SYNTHESIS, CHARACTERIZATION AND ISOMERIZATION ACTIVITY
STUDIES FOR MODIFIED SULFATED ZIRCONIA CATALYSTS

A Dissertation

Submitted to the Graduate School
of the University of Notre Dame
in Partial Fulfillment of the Requirements
for the Degree of

Doctor of Philosophy

by

Sameer Vijay, B. Tech.

________________________________________________________________________
Eduardo E. Wolf, Director

Graduate Program in Chemical and Biomolecular Engineering
Notre Dame, Indiana
March 2004
SYNTHESIS, CHARACTERIZATION AND ISOMERIZATION ACTIVITY STUDIES FOR MODIFIED SULFATED ZIRCONIA CATALYSTS

Abstract

by

Sameer Vijay

Sulfated zirconia (SZ) is an attractive alternative for use in industrial processes because of its good alkane activation potential as well as being a non-toxic replacement for liquid acid catalysts currently in use. Over the past 10 years, numerous studies have attempted to synthesize non-deactivating SZ-based catalysts by adding modifiers and/or promoters. In this work, a synthesis method is presented that is used to prepare a Pt-modified SZ catalyst, which shows exceptionally high and stable activity for n-pentane isomerization at atmospheric pressure.

A 3-step method consisting of calcining a sulfated zirconium hydroxide at high temperature prior to adding platinum, reduction of platinum followed by additional pretreatments is presented. The activity of such an SZ catalyst remains stable for up to 4 hours with conversion of n-pentane exceeding 70%. EXAFS studies showed that the active catalyst contains relatively large crystallites of platinum. Presence of Pt-S in the inactive catalyst gives evidence for the cause of deactivation of the samples prepared in the conventional manner. XANES analysis of the data also shows that the state of platinum in the active catalyst is that of a metallic platinum (Pt⁰). Using XPS data, it is shown that the surface undergoes rearrangements during the preparation.

Use of operando DRIFTS showed the sulfur-oxygen groups on the surface to be
more complex than previously reported as species different than just sulfates, were present. During the reaction, a particular species of OH group disappear. This species is replenished by the atomic hydrogen provided by the metallic platinum.

The experimental results give evidence of the changes in the catalyst surface during the preparation, pretreatment and the reaction itself. Based on the findings, a Site-Juxtaposition hypothesis is presented. This hypothesis is based on the hydrogen spillover occuring on the metallic crystallites, and the capability of this atomic hydrogen to hydrogenate coke species, thus arresting deactivation. The deactivation suppression is brought about by juxtaposition of the metal sites and the acid sites during the oxidation-reduction pretreatments. A simple math model is included that attempts to corroborates this phenomenon.
In the memory of my grandfather...

यह प्रबन्ध पूजनीय बाऊंजी को समर्पित …
CONTENTS

FIGURES .................................................................................. vi

TABLES .................................................................................. xii

ACKNOWLEDGMENTS ..............................................................xiv

CHAPTER 1: INTRODUCTION ................................................... 1
  1.1 Science of catalysis ......................................................... 3
  1.2 Solid acid catalysts ....................................................... 4
  1.3 Sulfated zirconia (SZ) .................................................... 5
    1.3.1 Introduction .......................................................... 5
    1.3.2 Preparation methods ............................................. 7
      1.3.2.1 2-step methods ................................................ 7
      1.3.2.2 1-step methods ............................................... 11
    1.3.3 Modified sulfated zirconia catalysts ......................... 13
  1.4 Characterization of SZ catalysts ....................................... 15
    1.4.1 Surface area ........................................................ 15
    1.4.2 Phase studies and calcination temperature ................. 16
    1.4.3 Temperature programmed studies .......................... 17
    1.4.4 Acid strength ...................................................... 20
    1.4.5 Hydration studies ............................................... 22
    1.4.6 Spectroscopic studies ......................................... 23
  1.5 Catalytic activity and deactivation ..................................... 24
    1.5.1 Isomerization activity ........................................... 24
    1.5.2 Role of modifiers and promoters ............................ 30
    1.5.3 Deactivation ...................................................... 31
  1.6 Objectives and organization of the thesis ......................... 32

CHAPTER 2: EXPERIMENTAL METHODS ............................... 35
  2.1 Introduction ................................................................ 35
  2.2 Catalyst synthesis ....................................................... 35
    2.2.1 Zirconium hydroxide synthesis .............................. 36
    2.2.2 Sulfation .......................................................... 39
    2.2.3 Addition of platinum ........................................... 40

iii
2.3 Catalytic activity and kinetic studies ..................................................... 41
   2.3.1 Reaction system ........................................................................ 41
   2.3.2 Gas chromatographic method ......................................................... 43
   2.3.3 Kinetic analysis ........................................................................ 45
2.4 Physical characterization techniques ....................................................... 45
   2.4.1 Nitrogen adsorption isotherm measurements .................................... 46
   2.4.2 X-ray diffraction ...................................................................... 47
   2.4.3 Thermal analysis ...................................................................... 48
   2.4.4 Sulfur analysis ........................................................................ 49
   2.4.5 Pulse chemisorption .................................................................. 50
   2.4.6 Platinum absorption study ........................................................... 51
2.5 Spectroscopic characterization methods .................................................... 52
   2.5.1 X-ray photoelectron spectroscopy .................................................. 54
   2.5.2 X-ray absorption spectroscopy ....................................................... 57
      2.5.2.1 EXAFS ........................................................................... 62
      2.5.2.2 XANES ........................................................................ 65
      2.5.2.3 XAS experimental setup ....................................................... 66
   2.5.3 Infrared vibrational spectroscopy ..................................................... 67
      2.5.3.1 Molecular Vibrations ........................................................... 69
      2.5.3.2 Diffuse Reflectance Infrared Spectroscopy ................................ 71

CHAPTER 3: CHARACTERIZATION AND n-PENTANE ISOMERIZATION
   ACTIVITY STUDIES ........................................................................... 77
3.1 Introduction ...................................................................................... 77
3.2 Physical characterization .................................................................... 77
   3.2.1 BET surface area measurements by nitrogen adsorption .................... 78
   3.2.2 TGA-DTA ............................................................................. 78
   3.2.3 X-ray diffraction studies .............................................................. 86
   3.2.4 Elemental analysis – sulfur and platinum ....................................... 90
   3.2.5 Pulse chemisorption .................................................................. 92
   3.2.6 Summary .............................................................................. 97
3.3 Evaluation of catalytic activity ............................................................... 98
   3.3.1 Catalysts prepared with 2-step method ......................................... 99
   3.3.2 Catalysts prepared with 3-step method ......................................... 106
   3.3.3 Effect of pretreatment on SZ$^{650}$-based catalysts .......................... 116
   3.3.4 Effect of the Zr(OH)$_x$ support .................................................. 120
   3.3.5 Summary .............................................................................. 122
3.4 Discussion ...................................................................................... 123

CHAPTER 4: SPECTROSCOPIC CHARACTERIZATION OF PLATINUM
   SUPPORTED ON SULFATED ZIRCONIA CATALYSTS ............................. 126
4.1 Literature review on the state of platinum .............................................. 126
4.2 X-ray photoelectron spectroscopy results ............................................. 128
   4.2.1 Effect of SZ calcination temperature ........................................... 128
   4.2.2 Effect of pretreatment on Pt in SZ$^{650}$-based catalyst ....................... 134
   4.2.3 Summary .............................................................................. 134
4.3 X-ray absorption spectroscopy results .................................................. 141
FIGURES

1.1 The *innovation* loop: Operational constraints require development of a new catalyst, resulting in a higher process efficiency .......................... 2
1.2 The science of catalysis represented as a prism, showing the three major sub-disciplines of catalysis on the macro-, meso- and microscopic level .................................................. 3
1.3 Schematic of the two-step method for preparation of sulfated zirconia 8
1.4 Schematic of 2-step method for preparation of Pt-containing \( \text{SO}_4^{2-}/\text{ZrO}_2 \) catalyst ................................................................. 12
1.5 Bed temperature versus oven temperature during calcination of Zr hydroxide ................................................................. 12
1.6 Thermal weight loss of the calcined samples in the temperature range between 20 °C and 1000 °C .................................................... 12
1.7 Acid strength of liquid and solid acids as determined by Hammett-indicator method .............................................................. 21
1.8 Conversion versus Time-on-stream for catalytic isomerization of n-butane on SZ catalysts ........................................................ 25
1.9 Typical reaction profile for n-butane isomerization at low temperature 25
1.10 Schematic of bimolecular mechanism of n-butane isomerization. The initiation step requires formation of carbenium ion. .......... 27
1.11 Reaction of n-pentane as a function of TOS over Pt/SZ catalyst at 206°C ................................................................. 27
1.12 Effect of addition of Pt to FMSZ and \( \text{H}_2 \) to the feed on the conversion of n-pentane to isopentane. (○) FMSZ, (□) PtFMSZ and (△) PtFMSZ with \( \text{H}_2 \) in feed. Arrows indicate time at which the total conversion declined to 3% of maximum. .. 29
2.1 Schematic of the 3-step synthesis method used in this thesis ...... 37
2.2 Schematic of the reactor system used in activity studies ........... 42
2.3 Schematic from which most techniques can be derived .......... 52
2.4 The electro-magnetic spectrum, along with common photon sources and a number of characterization techniques based on photons .. 53
2.5 The electronic transition involved in the photoemission of a electron and Auger process ......................................................... 55
2.6 Various processes occur when an incoming x-ray beam strikes a solid.

2.7 The absorption cross-section $\mu/\rho$ for several elements over the x-ray energy range of 1 to 100 keV.

2.8 Typical apparatus for transmission XFS experiment. $I_0$, $I_1$ and $I_2$ are ionization detectors. A minimal experiment requires $I_0$ and $I_1$. The addition of $I_2$ permits the XAS of a standard such as a metal foil to be measured. This standard XAS is used for accurate energy calibration.

2.9 Typical apparatus for a fluorescence XAS experiment. The fluorescence detector is usually an ionization detector or a solid-state detector. A minimal experiment requires only $I_0$ and the fluorescence detector.

2.10 X-ray absorption spectra for (a) transmission mode and (b) fluorescence mode for Pt-L$_{III}$ edge (11.564 keV) in Pt/SZ.

2.11 Various regions in an X-ray absorption spectrum – usually referred by their acronyms.

2.12 EXAFS occurs because the photoelectron can scatter from a neighboring atom. The scattered photoelectron can return to the absorbing atom, modulating the amplitude of the photoelectron wavefunction at the absorbing atom. This in turn modulates the absorption coefficient $\mu(E)$.

2.13 *Wiggles* arise due to destructive and constructive interference between outgoing and backscattered wavefunctions resulting in the fine structure.

2.14 Picture showing the EXAFS reactor tube and the sample holder.

2.15 The EXAFS reactor tube placed in the measurement hutch in the path of the x-ray beam.

2.16 Fundamental vibrations of several molecules.

2.17 Schematic of Diffuse reflectance mirror setup with IR beam path (courtesy Harrick Sci. Corp.).

2.18 Schematic of the reaction cell for in-situ DRIFTS.

2.19 Pictures of DRIFTS setup and the reactor chamber.

3.1 Thermogravimetric analysis of SZ$_{550}$ and SZ$_{650}$. The numbers along the length of the curves indicate the temperature in °C.

3.2 Rate of weight loss for samples of sulfated Zr hydroxide at 550 °C and 650 °C.

3.3 Effect of heating rate on the profile of loss in weight in SZ samples.

3.4 DTA profile for sulfated zirconium hydroxide when heated till 750 °C.

3.5 The temperature profile of the powder bed during the calcination of sulfated zirconium hydroxide till 650 °C. The bed height was 4 cm ($\phi = 2$ cm).

3.6 Short range order in sulfated Zr hydroxide as opposed to tetragonal SZ$_{650}$. 

vii
3.7 X-ray diffractograms for SZ550 and SZ650: Increased crystallinity due to higher calcination temperature ........................................ 88
3.8 X-ray diffraction plots for Pt(r)/SZ prepared from SZ calcined at different temperatures – 550 °C, 605 °C and 650 °C ...... 89
3.9 X-ray diffraction on SZ650 and Pt(o)/SZ650: Addition of Pt does not modify the phase of SZ ......................................... 90
3.10 Comparison of the diffraction patterns of amorphous S-Zr(OH)2, SZ650 which was reduced and re-oxidized and Pt(r)/SZ650 .................. 91
3.11 Hydrogen uptake in Pt(r)/SZ550 as function of temperature ...... 95
3.12 Hydrogen uptake in Pt(r)/SZ650 as function of temperature ...... 96
3.13 Equilibrium fractions of alkanes isomers of n-pentane as a function of temperature (P = 1 atm.) .............................................. 100
3.14 Conversion vs. TOS profile for SZ550 sample (a) constant PnC5 (b) varying partial pressure of n-pentane ................................. 102
3.15 Conversion vs. TOS for SZA600 and SZA650 samples ............ 104
3.16 Conversion vs. TOS for PtSZ650(o) and PtSZ650(r) catalysts .... 105
3.17 Conversion and isopentane selectivity vs. TOS for Pt(o)/SZ550: Effect of regeneration ......................................................... 107
3.18 Conversion vs. TOS for Pt(r)/SZ550: pretreatment at 300 °C and high hydrogen flow rate ....................................................... 108
3.19 Conversion vs. TOS for Pt(o)/SZ650 sample: Effect of regeneration . 110
3.20 Selectivity towards isopentane vs. TOS for Pt(o)/SZ650 sample: Effect of regeneration .......................................................... 110
3.21 Conversion vs. TOS for Pd-modified SZ650 and SZA650 samples . 111
3.22 Conversion vs. TOS for Pt(r)/SZ650 ........................................ 113
3.23 Selectivity towards isopentane vs. TOS for Pt(r)/SZ650 .......... 113
3.24 Conversion vs. TOS for Pt(r)/SZ650: pretreated at 300 °C and high hydrogen flow ............................................................. 114
3.25 Conversion vs. TOS for Pt(r)/SZ650 at 150 °C, 200 °C and 250 °C 115
3.26 Conversion vs. TOS for Pt(r1)/SZ650: effect of regeneration ...... 117
3.27 Conversion vs. TOS for Pt(rS,o), Pt(r1,o), Pt(rS,o,rS), Pt(rS,o,r1)SZ650-based catalysts ................................................................. 119
3.28 Conversion vs. TOS for Pt(rS)/SZ650 samples prepared from various types of SZ ............................................................... 121
4.1 Proposed model of platinum on SO42−/ZrO2 surface ............... 128
4.2 XPS spectra for O 1s, S 2s, Zr 3d and Pt 4f region for Pt(r)/SZ650 .. 130
4.3 XPS spectra for S 2s for SZ650- and SZ450-based samples .......... 131
4.4 XPS spectra for Pt 4f for SZ550- and SZ650-based samples .......... 132
4.5 Component ratio of elements in Pt/SZ550 and Pt/SZ650 catalysts ... 135
4.6 XPS spectra for O 1s, S 2s and Pt 4f region for catalysts prepared by 2-step method ........................................... 137
4.7 XPS spectra in O 1s, S 2s and Pt 4f region for catalysts prepared as per the 3-step method ........................................... 139
4.8 Surface concentration ratios (XPS) of sample components ........................................... 142
4.9 Magnitude of $k^2$ weighted FT of EXAFS data for a used Pt(o)/SZ$_{550}$ catalyst (solid line) compared with Pt(r)/SZ$_{550}$ (dashed line) ........................................... 144
4.10 Magnitude of $k^2$ weighted FT on EXAFS data. Comparison between Pt(r)/SZ$_{550}$ reduced ($\Delta k=3.01-10.45$ Å$^{-1}$) (solid line), Pt(r)/SZ$_{650}$ reduced ($\Delta k=2.75-13.80$ Å$^{-1}$) (dotted line) and Pt(r)/SZ$_{650}$ further oxidized (dashed line) ........................................... 145
4.11 Fit of isolated shell and raw data for Pt(r)/SZ$_{550}$[$r$], ($\Delta k=3.01-10.45$ Å$^{-1}$, $\Delta r=1.51-2.42$ Å). (bold solid–real part of FT raw data, thin solid–imaginary part of FT raw data, bold dotted–real part of the fitted data, thin dotted–imaginary part of the fitted data) ........................................... 145
4.12 Fit of isolated shell and raw data for Pt(r)/SZ$_{650}$[$r$] ($\Delta k=2.75-13.80$ Å$^{-1}$, $\Delta r=1.84-2.92$ Å). (bold solid–real part of FT raw data, thin solid–imaginary part of FT raw data, bold dotted–real part of the fitted data, thin dotted–imaginary part of the fitted data) ........................................... 147
4.13 Normalized XANES spectra. solid–Pt(r)/SZ$_{550}$[$r$], dotted–Na$_2$PtCl$_4$ (reference), dashed–H$_2$PtCl$_6$ (reference) ........................................... 149
4.14 Normalized XANES spectra. dotted– Pt(r)/SZ$_{650}$[$r$], dashed–Pt(r)/SZ$_{650}$[$r$,o] ........................................... 150
4.15 Magnitude of the Fourier transform of $k^2$-weighted EXAFS of PtSZ$_{650}$($o$) and PtSZ$_{650}$($r$) ........................................... 152
4.16 Normalized XANES spectra: PtSZ$_{650}$($o$) and PtSZ$_{650}$($r$) ........................................... 153
4.17 Magnitude of FT of $k^2$-weighted EXAFS of Pt(o)/SZ$_{650}$, Pt(r$_s$)/SZ$_{650}$ and Pt(r$_l$)/SZ$_{650}$ ........................................... 155
4.18 Normalized XANES spectra: Pt(o)/SZ$_{650}$, Pt(r$_s$)/SZ$_{650}$ and Pt(r$_l$)/SZ$_{650}$ ........................................... 156
4.19 Magnitude of FT of $k^2$-weighted EXAFS of Pt(o)/SZ$_{650}$, Pt(r$_s$,o)/SZ$_{650}$ and Pt(r$_s$,o)/SZ$_{650}$ ........................................... 158
4.20 Normalized XANES spectra: Pt(o)/SZ$_{650}$, Pt(r$_s$,o)/SZ$_{650}$ and Pt(r$_l$,o)/SZ$_{650}$ ........................................... 160
4.21 Magnitude of FT of $k^2$-weighted EXAFS of Pt(r$_s$,o,r$_s$)/SZ$_{650}$ and Pt(r$_s$,o,r$_l$)/SZ$_{650}$ ........................................... 161
4.22 Normalized XANES spectra: Pt(r$_s$,o,r$_s$)/SZ$_{650}$ and Pt(r$_s$,o,r$_l$)/SZ$_{650}$ ........................................... 162
4.23 Magnitude of FT of $k^2$-weighted EXAFS of samples prepared from Zr hydroxide from Aldrich and MEI ........................................... 164
4.24 Magnitude of FT of $k^2$-weighted EXAFS of (a) Pt(r)/SZ$_{650}$(Na), (b) Pt(r)/SZ$_{650}$-Na(l) and (c) Pt(r$_s$,o,r$_s$)/SZ$_{650}$(MEI) ........................................... 166
4.25 Magnitude of Fourier Transform of $k^2$-weighted EXAFS of an active
catalyst versus inactive catalyst .................................................. 169
4.26 Magnitude of FT of $k^2$-weighted EXAFS of inactive samples A, B
and C ............................................................................................. 170
4.27 Three regimes in a typical adsorption model ............................... 173
4.28 pH shift measurement: experimental data and model fit for $\text{SZ}_{550}$,
$\text{SZ}_{650}$ and $\text{ZrO}_2$(MEI) [basis: 500 m$^2$/l] ................................. 174
4.29 pH shift measurement: experimental data and model fit [basis: 1000
m$^2$/l] ......................................................................................... 175
4.30 Adsorption of platinum from t-APCl solution onto $\text{SZ}_{550}$ and $\text{SZ}_{650}$
support (surface loading = 1000 m$^2$/l) ........................................ 177
4.31 Adsorption of platinum from CPA solution over $\text{SZ}_{550}$ and $\text{SZ}_{650}$
support (surface loading = 500 m$^2$/l) ........................................... 178
5.1 Transmission spectra of $\text{SZ}$ samples ....................................... 187
5.2 DRIFTS spectra for $\text{SZ}$ (MEI) samples ................................. 188
5.3 DRIFTS spectra for Pt-modified $\text{SZ}_{650}$ samples ...................... 191
5.4 DRIFTS spectra of the inactive samples A and B (Table 4.17) .... 193
5.5 Background-corrected DRIFTS spectra obtained during reduction of
unmodified $\text{SZ}_{650}$ ................................................................. 197
5.6 Intensity of bands at selected wavenumbers during reduction of $\text{SZ}_{650}$ 198
5.7 Background-corrected DRIFTS spectra obtained during reduction of
Pt-loaded $\text{SZ}_{650}$ ................................................................. 200
5.8 Intensity of bands at selected wavenumbers during reduction of Pt-
loaded $\text{SZ}_{650}$ ................................................................. 201
5.9 Background-corrected DRIFTS spectra obtained during reduction of
Pt($r_s,o$)/$\text{SZ}_{650}$ ................................................................. 202
5.10 Intensity of bands at selected wavenumbers during reduction of Pt($r_s,o$)/
$\text{SZ}_{650}$ ................................................................. 203
5.11 Background-corrected DRIFTS spectra obtained during n-pentane
isomerization on unmodified $\text{SZ}_{650}$ ........................................... 206
5.12 Intensity of bands at selected wavenumbers during n-pentane isomer-
ization on unmodified $\text{SZ}_{650}$ ........................................... 207
5.13 Background-corrected DRIFTS spectra obtained during n-pentane
isomerization on Pt($r_s$)/$\text{SZ}_{650}$ sample .................................... 209
5.14 Intensity of bands at selected wavenumbers during n-pentane isomer-
ization on Pt($r_s$)/$\text{SZ}_{650}$ ........................................... 210
5.15 Background-corrected DRIFTS spectra obtained during n-pentane
isomerization on Pt($r_s,o,r_s$)/$\text{SZ}_{650}$ .................................... 212
5.16 Intensity of bands at selected wavenumbers during n-pentane isomer-
ization on Pt($r_s,o,r_s$)/$\text{SZ}_{650}$ .................................... 213
5.17 Background-corrected DRIFTS spectra obtained during n-pentane isomerization on inactive sample A (cf. Table 4.17) .................................. 215
5.18 Intensity of bands at selected wavenumbers during n-pentane isomerization on inactive sample A (cf. Table 4.17) .................................. 216
6.1 Schematic of spillover and reverse spillover phenomenon .... 223
6.2 Sulfided and subsurface platinum are not able to act as proton/hydride provider ............................................................. 227
6.3 Separation of metal and acid site causes slow supply of H-spillover species, which leads to decreased deactivation. .......... 227
6.4 Rapid transfer of spilled-over H can occur if the metal and the acid sites are juxtaposed ...................................................... 228
6.5 Conversion vs. TOS obtained by solving the model described above with \( k'_A = 0.86 \text{ s}^{-1} \), \( k'_P = 8.8 \text{ s}^{-1} \text{ atm.}^{-1} \). The steady state conversion value rises with increasing value of \( k'_{-P} \). The plots shown correspond to \( k'_{-P} = 1.0, 1.5, 2.0, 3.0 \) and \( 3.8 \text{ s}^{-1} \text{ atm.}^{-1} \) .... 233
TABLES

1.1 SULFATE ZIRCONIA CATALYSTS SYNTHESIZED BY SOL-GEL METHODS .................................................. 13

2.1 POSSIBILITIES FOR SPECTROSCOPIC ANALYSIS IN CATALYSIS .......................................................... 54

2.2 CLASSIFICATION OF INFRARED RADIATION ................................................................. 69

3.1 BET SURFACE AREA OF SELECTED SAMPLES ............................................................. 79

3.2 SULFUR CONTENT (wt%) OF SZ SAMPLES CALCINED AT 550 °C AND 650 °C ........................................ 92

4.1 SURFACE COMPOSITION FOR Pt(r)/SZ_{650} AND Pt(r)/SZ_{650} SAMPLES, BEFORE AND AFTER A REACTION (-T), ON A CARBON-FREE BASIS ............................................................. 133

4.2 NOMENCLATURE AND CONDITIONS FOR PREPARATION OF Pt/SZ_{650} CATALYSTS ........................................ 136

4.3 SURFACE CONCENTRATION AS CALCULATED FROM XPS ANALYSIS .................................................. 140

4.4 PARAMETERS USED IN EXAFS FITS ................................................................. 146

4.5 XANES FITS DATA (ERROR ESTIMATE: 5-10%) ................................................................. 149

4.6 PARAMETERS USED IN THE EXAFS FIT OF PtSZ_{650}(o) AND PtSZ_{650}(r) .................................................. 153

4.7 XANES ANALYSIS DATA (fractions) ................................................................. 154

4.8 PARAMETERS USED IN THE EXAFS FIT OF Pt(o)/SZ_{650}, Pt(r_s)/SZ_{650} AND Pt(r_1)/SZ_{650} .................................................. 156

4.9 XANES ANALYSIS DATA (fractions) ................................................................. 157

4.10 PARAMETERS USED IN THE EXAFS FIT OF Pt(r_s,o)SZ_{650} AND Pt(r_1,o)SZ_{650} .................................................. 158

4.11 XANES ANALYSIS DATA (fractions) ................................................................. 159

4.12 PARAMETERS USED IN THE EXAFS FIT OF Pt(r_s,o,r_s)/SZ_{650} AND Pt(r_s,o,r_1)/SZ_{650} .................................................. 161

4.13 XANES ANALYSIS DATA (fractions) ................................................................. 162

4.14 LIST OF SAMPLES PREPARED FROM DIFFERENT Zr HYDROXIDE PRECURSORS .................................................. 164
4.15 PARAMETERS USED IN THE EXAFS FIT OF Pt(r)/SZ_{650}(Aldrich) AND Pt(r)/SZ_{650}(MEI) .............................................................165
4.16 PARAMETERS USED IN THE EXAFS FIT OF Pt(r)/SZ_{650}(Na), Pt(r)/SZ_{650}-Na(l) AND Pt(r_{s,o,r_{s}})/SZ_{650}(MEI) .............................................167
4.17 INACTIVE CATALYSTS .................................................................168
4.18 PARAMETERS USED IN THE EXAFS FIT OF THE INACTIVE Pt/SZ SAMPLES, A, B AND C .............................................................170
5.1 INFRARED BAND POSITIONS IN SZ SAMPLES ..............................184
6.1 SIMPLIFIED REACTION PATHWAY FOR n-PENTANE ISOMERIZATION .................................................................229
ACKNOWLEDGMENTS

My biggest “Thank you!” is to my advisor during my studies at Notre Dame, Dr. Eduardo E. Wolf, for providing guidance, motivation and always being available for discussions. I have learned this much because he is a fine teacher.

I am much obliged by Dr. H.-C. Chang, Dr. D. A. Hill, and Dr. W. C. Strieder, for agreeing to review this research at short notice and I thank them as well. My gratitude to Dr. Stanisic for kindly agreeing to be the chair for my thesis defense.

“Muchas gracias” to my colleagues in the Catalysis and Reactor Engg. Lab, especially Francisco, Javier and Sichem. They compensated in ample the lack of windows in the labs. Many thanks to Gabriela for her friendship.

I am particularly grateful to Dr. J. T. Miller (BP), for EXAFS data analysis as well as his insightful comments on my work and the art of catalyst tweaking and Dr. A. J. Kropf (CMT, ANL) for help in the X-ray beam alignment.

I also acknowledge the Dept. of Chemistry and Biochemistry (Dr. M. Leiberman), CEST (D. Birdsell) and CMEM (Dr. P. McGinn) for trusting me to play with various instruments in their laboratories for my research.

Partial support for my research from the National Science Foundation and the department is gratefully acknowledged.

Sincere thanks to the support staff of our department - Marty, Jeanne and Karen for their help in million ways; as well as Jim Kirksey and Jim Smith, for their advice and excellent technical skills.
The tremendous support of my family and friends helped make this dream a reality and I acknowledge their love and care...

To my grandmother and my parents in India: मेरी सफलता का श्रेय आपके आशीर्व, पैर्यं, प्यार एवं प्रोत्साहन को ही है।

To Magdalena: Ganz herzlichen Dank für alle die Liebe und die Aufmunterungen.

To all the friends in Notre Dame: I am truly grateful for your company, warmth and generosity. You made this experience a really wonderful one!
CHAPTER 1

INTRODUCTION

The expansion of the chemical process industry finds its roots in scientific innovations at the beginning of the 20th century. An important development amongst these was the origin of industrial heterogeneous catalysis. Large scale continuous processes were made possible by the introduction of heterogeneous catalysis in flow reactors, where products were continuously separated from the catalyst. During the past century, development and progress in catalysis was driven due to either changing industrial needs or societal requirements, such as availability of raw materials, the need to reduce process side-effects, or the demands for new products.

Besides the discovery of new catalysts, first for the coal-based followed by the oil-based and currently the natural gas-based chemical industry, environmental concerns have led to the development of gas treatment catalysts to reduce emissions from stationary sources (e.g. electricity generation plants) as well as automobile exhausts. Whereas such applications of catalytic clean-up technology are of obvious importance, there is an increasing need to develop new catalytic processes that produce less or no waste products. Developments in catalysis and chemical process engineering are thus linked in an innovation loop as sketched in Figure 1.1.

Catalyst technology, besides being a backbone of the chemical processing industry is very critical to petroleum refining industry and comprises a multi billion dollar industry worldwide with an ever increasing annual growth. It plays a major
Figure 1.1. The *innovation* loop: Operational constraints require development of a new catalyst, resulting in a higher process efficiency
Figure 1.2. The science of catalysis represented as a prism, showing the three major sub-disciplines of catalysis on the macro-, meso- and microscopic level role in all economic development, in general, either by itself (catalyst production) or by its use in processes for production of value-added chemicals. The science and technology of catalysis are therefore of central practical importance.

1.1 Science of catalysis

Catalysis as a science has developed along three major directions: kinetics, catalyst characterization and the synthesis of catalysts. These three ingredients can all be recognized on three different fundamental levels, as schematically summarized in Figure 1.2.

At the microscopic level, catalysis deals with elementary reaction steps of molecules on the surface of the catalyst, spectroscopic and theoretical studies on surface species
and reactive sites, and the synthesis of active sites and reaction intermediates. The *mesoscopic* level is that of measuring catalytic activities and selectivity, characterization of catalysts by spectroscopy, diffraction, microscopy and other methods, and of catalyst preparation by impregnation or precipitation, reduction or sulfidation. The *macroscopic* level is that of reaction engineering, texture determination and shaping catalysts in extrudates, as powders for fluid beds or in monoliths.

In this thesis, the primary emphasis is on the mesoscopic aspects of catalyst science involving sulfated zirconia catalysts in the above mentioned broad directions along with some details of microscopic levels of understanding.

1.2 Solid acid catalysts

Depending on the chemical nature of the catalyst being used, the catalytic processes can be broadly classified into oxide-reduction and acid-base ones. Solid acid catalysts form a part of the acid-base catalysts. Solid acids are of the same chemical nature as the liquid inorganic acids such as hydrochloric or the sulfuric acid. The solid acids are not as aggressive as the liquid acids, even though being stronger, since the acid sites are hidden inside the well-developed catalyst pore structure. Among the widely known solid-acid catalysts are the fluidized catalytic cracking (FCC) catalysts and the zeolites.

A wide range of liquid-phase industrial reactions still rely on the use of the inorganic or mineral acids. While many of these process are catalytic, some (e.g. acylation with AlCl₃) require stoichiometric amounts of acid. Final isolation of the product in these process necessitates aqueous quenching and neutralization steps to remove the acid, resulting in enormous quantities of hazardous waste. The cost of disposal of the waste often outweighs the value of the product. The tightening legislation on emission control is then driving the industry toward the implementa-
tion of innovative clean technology or cleaner-by-design processes including the use of alternative heterogeneous catalyzed processes. Solid acids, thus, form an attractive alternative to replace the homogeneous catalytic routes. The chemical industry and the Office of Industrial Technologies (OIT) of the U.S. Department of Energy (DOE) outlined a vision for the industries of future in their report – Technology Vision 2020: The U.S. Chemical Industry, and emphasized development of new viable solid acid alkylation catalysts with sustained activity as a critical need area [2].

Since the past 10 years, many classes of solid acid catalysts have been investigated, including Mobil’s M41S molecular sieves and the MCM-family of materials, zeolites (H-β, H-US-Y etc.), sulfonated resins (e.g. Nafion-H), Keggin-type heteropoly acids (HPAs) and the mesoporous zirconia-based substances (e.g. sulfated and/or tungstated zirconia), for use in various hydrocarbon reactions.

1.3 Sulfated zirconia (SZ)

1.3.1 Introduction

Earliest report of a modified zirconia-gel based catalyst comes from a patent assigned in 1962 to Phillips Petroleum Company [3] in which Holm and Bailey reported the use of sulfate-treated zirconia-gel catalysts for the isomerization and alkylation of hydrocarbons. These authors also reported first use of a platinum containing sulfated zirconia-gel catalyst as an alternative for the chlorided alumina catalyst for isomerization of n-pentane. The reaction was carried out at 500 psig and 261°C with a 36-38% iso-pentane yield.

Almost two decades later, Arata and co-workers [4, 5] generated renewed interest among researchers by reporting a zirconia catalyst treated with sulfuric acid or ammonium sulfate that had extremely strong acidity and was capable of catalyzing isomerization of n-butane to isobutane at room temperature. They claimed that
sulfated zirconia (denoted as SZ hereafter) is an acid 10,000 times stronger than 100% sulfuric acid and hence is a superacid. However, this claim is not without controversy and has been debated as well as questioned by various groups [6, 7].

The ever increasing need for environmentally benign processes and safety has led researchers, in both industry and academia, to look for alternatives for the existing chemical and refining technologies involving acid catalysis. The processes employing highly corrosive, hazardous and polluting liquid acids are being replaced with solid acids, for instance, acid-treated clays, zeolites, ion-exchange resins and metal oxides.

In general, metal oxides have been used extensively either as such or as supports in conjunction with other active components for many industrial oxidation and acid-base-catalyzed reactions. The surface of zirconia (zirconium oxide, ZrO$_2$) is known to be active for all these catalytic phenomena. Modification by anions, such as sulfate ions, makes it a strong acid catalyst that has superior catalytic activity for many reactions. Over the past years, SZ has been investigated as a potential catalyst for numerous hydrocarbon conversion processes such as hydroisomerization, alkylations (e.g. alkylation of isobutane with butene to form gasoline alkylates), oligomerization, methanol conversion to hydrocarbons, condensation, etherification, nitration among many others. As seen above, due to their potential for use in numerous reaction schemes, SZ and modified SZ form an important class of catalysts that holds promise for providing environmentally clean processes for the chemical industry of the future.

On the other hand, since the SZ-based catalysts possess high acidic strength, they suffer from drawbacks such as poor stability and low isomerization activity for C$_7$+ hydrocarbons. Deactivation due to coke formation at high reaction temperature has been overcome only to a small extent by modifying SZ with various transition metals, like platinum, nickel, copper etc. of which platinum-modified SZ is very
widely studied and operation under high pressure conditions.

Numerous studies have been devoted to the preparation of SZ and to the characterization of its physiochemical properties and catalytic performance in various chemical reactions. A large number of research publications have appeared on this subject in recent years. An authoritative review of the zirconia-based solid acid catalysts was published by Song and Sayari in 1996 dealing with the large body of information published since 1990. The following subsections detail the state of the art known on the preparation and characterization of these modified SZ catalysts. Many of the references cited here were reported during the course of this work itself.

1.3.2 Preparation methods

Various methods have been used by different researchers in order to get a catalyst with even higher activity. The methods reported in the literature can all be classified into two categories – (a) two-step methods, and (b) one-step methods.

1.3.2.1 2-step methods

The conventional preparation of sulfated zirconia includes (i) synthesis of precursor, i.e., zirconium hydroxide gel, and (ii) sulfation of Zr(OH)$_4$ to load the sulfur species and calcination of obtained zirconium hydroxide. This is the so-called 2-step method defined by Song and Sayari. Figure 1.3 illustrates the steps involved in this method.

The classical preparation of Zr(OH)$_4$ proceeds by precipitation of an aqueous zirconium salt with a base in solution. Although this procedure apparently provides a simple and easy way to prepare the catalyst, a successful preparation needs much attention to details. Many factors during this step itself could affect the precursor structure, which results in differing catalytic activity in the final catalyst. Different zirconium sources such as zirconium nitrate, zirconium chloride, zirconyl chloride,
Figure 1.3. Schematic of the two-step method for preparation of sulfated zirconia

Step 1

Zirconium Salt

Base

Step 2

Zr(OH)$_x$

Source of Sulfur

Sulfur-containing Zr(OH)$_x$

Caclination at 600-650°C

SZ
zirconium oxynitrate and Zr propoxide have been used as zirconium sources \[9,10\], each resulting in significantly different activity. The influence of the nature of the Zr salt has been questioned, suggesting that the final crystalline phase only is important to the catalytic activity \[11\]. In addition, various types of precipitating agents such as aqueous ammonium hydroxide, and urea have been suggested \[12\]. The final pH value of the gel obtained after the hydrolysis of the hydrated Zr precursor strongly affects the morphology and crystalline nature of the catalyst after calcination \[13\]. Optimum value for the final pH is between 7 and 10 \[14\]. The gel is then decanted and aged for a certain period of time varying between 30 minutes to 12 hours, in order to get a stable texture. Risch and Wolf \[15\] used a pH adjusted reflux of freshly precipitated Zr(OH)\(_4\) gel for 20 hours at 90°C to obtain sulfated zirconia that exhibited higher n-butane isomerization activity than an un-refluxed preparation. This is more likely due to higher surface area in the case of refluxed Zr(OH)\(_4\).

Sol-gel methods have also been used to prepare the Zr hydroxide. Briefly, in this method, a metal alkoxide undergoes hydrolysis and subsequent condensation in an alcohol solvent, forming a polymeric oxide network referred to as alcogel. Removal of the solvent under conventional air drying generates a liquid-vapor interface inside the pores, and the corresponding high surface tension collapses the porous oxide network, thus reducing the area. The resultant material is called a xerogel. The formation of the liquid-vapor interface may be avoided by removal of the solvent under supercritical conditions. The resulting high surface area gel is called aerogel. Morterra et al. \[16\] prepared a xerogel by means of Zr propoxide (Zr(OC\(_3\)H\(_7\))\(_4\)). Clearfield et al. \[17\] synthesized an aerogel from Zr isopropoxide, acetic acid and propanol.

The sulfation procedure is normally performed by immersion of the Zr(OH)\(_4\) powder in a solution of sulfating species such as sulfuric acid or ammonium sulfate.
Sulfation of crystallized zirconium oxide does not produce an active catalyst [18, 19]. Sohn and Kim [20] and later Davis et al. [10] used various sulfating agents including H$_2$SO$_4$, (NH$_4$)$_2$SO$_4$, H$_2$S, SO$_2$ and CS$_2$ but reached different conclusions. Sohn and Kim observed that the acidity of the catalyst was independent of the sulfating agent whereas Davis et al. found that sulfation by sulfuric acid results in a catalyst with better catalytic performance for n-butane isomerization. It has also been found that, for sulfate concentrations above an average half monolayer, sulfation with sulfuric acid leads to contents of sulfate that are appreciably lower than the nominal concentration. Parera [21] has compared the surface sulfate concentration and the surface area of the catalysts when the sulfation is accomplished using sulfuric acid and ammonium sulfate. It is seen that higher sulfate concentrations and surface area are obtained with sulfuric acid than with ammonium sulfate [10, 21]. Higher concentrations of the sulfating agent used also result in higher tetragonal content of the catalyst. Most of the excess sulfur is, however, lost during the thermal activation of the catalyst. These sulfates thus represent the thermally most labile forms of the grafted sulfates. Morterra et al. [22] studied the effect of sulfate concentration on the Brønsted acidity of the catalyst. Their results suggest an increase in Brønsted acidity with sulfate concentration up to a certain maximum, after which the amount of Brønsted acidity remains constant.

In addition to the fact that strong acidity can only be generated by impregnation of Zr hydroxide and not by impregnating crystalline zirconia, the final crystalline structure depends upon the calcination method. The calcination in either air or in oxygen between a range of 550°C to 650°C was found to transform from amorphous hydroxide to tetragonal phase oxide [10]. Upon calcining to a higher temperature, further transformation to a monoclinic phase takes place, as well as a loss of sulfur species from the surface leading to a reduction of its catalytic activity. This loss
occurs in the form of decomposition of sulfates to SO$_2$ and SO$_3$ [14, 23]. Apparently, the tetragonal phase in sulfated zirconia could be correlated with catalytic activity for isomerization [13, 24]. Ward and Ko [25] reported a monoclinic sulfated zirconia sample with weak n-butane isomerization activity. More recently, Stichert et al. [26, 27] have obtained a catalytically active high surface area monoclinic sulfated zirconia by carefully adjusting the precipitation procedure and aging conditions. Thus, it seems that the crystalline phase of sulfate zirconia is not as important with respect to its activity as the content of acid sites.

The final sulfur content over calcined sulfate zirconia has significant impact on the activity. In a systematic study, Sparks et al. [28] developed a method to control sulfur content simply by changing the activation temperature, which can also affect other properties, especially the crystallinity. A relationship between the sulfur content and the ratio of Brønsted to Lewis acid centers shows a maximum in catalytic activity. In their extensive analysis of the influence of the sulfur content, Farcasiu et al. [29, 30] found that the content of sulfur can also be controlled by carefully controlled calcination.

In a similar fashion, platinum-containing SZ catalyst is prepared by adding platinum solution (usually chloroplatinic acid or tetra-ammonium salt of Pt) either by absorption or impregnation, to the sulfur-containing zirconium hydroxide before calcination to activate the acid sites (see Figure 1.4). This is the most frequently used method in various studies on state of Pt and activity for n-pentane isomerization.

1.3.2.2 1-step methods

Arata and coworkers reported the first attempt in preparing the catalyst from Zr sulfate as a starting material. This procedure did not allow a good control of sulfate content as observed by Farcasiu and Li [31]. Ward and Ko [32] reported on
Figure 1.4. Schematic of 2-step method for preparation of Pt-containing $\text{SO}_4^{2-}/\text{ZrO}_2$ catalyst
TABLE 1.1
SULFATE ZIRCONIA CATALYSTS SYNTHESIZED BY SOL-GEL METHODS

<table>
<thead>
<tr>
<th>Catalyst Description</th>
<th>Catalytic Properties</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/SO$_4^{2-}$/ZrO$_2$ &amp; SO$_4^{2-}$/ZrO$_2$ One-step sol-gel using ZrOCl$_2$ + H$_2$SO$_4$ + CH$_3$COOH</td>
<td>Active for n-hexane isomerization at 150°C and n-butane isomerization at 250°C</td>
<td>[33]</td>
</tr>
<tr>
<td>Pt/SO$_4^{2-}$/ZrO$_2$ One-step sol-gel using Zr(OPr)$_4$ + H$_2$SO$_4$ + i-PrOH</td>
<td>Active for n-butane isomerization at 150°C and 250°C</td>
<td>[35]</td>
</tr>
<tr>
<td>SO$_4^{2-}$/ZrO$_2$ Colloidal sol-gel + sulfation</td>
<td>Both strong Lewis and Brønsted sites</td>
<td>[36]</td>
</tr>
</tbody>
</table>

a preparation of SZ in a single step using a sol-gel method. They found that sulfate ions were trapped in the bulk of the aerogel but expelled onto the surface and transformed into catalytically active species after calcination and crystallization. Tichit et al. [33] also used this approach and investigated the preparation and activation treatments on the catalytic activity of sulfated zirconia.

Morterra and coworkers [34, 35] have reported similar one-step preparations of platinum containing SZ catalyst by sol-gel technique.

Table 1.1 presents some recent preparations of sulfated zirconia catalysts by sol-gel methods.

1.3.3 Modified sulfated zirconia catalysts

Although SZ is known to possess the highest acidity amongst all known solid acid catalysts, a considerable amount of research is centered on further improvement of catalytic activity and stability towards deactivation. It has been found to be
more active than zeolites for isomerization and alkylation at low temperatures [37], however, it possesses lesser resistance to deactivation than zeolites. In this context, SZ catalysts modified with addition of various transition metals such as Pt, Pd, Fe, Ir, Mn, etc. have been found to exhibit better catalytic activity. Among the metals added, Pt, Fe and Mn exhibit better activity.

Hsu et al. [38] observed that the activity of SZ for isomerization of n-butane could be greatly enhanced by addition of Fe and Mn, and attributed the enhancement to generation of additional sites with higher acid strength than those of the parent SZ. On the contrary, Adeeva et al. [7] have proposed that the rate enhancement is not caused by an increase in acid strength but rather by an increased production of alkenes which may participate in the reaction. According to this mechanism, isomerization proceeds via β-scission of an intermediate C₈ carbenium ion formed by oligomerization of a C₄ carbenium ion and a butene molecule. Modification of SZ with Fe and Mn increases the reaction selectivity for isomerization by minimizing the disproportionation reaction [38]. It has been suggested that the presence of transition metals may attract olefin molecules which form an alkene pool that enhances the local concentration of the olefins near the acid sites. Under such a condition, the rate-limiting oligomerization step would be greatly accelerated by the higher surface concentration of the olefins. These catalysts however suffer from rapid deactivation [39].

It has also been found that the Pt-modified SZ shows higher rate for alkane isomerization than Pt-containing unpromoted zirconia and even zeolite and mesoporous aluminosilicates. Modification by platinum has also been found to increase the stability of the catalyst towards deactivation during isomerization of the catalysts [40] in the presence of H₂ and cracking of alkanes. Cleansing of sites by the hydrogenation of coke that causes deactivation has also been suggested as a possible
role of the supported platinum \cite{41}. Details of the studies done on the role and state of platinum are included as literature review in Chapter 4.

It has been found that the activity of SO$_4^{2-}$/ZrO$_2$ is significantly decreased in a hydrogen atmosphere, but after supporting Pt onto these catalysts, both the activity and selectivity towards isomerization increased \cite{42}. On the basis of IR studies, Gao et al. concluded that sulfates on the surface of ZrO$_2$ may be partially reduced leading to a decrease in the acidic sites. Pt loading reduces the inhibition observed in SO$_4^{2-}$/ZrO$_2$ in hydrogen and hence the activity of the catalyst is retained. These authors also suggested formation of new strong Lewis and Bronsted acid sites with the addition of Pt in the presence of hydrogen.

1.4 Characterization of SZ catalysts

Extensive studies have been carried out using various characterization techniques in order to gain insight into a number of important properties of SZ catalysts including: (i) the nature of acid sites, (ii) the crystalline structure of the catalysts, (iii) the state and role of the added noble metals (such as Pt). The following is a summary of the most recent reports on characterization of SZ-based strong solid acid catalysts.

1.4.1 Surface area

The surface area of a sulfated zirconia is larger than that of an unsulfated zirconia calcined at the same temperature \cite{14, 20, 43}. The addition of sulfate ions to hydrous zirconia is known to stabilize zirconia upon crystallization and retard the crystal growth as well as sintering \cite{18} that normally decreases active surface area \cite{44}. Addition to sulfate ions to zirconia is essentially beneficial on this respect. In addition it also lead to creation of the acidic function on the zirconia surface.

Surface areas for SZ calcined at temperatures between 550°C to 650°C range from
90 - 120 m²/gm. The amorphous zirconia precursor usually has a surface area in the range of 200-250 m²/gm, indicating loss of surface area that accompanies calcination. Jaenicke and coworkers [45, 46] have proposed that digestion of zirconium hydroxide gel for longer time increases the surface area of the amorphous hydroxide. The surface area could be further increased by digestion in the presence of an alkali such as NaOH. Zr(OH)₄ with surface area exceeding 350 m²/gm have been reported. Loss in surface area upon calcination of the zirconia precursor increases as the calcination temperature is increased.

A number of research groups have reported successful preparation of mesoporous SO₄²⁻/ZrO₂ with higher than usual surface areas by various methods including refluxing [15], surfactant-assisted synthesis [47], liquid-crystal templating [48] and most recently by Sun et al. [49] who supported SO₄²⁻/ZrO₂ onto a MCM-41 material.

1.4.2 Phase studies and calcination temperature

SZ is most active when it has been prepared by calcination between a temperature of 500 to 650°C [8]. Using x-ray diffraction, it has been observed to exist in a meta-stable tetragonal crystalline phase [11, 32, 43]. Lower calcination temperature (less than 500°C) does not lead to crystallization and renders the catalyst amorphous. At higher calcination temperature (>800°C), oxidation and loss of sulfur species from the surface cause the zirconia to experience phase change to a thermodynamically more favorable monoclinic phase [37]. The zirconia samples with increasing sulfate content display increasing resistance to crystallize to the meta-stable tetragonal and then to the monoclinic phase [8, 43]. Norman et al. [44, 50] have suggested that the presence of bridging sulfate in SO₄²⁻/ZrO₂ causes a) improved thermal stability over hydroxyl bridges, and b) change in Zr-Zr separation.
to 3.5-4.3 Å for the sulfate bridges from 3.3-3.7 Å for hydroxyl bridges due to replacement of SO$_4^{2-}$ for OH$^-$.

Morterra et al. [51] have suggested that presence of the tetragonal crystalline phase is necessary for catalytic activity. However, Farcasiu et al. [52] reported that only the calcination temperature is important for creating catalytically active sites. More recently, Stichert and Schüth [26] reported a catalytically active catalyst with high surface monoclinic phase. It seems that crystalline phase is not particularly relevant for attaining good activity of the catalyst.

1.4.3 Temperature programmed studies

Temperature-programmed desorption (TPD) method is usually used for the estimation of the chemisorption uptake by the integration of TPD peaks. Depending on the probe molecule used, this technique may provide information on the dispersion of active surface of the metal component, the strength and the relative amount of acid sites etc. In the case of SZ catalysts, bases such as ammonia [13], pyridine [53], and benzene [54] have been used for probing the acid sites. However, for SZ-based catalysts, the strong interaction between the adsorbate molecules and the surface sulfate ions preclude the use of TPD to investigate acidity. In addition, due to the strong oxidizing ability of the sulfate groups, the adsorbed species decompose oxidatively under TPD conditions at temperatures that do not correlate to the acid strength. Even then, TPD of small and stable molecules such as CO and H$_2$ is still used.

Temperature programmed oxidation (TPO) is another similar method commonly used to investigate the carbonaceous species that result in catalyst deactivation. Alvarez et al. [55] measured CO$_2$ signal during TPO of deactivated metal-modified SZ catalysts to obtain information of coke deposition. They found that Pt inhibited
the coke formation significantly more than Fe/Mn or Ni.

Using temperature-programmed reduction (TPR) of SZ and Pt/SZ catalysts, Xu and Sachtler [56] found that up to 50% of sulfate groups were reduced to SO$_2$ and the remaining reduced to S$^-$ species. In the presence of Pt, they observed formation of H$_2$S alone. Complete reduction of sulfate groups resulted in loss of catalytic activity possible due to a marked decrease in Brønsted acid strength.

Wei et al. [57] used TGA-DTA-MS coupled technique to study thermal decomposition of Zr$_2$(SO$_4$)(OH)$_6$. They noticed a rapid mass loss in three stages: a) until 403°C, b) between 403 to 570°C, and c) 570 to 880°C. They also report evolution of sulfur in the form of SO$_2$ and SO near the temperature 575°C.

Song and Sayari [8] briefly mentioned DTA of Zr(OH)$_4$ and sulfated Zr(OH)$_4$ in which an exothermic peak attributed to crystallization of ZrO$_2$ shifts from 410°C to a higher temperature of 530°C after addition of sulfur. The so-called glow phenomenon and its role during the calcination of sulfated Zr hydroxides has been investigated recently [58] (see Figure 1.5) and seems to play some role in the final catalyst and its activity. Tatsumi et al. suggested use of the isothermal peak in estimating the catalytic activity of the SZ catalysts [59].

Stichert et al. [27] who reported an active monoclinic sulfated zirconia, performed TGA on variously aged samples and observed two distinct regions of weight loss (Figure 1.6). The loss between room temperature to about 200°C is due to loss of physisorbed water, whereas the second one is due to loss of sulfate groups. Using a MS, they detected SO$_2$ and its fragmentation products corresponding to the loss in weight at a temperature above 550°C (823K). The loss of weight from the uncalcined samples continued up to 1000°C.
Figure 1.5. Bed temperature vs. oven temperature during calcination of zirconium hydroxide [58]. Left: A – Zr hydroxide, B – sulfated Zr hydroxide, C – 2 wt% Fe, D – 2 wt% Mn. Right: Sulfated zirconium hydroxide with 2 wt% Mn, A – 25gm, B – 12gm, C – 3gm.

Figure 1.6. Thermal weight loss of the calcined samples in the temperature range between 20°C and 1000°C [27] (SZ-1 to SZ-5 have increasing aging times during their preparation).
1.4.4 Acid strength

The Hammett Acidity function ($H_0$) is a thermodynamic measure of the potential of an acid to donate a proton to a neutral base. It is defined as [60]:

$$H_0 = pK_{BH^+} - \log \left( \frac{[BH^+]}{[B]} \right)$$

(1.1)

where $[B]$ is the concentration of indicator B, $[BH^+]$ is the concentration of its conjugated acid $BH^+$, and $pK_{BH^+}$ is equal to $-\log(K_{BH^+})$. $K_{BH^+}$ is the equilibrium constant for

$$BH^+ \rightarrow B + H^+$$

(1.2)

Acid strength of solutions are typically measured with a family of indicators of varying base strengths, i.e., Hammett indicators. Color changes indicate whether the indicators are protonated, and spectroscopic measurements provide a measure of the degree of protonation. Typically, the solid is covered with an indicator and titrated against a base to determine the value of $H_0$. The lower the value for $H_0$, stronger the acid. 100% pure sulfuric acid has an $H_0$ value of −11.94. A superacid is defined as an acid with Hammett Acidity function lower than that of 100% Sulfuric acid [61]. Acid strengths of some strong liquid and solid acids are indicated in Figure 1.7. Arata et al. [4] measured $H_0$ of −14.52 and later reported a value of −16.04 [5], thus claiming SZ as a superacid with acidity almost 1000 times stronger than that of 100% sulfuric acid.

Measurement of acidity with Hammett indicators is not suitable for solid acids because of the following reasons – (a) solids acid are usually opaque and/or colored solids and do not allow easy observation of color change of Hammett indicators, (b) usually the acid sites on the surface of varying strength and only a few very active
Figure 1.7. Acid strength of liquid and solid acids as determined by Hammett-indicator method. [92]
sites act in the catalysis of hydrocarbon reactions and (c) many solid acids (including SZ) possess very strong oxidation capability and can oxidatively interact with the Hammett indicators leading to uncertain color change. Alternate, acidity measuring techniques have been used instead. These include temperature programmed desorption of adsorbed pyridine coupled with infra-red measurements [37], adsorption of acetonitrile with FT-IR and proton NMR [7] among others. It is now commonly accepted that SZ does not have superacidity but is comparable to that of some zeolites such as H-M and ZSM-5.

Detailed studies with the aim of clarifying the origin and the nature of the active sites on SZ, have been performed and a number of structural models have been put forward. Yadav and Nair [63] recently reviewed this subject in much detail. Various researchers have claimed that the isomerization activity is due to the presence of only Lewis acid sites [12, 64], or mainly Lewis acid sites with some Brønsted acidity [24, 65], and others [17, 20] claiming presence of both types of acid sites on the surface.

1.4.5 Hydration studies

The extent of hydration of the catalyst surface has been suggested to be one of the determining factors governing ratio of Brønsted acid sites to Lewis acid sites [66]. An activation treatment to remove absorbed water before reactions is found to be necessary for high activity. Gonzalez et al. [67, 68] have performed extensive studies on the hydration state of the commercial SZ catalysts. They found that too much water on the surface or too little OH groups decrease the overall activity and concluded that an optimum temperature for drying is important.

Vedrine and co-workers [69] suggested that surface sites on SZ catalyst may need an optimum quantity of water to be active, and proposed that a combination
of Brønsted acid sites and surface bound water is needed to for catalytic activity. On the other hand, Morterra et al. [16] as well as Davis and co-workers [70] showed that presence of water poisons the acid sites. Babou et al. [69], Comelli et al. [11] and Zhang et al. [71] found in spectroscopic studies of adsorbed basic probe molecules that water transforms Lewis acid sites into Brønsted acid sites. In contrast, Dumesic and co-workers [72, 73] used microcalorimetric and infrared measurements to show that surface rehydration does not alter the number or the strength of the acid sites. According to them, addition of water to a dehydrated catalyst did not convert Lewis acid sites to Brønsted acid sites.

1.4.6 Spectroscopic studies

Infrared spectroscopy is widely used to investigate the nature and strength of Lewis and Brønsted acids on solid catalysts. Weak bases such as CO, H$_2$O, pyridine etc. are routinely used as probe molecules. Using in-situ IR spectroscopy during calcination, activation, reaction and deactivation can provide reliable information on the properties of active sites and acid sites on catalysts. Detailed literature review on IR spectroscopy with SZ-based catalysts is included in the chapter 5.

X-ray photoelectron spectroscopy is another tool routinely used to investigate the state of elements in the near surface region of solids. The state of platinum in activated Pt/SZ is still being debated. Pt on SZ is unusual since it does not adsorb CO or H$_2$ appreciably nor does it show hydrogenation or hydrogenolysis activity [74].

Enhanced X-ray Absorption Fine Structure Spectroscopy (EXAFS) and X-ray Absorption Near-Edge Spectroscopy (XANES) are relatively newer addition to set of tools available for characterizing bulk materials. By monitoring absorption of highly energized x-ray over the catalyst particle, one can extract information about
the order and neighbors of a particular element, bond length and chemical state of
the element.

More details about published works done on characterizing Pt is reviewed in chapter 4.

1.5 Catalytic activity and deactivation

Although, the SZ-based catalysts have been found suitable for catalyzing nu-
merous industrial reactions [63], the following sections selectively highlight the use
of such catalysts for n-alkane isomerization reactions.

1.5.1 Isomerization activity

The catalytic performance of conventional SZ catalysts for n-alkanes, in partic-
ular – n-butane isomerization has been studied extensively [8, 63]. The catalyst
exhibits a high initial activity over a wide temperature range of 100-300°C but
deactivates quickly. Figure 1.8 presents a typical profile for n-butane conversion
versus reaction time-on-stream (TOS). It is believed that coke formed during the
catalyst deactivation blocked the acid sites and other active sites on the catalyst
surface [54]. Addition of Pt and the presence of hydrogen in the reaction system can
somewhat inhibit the formation of carbonaceous species thus prolonging the catalyst
life. However H₂ has a negative effect on the isomerization of n-butane. Increase in
temperature favors the conversion of hydrocarbons, but at the same time results in
more cracking products at the expense of isomerization.

By using modifiers such as Fe and/or Mn, it has been possible to achieve reaction
rates that are up to 3 orders of magnitude that that for pure SZ. The reaction can
be carried out at much lower temperatures [75, 76] as well. It is found that the
low-temperature n-butane conversion vs. reaction time-on-stream has an induction
period as shown in Figure 1.9. The conversion profile at low temperatures is com-
Figure 1.8. Conversion vs. TOS for catalytic isomerization of n-butane on SZ catalysts [15]

Figure 1.9. Typical reaction profile for n-butane isomerization at low temperature [15]
prised of two distinct regimes – a break-in period followed by a slow deactivation period. It is now well accepted that the period leading to the maximum conversion during induction period corresponds to the formation of reaction intermediates, which then get consumed in a competition between formation and consumption. Resasco and co-workers found that the induction period is a strong function of the reaction temperature and the partial pressure of n-butane \([77, 78]\). Zarkalis et al. \([79]\) found that higher reaction temperature usually resulted in shorter induction period for n-butane isomerization.

Similar extensive studies have been also conducted for catalytic isomerization of higher alkanes such as n-pentane \([41, 80]\), n-hexane \([81, 82]\), n-heptane \([83, 84]\) and n-hexadecane \([83, 85]\) among others. In each case, SZ-based catalysts had a higher activity than the chlorided-alumina or other prevalent acid catalysts. SZ-based catalysts also suffer due to deactivation in each of these studies except when the catalytic tests were carried out under high pressure conditions in the presence of hydrogen.

It has been suggested that the pathway for isomerization for n-butane is different than that for higher alkanes. For n-butane, the pathway agreed to by most is that of a bi-molecular or inter-molecular mechanism wherein a n-butene intermediate is formed which isomerizes to isobutene by \(\beta\)-scission of alkylated C\(_8\) intermediate, \([86]\) (Figure 1.10). For n-pentane isomerization, the opinion of the researchers is not unanimous and contrasting opinions abound. It has been suggested that the pathway in case of n-pentane isomerization is a monomolecular and that isomerization proceeds via a protonated dimethylcyclopropane intermediate \([80, 87]\).

Liu and Sachtler \([80]\) were among the first to report a stable isomerization activity for n-pentane with Pt/SZ catalysts (Figure 1.11), however the conditions used were extreme – very high hydrogen to alkane ratio (2.2:0.054 bar), high total pressure.
Figure 1.10. Schematic of bimolecular mechanism of n-butane isomerization. The initiation step requires formation of carbenium ion.

Figure 1.11. Reaction of n-pentane as a function of TOS over Pt/SZ catalyst at 206°C. [80]
(11 bar) and temperature (200°C). By comparing the isomerization of n-pentane and n-butane over Pt-modified commercial SZ catalysts and they reported on the effects of varying hydrogen pressure on the activity. They found that isomerization rate for n-pentane was unaffected by the hydrogen partial pressure. They also reported that isomerization of n-pentane to isopentane was not a function of the formation of isopentene based on their calculation of the equilibrium concentration of n-pentene gas phase intermediate at the catalyst surface. Thus, they suggested that Pt modification aided in decreasing the extent of deactivation without interfering in the actual isomerization mechanism.

In contrast, Smith et al. [88] reported very low n-pentane conversion (~3-5%) for Pt/SZ catalysts for isomerization carried out at 70-130°C and low pressures. These authors prepared the catalyst used in their study with an “oxidative redispersion” stage.

Gates et al. used commercial SZ promoted with Fe and Mn to study the isomerization of n-pentane and n-butane [89]. They found that Fe/Mn promotion increased the reaction rate by up to two orders of magnitude. In addition, they also observed that addition of Pt and introduction of hydrogen in the feed stream decreased the rate of deactivation. During isomerization of n-pentane on Fe/Mn-promoted SZ-based catalysts, a different activity profile is seen. An induction period similar to the one observed for n-butane has been reported (Figure 1.12). It was suggested that monomolecular and bimolecular mechanisms were operative during the reaction and that both isomerization and disproportionation reactions were occurring. The maximum in conversion achieved was about 5-6% at 50°C.

Arata and co-workers [59] investigated the effect of the pH of the mother solution in the preparation of SZ catalysts. They suggested that the activity of the SZ catalyst could be estimated from the exothermic peak in the DTA.
Figure 1.12. Effect of addition of Pt to FMSZ and H\textsubscript{2} to the feed on the conversion of n-pentane to isopentane. (○) FMSZ, (□) PtFMSZ and (△) PtFMSZ with H\textsubscript{2} in feed. Arrows indicate time at which the total conversion declined to 3% of maximum.

Other groups have used various kinds of solid acid catalysts to investigate the isomerization of n-pentane. Petkovic et al. [90], Scheithaur et al. [91–93], Vartuli et al. [94] have used different types of characterization methods to investigate tungstated-zirconia catalysts with n-pentane isomerization. The isomerization of n-pentane has also been studied over H\textsubscript{3}PW\textsubscript{12}O\textsubscript{40} heteropolyacids, Mordenite zeolites as well as hybrid catalysts.

Based on the available published reports on n-pentane isomerization over SZ-based catalysts, it is obvious that no one has reported a SZ-based catalyst that can sustain high activity and selectivity during n-pentane isomerization, in particular, to be of use in practice. An unclear understanding of the pathway followed, makes the search of such a catalyst further complicated and challenging. A further contentious issue is the role played by the modifiers and promoters in inhibiting the deactivation of SZ catalysts.
1.5.2 Role of modifiers and promoters

Addition of metals such as Pt, Pd to SZ catalyst can significantly improve the catalytic performance by (a) increasing activity, (b) increasing selectivity towards isomerization products and (c) stabilizing catalytic activity. In an earlier work done in our group, Risch and Wolf [95] have shown that addition of Pt to an unmodified SZ catalysts inhibits the deactivation suffered by SZ catalyst during n-butane and n-pentane isomerization. Similar results have been reported for other Group VIII metals as well [8].

The beneficial effect of Pt is postulated to be due to either its participation in a bifunctional manner or to its dissociative capability in the presence of hydrogen, which spills over the surface forming H\(^+\) that participates in the reaction sequence. In their investigation on the role of Pt on SZ, Tabora and Davis [76] found that Pt is able to stabilize catalytic activity, even in the absence of hydrogen.

Usually Pt-modified catalysts are normally prepared with approx. 1-2% Pt. However, Hino and Arata [96] achieved maximum activity for n-butane isomerization under mild pulse-reaction conditions with Pt content of almost 7.5%. In contrast, Tabora and Davis [76] found the optimum loading of Pt for isomerization at 50\(^\circ\)C to be 0.74 wt%. A further increase in Pt loading did not result in any significant change. They attributed this to aggregation of reduced Pt which did not contribute to the catalytic activity.

Other noble metals have been added as modifiers. Occelli et al. used Cu on SZ for n-pentane isomerization. Ir is also found to have similar effect as that of Pt to the catalytic performance of SZ [18]. Another class of elements added to SZ can be classified as promoters, which enhance the activity at low temperatures as opposed to modifiers, which in effect, decrease the rate of deactivation. Fe, Mn and Ga are such promoters. Their role is certainly not very clear. Currently, most
researchers do not consider n-butane isomerization at low temperature to be entirely acid catalyzed. Fe and Mn, present as oxides, have strong dehydrogenation potential to initialize butane isomerization. At the same time, it has also been suggested that Fe and Mn may not be catalytically involved in the isomerization reactions.

1.5.3 Deactivation

SZ-based catalysts undergo deactivation during isomerization of alkanes due to reasons including – (a) elimination of acid sites, (b) loss of surface sulfur species, (c) a change in catalyst structure and (d) formation and deposition of coke.

Ng and Horvat [97] observed hydrogen sulfide as one of the reactor effluent gas in n-butane isomerization at 250°C and concluded that deactivation is at least partly due to reduction of surface sulfur by either n-butane or by in-situ generated hydrogen and its subsequent loss. Xu and Sachtl and others have shown that sulfate groups can be reduced in presence of hydrogen [56, 75, 98]. However, the catalytic activity of a used SZ-based catalyst can be regenerated upon calcination in air. The loss of sulfur from the catalyst due to reduction during reactions seems to have a minor effect on the catalyst deactivation.

Li and Stair [99] demonstrated that a phase of deactivated sulfated zirconia was nearly identical to that of the monoclinic phase whereas the active catalyst surface was dominated by the tetragonal phase. Regeneration in air seems to restore the tetragonal structure.

Most of the published papers on deactivation consider coke formation during isomerization to be the dominant reason for deactivation. It is now widely accepted that n-butane isomerization occurs via a bi-molecular pathway, in which n-butane undergoes dehydrogenation to form unsaturated intermediates. These intermediates subsequently lead to the formation of coke. Dumesic and co-workers [100] compared
the deactivation observed during n-butane and iso-butane isomerization under same conditions. Since branched C\textsubscript{4} species cannot form conjugated C=C, they attributed the rapid deactivation during n-butane isomerization primarily to coke formation. Gonzalez et al. used XPS on active as well as deactivated SZ catalysts and concluded that the deactivation occurs due to carbon deposition \[101\].

For deactivation during higher molecule (C\textsubscript{5+}) isomerization, it is understood that carbonaceous species formed by the cracking of molecules over the strong acid sites are the precursors of coke. Paal and co-workers \[102\] attributed reversible deactivation of Pt/\text{SO}_4^{2-}/\text{ZrO}_2 during n-hexane isomerization to carbon accumulation and slight removal of surface sulfur on continued reaction. However, in a recent paper \[103\], they suggest deactivation in the same reaction due to partial reduction of sulfate groups rather than carbon accumulation, on the basis of careful XPS studies. Another paper \[7\] claimed that the presence of Pt and hydrogen promoted the reduction of sulfates to sulfide. This species supposedly remains on the catalyst as Pt sulfide \[104\]. It has also been suggested that in a deactivated catalyst, platinum undergoes re-dispersion and gets buried under zirconia support layers \[105\]. Lack of sufficient Pt on the surface thus leads to hindrance in hydrogen transfer leading to accumulation of surface carbon deposits.

1.6 Objectives and organization of the thesis

Sulfated zirconia is known to be a versatile catalyst with good activity for alkane activation even at low temperatures. In spite of numerous research papers and reports available since the early 90s, there is still no clear understanding of either the nature of acid sites and the state or the role of promoters.

The present study is focused on the following aspects:

1. Synthesis of highly active Pt-containing SZ-based solid acid catalyst.
2. Evaluating the activity of the SZ catalysts for n-pentane isomerization and effect of different parameters.

3. Characterization of the obtained SZ catalysts by techniques that probe the structure of the catalysts.

4. Characterization of the Pt modifier used on the SZ catalysts and its effect on the support.

5. Basic understanding of the simple aspects of deactivation leading to a mechanistic model.

The thesis is presented in seven chapters. This chapter was an attempt to cover the science and catalysis of SZ-based catalysts in some detail. Chapter 2 provides a detailed description of the experimental methods used during the course of this work for preparation, characterization and evaluation of catalytic activity.

In Chapter 3 the results of the synthesis and characterization tests performed on the obtained catalyst are presented. The results of activity of the catalysts during n-pentane isomerization as well as effect of some variables on the conversion and selectivity are provided. Chapter 4 deals with the characterization of platinum by means of X-ray photoelectron spectroscopy and X-ray absorption fine structure spectroscopy. Effects of the preparation procedure on the state of Pt in the catalysts are elucidated. In-situ diffuse reflectance studies on various SZ catalysts, during pretreatments and under reaction conditions are detailed in Chapter 5.

Chapter 6 explains a hypothetical model that attempts to elucidate the results of preparation and activity studies. A mechanistic model based on the hypothesis is used to simulate the results obtained for activity studies on the basis of results of characterization methods.
Finally, a summary of the work presented in the thesis and recommendations for future work are put forward in Chapter 7.
2.1 Introduction

The methods and apparatus described in this chapter were utilized to obtain the experimental data presented in the subsequent chapters. Each section describes the respective equipment as well as the procedure followed. The catalytic activity of modified sulfated zirconia catalysts is affected by the preparation method used to prepare sulfated zirconia which in turn is affected by a large number of variables, including starting compounds, preparation conditions, acid site density, pretreatment procedure and reaction conditions. Synthesis procedures used were adopted from a comprehensive survey of synthesis methods reported in the literature and from a previous work [106]. New synthesis procedures were later devised and further improved to prepare new catalysts that yield higher activity and stability against deactivation.

2.2 Catalyst synthesis

Synthesis of the catalysts was done at ambient atmospheric pressure by a standard solution precipitation method in glass vessels. Sulfated zirconia catalyst was prepared by a two step method and Pt-containing catalysts requiring one more step as shown in the schematic for a 3-step catalyst synthesis method Figure 2.1. Since the preparation of the SZ catalyst is sensitive to numerous parameters, it is
described in full detail below.

2.2.1 Zirconium hydroxide synthesis

The catalyst was precipitated from titration of acidic zirconium salt (ZrOCl$_2$) with a basic solution (30% ammonium hydroxide solution) until the desired pH of 8-9 was attained. Constant heavy stirring was maintained to ensure proper mixing and to avoid settling of the precipitate. The pH was monitored in-situ during the titration with an pH/mV/°C meter (Oakton) connected to a sealed combination electrode with silver/silver chloride reference (Cole-Parmer). The meter and the electrode were calibrated prior to use by washing with tap water and using buffer solutions of pH = 4.0, 7.0 and 10.0 (Aldrich). The calibration was repeated at least 3 times to ensure quick and accurate response. After attaining the desired final pH, the precipitate was left under stirring for ca. 30 minutes. No heating was employed, however, the heat of reaction of zirconium salt and ammonium hydroxide caused an increase of temperature from room to ca. 35°C.

Vacuum filtration procedure was used to recover the zirconium hydroxide powder from the synthesis slurry. The apparatus consisted of a Buchner funnel and an Erlenmeyer flask with a sidearm. Two sheets of filter paper (Whitman) were placed in the funnel and wetted prior to filtering the gel-like slurry. Distilled and de-ionized (DD) water was used to ensure proper filtration and to avoid formation of a dense cake.

After filtering, the zirconium hydroxide cake was washed by pouring DD water over it. This step led to elimination of excess ions from the synthesis products. The concentration of ions was measured by the pH meter to ensure almost full elimination. Approximately 1 liter of DD water was used to obtain a gel with no residual ions in it. Once all the water had passed through, the filter cake was placed
Figure 2.1. Schematic of the 3-step synthesis method used in this thesis
in a petri dish and kept in an oven to dry in air for at least 3-4 hours at a temperature of 95°C.

The volume of the dried cake was almost 75% less than that of the filtered, washed cake. The dried cake was ground and the resulting powder is referred as zirconium hydroxide. Gmelin’s *Handbook of Inorganic Chemistry* does not attribute any definite formula to this compound [107]. Instead a ZrO$_2$.xH$_2$O ($x = 2$ or more) formula was suggested. Hereafter, Zr(OH)$_2$ or Zr(OH)$_x$ also refers to the same substance.

In some synthesis schemes, ammonium hydroxide was replaced by sodium hydroxide as a precipitant. This resulted in a zirconium hydroxide gel which had sodium as part of its matrix structure as explained later (Chapter [3]).

In other catalyst synthesis, high surface area commercial zirconium hydroxide supplied by MEI Inc. was used after suitable treatments. The zirconium hydroxide obtained was refluxed at 100°C without stirring in a 5M sodium hydroxide (NaOH) solution added in 1:10 ratio (i.e. 10 ml of NaOH sol. per gram of zirconium hydroxide). The slurry was then filtered and washed with 0.1M ammonium nitrate solution (100 cc per gm of zirconium hydroxide used initially). This step ensured removal of excess sodium hydroxide from the slurry. The filtrate cake was then left in ambient environment to dry for 24 hours. The zirconia thus prepared is referred to with a suffix -Na.

To eliminate sodium from the zirconium hydroxide matrix, the hydroxide slurry resulting from refluxing and filtration with 0.1M ammonium nitrate solution was further washed with 20 cc/g of 2.25M ammonium nitrate solution at 100°C in a conical flask for at least 3 hours. The ammonium nitrate solution was decanted and the process was repeated 2 more times. Doing so ensured that all sodium is completely leached from the hydroxide slurry. The slurry was recovered by filtration.
as above and dried to be used for sulfation. A suffix of -$Na-\ell$ is used to refer to the catalyst prepared as described above.

In other cases, the high surface area commercial zirconium hydroxide (MEI, Grade FZO-922/01) was refluxed at 100 °C without stirring in a flat bottom conical flask. The refluxing was carried out in solutions of ammonium hydroxide (pH=12), distilled water (pH=7.0) and zirconium oxy-nitrate ($\text{ZrO(NO}_3\text{)}_2$, pH=1.8) added as 10 ml/g of Zr hydroxide used. This refluxing was carried out for a period of 24 hours. The slurry was then filtered and washed with excess of DD water. The filtered cake was then dried in stagnant air in an oven maintained at a temperature of 95 °C. The dried powder was then used for sulfation to make sulfated zirconia. These catalysts are referred to by adding a suffix -$R$ to SZ and their pH as subscript.

2.2.2 Sulfation

A 0.5M solution of sulfuric acid is used to add sulfate group to zirconium hydroxide. The volume of the solution used is such that sulfur loading on the dried powder is 4% by weight. The impregnation method used is incipient wetness which means that the solution is added drop wise till the zirconium hydroxide powder is just wet. This is done in at least 3 stages of adding sulfuric acid solution and drying in the oven for 60-90 minutes before further sulfur addition. The final dried sulfated zirconium hydroxide is then calcined in a quartz tube in dry air flowing at 40 cc/min., ramping up to the desired temperature (550-650 °C) in 60 minutes and maintained at that temperature for 3 hours. The catalyst powder is then allowed to cool in flowing air. The resulting powder is termed as sulfated zirconia or SZ. The temperature used for calcining the sulfated zirconia is written as subscript to SZ (e.g. $\text{SZ}_{650}$).
2.2.3 Addition of platinum

Platinum was added to the SZ powder by means of precursors such as chloroplatinic acid (CPA), salts of tetra ammonium platinum (t-AP) or platinum nitrate. An amount of salt corresponding to a loading of 1% by wt. platinum on SZ is dissolved in 5-10 ml. of DD water. To perform the impregnation, the catalyst is spread evenly in an evaporating dish and the metal salt solution is added drop wise via a pipette till incipient wetness. The catalyst is dried at 95 °C for 60-90 minutes before repeating the process till all the solution is used up.

The platinum loaded SZ catalyst is then either (a) reduced in hydrogen flow or (b) oxidized in air. Oxidation was carried out in air flowing at a rate of 40 cc/min. with temperature ramping from room temperature till 500 °C in 60 minutes followed by a soak at the temperature of 500 °C for 180 minutes. Reduction was carried out in high hydrogen flow rate on 150 cc/min. The temperature was ramped till 170 °C in 30 minutes, followed by a slow ramping till a temperature of 300 °C in 120 minutes and keeping the temperature unchanged at 300 °C for further 120 minutes. For longer reduction \(r_l\), the ramping and maintaining at 300 °C lasted for 240 minutes each instead of 120 minutes.

The platinum-containing catalysts prepared by reduction are referred to with the suffix \(r\) with a subscript of \(s\) for short reduction and \(l\) for longer reduction. The oxidized catalysts have \(o\) as suffix to Pt in Pt/SZ.

Thus a catalyst named Pt\((r_s,o)\)/SZ\(_{650}\)-Na describes a catalyst prepared from zirconium hydroxide that was refluxed with sodium hydroxide (no leaching), sulfated and calcined at 650 °C. After addition of platinum, the catalyst was reduced for short duration (4 hours) followed by oxidation.
2.3 Catalytic activity and kinetic studies

2.3.1 Reaction system

The reactor system used for activity studies is as shown in Figure 2.2. The reactor flow system comprised of four mass flow controllers (5850 series, Brooks Instruments) for allowing measured flows of pure or mixed gases to the reactor. The flow meters were automated and computer controlled (LabVIEW2, National Instruments). All lines used were constructed of 1/8 in. SS 316 grade steel tubes. The piping consisted of a reactor line and a bypass line of equal length such that pressure drop across each line was similar. This was an important consideration to ensure smooth switching of gas flow between the two lines at the start of the reaction after the feed composition and flow rate had been established through the bypass line. The reactor type used for all studies is a fixed bed, isothermal, downward flow reactor.

The reactor and the bypass lines converged at a three way valve downstream from the reactor. The effluent passed through a 6-port sampling valve and then to soap bubble flow meter, used to measure flow rates, and finally to the vent line.

Air, oxygen and nitrogen were first passed through a gas purifier (Alltech) that consisted of calcium sulfate and 5Å molecular sieve in series. HP grade helium was used as carrier gas and diluent gas for activity studies, and was passed through an Alltech oxy-trap also. n-Butane was used in its as received form. n-Pentane was obtained from Aldrich Chem. with 99% purity.

The reactor was heated with a custom heating jacket (Amptek) controlled by a temperature controller (Omega CN-2010 model). A K-type chromel-aluminum thermocouple placed in a glass tube in the reactor was used to measure the catalyst bed temperature. The reactor effluent lines were wrapped with flexible electric heating tapes (BriskHeat) maintained at a temperature of 75 °C to avoid condensa-
Figure 2.2. Schematic of the reactor system used in activity studies
tion of heavier reaction products in the lines. The power output for the tapes was controlled with a variac set at 30% output.

The reactor consisted of a quartz tube 3/8 in. ID and 19 in. long with indentations in the wall 12 in. from the top that were used to support the catalyst bed. The top consisted of a 1/4 in. tube fitting for the feed gases and a thermocouple well 12 in. long and 1/8 in. diameter, which was submerged in the catalyst bed. The bottom was also fitted for a 1/4 in. tube fitting. A rubber o-ring was placed between each of the top & bottom pieces and the reactor body. The pieces were then held with the reactor body with c-clamps.

In some experiments, a single sample loop (25 µL) was used to collect and analyze the effluent gases from the reactor. The sampling was limited by the gas chromatographic analysis which took up to fifteen minutes to complete and only 3-4 samples could be collected during a run lasting 60 minutes.

2.3.2 Gas chromatographic method

The gas chromatographic analysis was optimized to provide as fast as possible results without sacrificing accuracy. Product analysis was performed on (a) a HP 5710A Gas Chromatograph equipped with two flame ionization detectors and (b) an HP 5890 Series II Gas chromatograph equipped with both a thermal conductivity detector (TCD) and a flame ionization detector (FID). The results reported in subsequent chapters were analyzed by using an FID. Two different kinds of separation packed columns were used. Column A was a seven foot, one-eighth inch stainless tubing (SS) wound in a six inch coil packed with 0.19% Picric acid supported on Graphpac-GC, 80/100 support (Alltech). Later, a ten foot, one-eighth inch coiled SS tubing (column B) packed with Hayesep D 100/120 (Alltech) was used. Helium carrier gas flow rate was maintained at 35 cc/min throughout the analysis. Inlet
helium pressure to the GC was set at 60 psi to maintain constant carrier gas flow. For maximum FID sensitivity, air flow was set at 400 cc/min and hydrogen was set at 30 cc/min.

A temperature programmed ramp was employed during the analysis for faster elution of heavier (C$_5$, C$_6$) hydrocarbons. For each sample, the column A was held at 60°C for 2 minutes and then heated at a rate of 10°C/min to a final temperature of 100°C and maintained at that temperature until all C$_5$ and C$_6$ species were analyzed. The detector was maintained at a temperature of 300°C. The following settings of the detector were employed: attenuation = 8, range = 10. For column B, the temperature was ramped to 200°C from 120°C at a rate of 10°C/min and the total analysis took 20 minutes. The temperature of the detector was maintained at 200°C and auxiliary temperature was set at 150°C. The detector attenuation and range were both set at 0. The results from each analysis were scaled to that with attenuation of eight to obtain consistent results.

Peak position and detector response for the individual product species were calibrated using standardized gas mixtures. Scotty II analyzed gas (Scotty Specialty gas mix 219) consisting of C$_1$ - C$_6$ in nitrogen and Matheson MicroMat 14 #GMT-10407TC (Alltech #19774) was used. The gas was fed at a flow rate of 20 cc/min through the reactor system and samples were taken using a single loop sample valve. Calibration was performed at least three times to ensure reproducibility. An identical procedure was used to calibrate peak position and detector response for isomers of C$_4$, C$_5$ and C$_6$ (Matheson gas #GMT-10411TC, Alltech #M7018).

Peak analysis was performed with a Hewlett-Packard Integrator 3395 and HP Chemstation software. The detector response was also sent to a chart recorder. The following settings were used on the integrator: attenuation = 0, area rejection = 0,
threshold = 0 and peak width = 0.04.

2.3.3 Kinetic analysis

The conversion, isomerization rate and isomerization selectivity were calculated based on the areas of GC signals of reaction products integrated by Chemstation software suite (HP). The peak area of each component in the product was normalized using calibration factors as obtained from the analysis of standard samples. This ensured that the peak-area ratios correspond to molar ratios of products. n-Pentane conversion was defined as

\[
\text{conversion (\%)} = \frac{A_{n-C_5,i} - A_{n-C_5,f}}{A_{n-C_5,i}} \times 100 \tag{2.1}
\]

where \(A_{n-C_5,i}\) and \(A_{n-C_5,f}\) represent the areas of the initial and final concentrations of n-Pentane, in other words, n-Pentane concentration before and after the reactor.

The selectivity towards isopentane was calculated as

\[
\text{selectivity (\%)} = \frac{A_{i-C_5}}{A_{n-C_5,i} - A_{n-C_5,f}} \times 100 \tag{2.2}
\]

where \(A_{i-C_5}\) represents the concentration of isopentane in the reactor exit stream.

The isomerization reaction rate was defined by the following equation:

\[
\text{isomerization rate (mol}^{-1} \cdot \text{gcat}^{-1} \cdot \text{s}^{-1}) = \frac{V \times C_t}{W \times 22400 \times 60 \times 100} \tag{2.3}
\]

where \(V\) represents the volumetric flow of n-pentane through the catalyst bed in cc per minute, \(C_t\) is the % conversion at time on stream \(t\), \(W\) is the catalyst weight. The number 22400 is the molar volume of an ideal gas.

2.4 Physical characterization techniques

The catalytic properties of a surface are determined by its composition and structure on the atomic scale. From a fundamental point of view, the ultimate goal
of catalyst characterization is to look at the surface atom by atom, and preferably under the reaction conditions or *in-operando*.

Establishing empirical relations between the factors that govern catalyst composition, particle size and shape, and pore dimensions on one side, and catalytic performance on the other are extremely useful in the process of catalyst development, although such relations may not give much fundamental insight on how the catalyst operates at a molecular level. Catalyst characterization in industrial research deals with the material science of the catalysts at a mesoscopic scale, whereas the fundamental catalysis research focuses on characterizing the surface of a catalyst at the microscopic or the atomic scale (Figure 1.2).

With the aim of characterizing the catalysts synthesized in the course of this work, the following characterization methods were employed. For the sake of clarity, the spectroscopic methods are presented in a separate section.

### 2.4.1 Nitrogen adsorption isotherm measurements

Nitrogen adsorption isotherm measurements were used to determine the surface area of the synthesized catalysts. The amount of nitrogen adsorbed by a porous material as a function of the partial pressure of nitrogen can be used to determine its surface area and the pore size distribution. Using N\textsubscript{2} adsorption, the mesoporosity of a catalytic material can be quantified.

These measurements were performed on a Quantachrome Monosorb unit operating at a nitrogen partial pressure of 0.3 in helium. Approximately 50 mg of sample was outgassed either in a U-shaped analysis tube or a Quantachrome flat bed sample holder. The degassing temperature of 200°C was maintained for 3 hours prior to each measurement. The tube containing the sample was then submerged in liquid nitrogen to adsorb gaseous nitrogen from the flow mixture and then heated by hot
air once the catalyst surface was saturated. The measurements were repeated at least three times on each sample to ensure accuracy. The BET surface area of the amount of the sample was displayed directly on the instrument. This value was then converted to specific surface area by normalizing with respect to weight of sample loaded. The Monosorb unit used 1-point method for evaluating the adsorption isotherm and did not yield any other information. Some of these BET surface areas were also measured on a Quantachrome Autosorb 1 unit which could perform a multi-point isotherm evaluation.

2.4.2 X-ray diffraction

X-ray diffraction (XRD) was used to determine the crystallinity and phase formation of the active sulfated-zirconia catalysts. The ordered tetragonal structure in sulfated-zirconia has a distinct diffraction peak characteristic of its d-spacing.

X-ray diffraction patterns were analyzed on a Scintag X-1 diffraction system equipped with Cu-Kα radiation and Peltier cooled solid state detector. Using XRD data, Bragg’s law is used to determine the inter-planar spacing form the diffraction peak angular location

\[
n\lambda = 2d_{hkl} \sin \theta
\]  

where \( n \) is the order of reflection (usually assumed 1), \( \lambda \) is the wavelength of Cu-Kα radiation, \( d_{hkl} \) is the inter-planar spacing and \( \theta \) is the Bragg’s angle at which diffraction occurs. Average crystallite size of the active catalyst was calculated using the Debye-Scherrer relationship which relates the diffraction peak width to the size of the crystal in [hkl] direction:

\[
L_{hkl} = \frac{K \lambda}{\beta_{hkl} \cos \theta}
\]  

where \( L_{hkl} \) is the average size of the crystal in [hkl] direction and \( K \) is the shape
factor (usually taken as 0.9). $\beta$ is the corrected peak width in radians, defined as $B - b$, where $B$ is the measured width of the diffraction line at half-height and $b$ is the instrumental broadening.

X-ray diffraction samples were prepared by first grinding the catalyst to a fine powder and then filling a Plexiglas sample holder to excess. The surface of the sample was then made smooth by carefully passing the side of a glass slide over the sample and removing the excess material. The sample holder with the sample powder was the placed upright in the Scintag diffractometer’s sample plate.

For measuring the crystallinity of the catalyst, the standard slit sizes were used. These included: source slit, 2°, source scatter slit, 4°, detector scatter slit, 0.5°, and detector slit, 0.3°. The diffraction patterns were recorded in a step mode at a scanning rate of 2°/minute.

2.4.3 Thermal analysis

Thermal gravimetric analysis (TGA) of selected samples was carried out to evaluate the losses of surface and bulk species due to combustion, dehydration or hydration with the increase in temperature. Differential thermal analysis (DTA) of sulfate loaded zirconium hydroxide was performed in a DTA-TGA equipment (TA Instruments, model SDT 29600).

Approximate 10-12 mg of sulfated zirconium hydroxide was loaded in a ceramic sample holder pan which was placed on the sample arm of the instrument. A ceramic pan with an alumina standard was placed on the reference arm. Both the sample and the standard were heated at a constant rate of 5°C/min till either 550°C or 650°C followed by a soak at the specific temperature for 1 hour. Air flow of 100 cc/min NTP was maintained throughout the analysis. The data gathered from the analysis includes the weight and temperature difference between the sample and the
reference standard as a function of both time and temperature of the oven.

Similar analysis was also carried out on a Cahn Microbalance RG 113 TGA system. The electrobalance was set at a mass dial range of 10 and recorder range of 1. The sample holder basket was modified to allow for flow of air through the sample. The weight of the basket was zeroed by balancing it with equivalent amount of weights on the balancing arm of microbalance. Air flow was maintained at 50 cc/min NTP throughout the analysis. A positive flow of air was also maintained on the microbalance arm in order to avoid drift effects. The temperature programming included a ramp to 650°C in 125 minutes from room temperature, equivalent to 5°C/min and maintaining at that temperature for 30 more minutes. Only the weight of the sample as a function of time is available using this microbalance and was collected on a computer using a data acquisition software (Labview).

2.4.4 Sulfur analysis

Since there is a presence of labile sulfur species present on the surface, it is important to know the final sulfur content of the catalyst at different stages of preparation and use. Knowing the sulfur content can provide a clue to changes occurring during pretreatments and reaction itself.

Sulfur analysis was performed in an elemental combustion analyzer (Costech Instruments, ECA 4010) at the Center for Environmental Science and Technology (CEST), Notre Dame. A known weight (5-20 mg) of the sample was packed in tin foil cups. The cups were then contacted with air at high temperature (over 1000°C) which cause oxidation of S to SO\(_3\). The exhaust gases are analyzed in a specially adapted GC column for CO\(_2\), NO\(_2\) or SO\(_3\) from which the elemental concentration can be calculated. Each sample was analyzed at least twice to ensure accuracy. Sulfanilimide (18.62% wt S) was used as the standard in order to obtain a linear
calibration plot before each test. Each of the sample was analyzed at least 3 times in order to obtain reliable results.

Some of the samples were also analyzed by Galbraith Labs. Inc. (Knoxville, TN). They also used a combustion-based analysis according to the ASTM standards and methods. The results of the analysis performed at Galbraith validated the analysis performed with the elemental analyzer at CEST.

2.4.5 Pulse chemisorption

Using absorption of CO or H₂, the active surface area and subsequent dispersion of the metal on the supported catalyst can be determined. In this work, hydrogen was used as a chemisorbing gas onto the Pt/SZ catalysts. This was accomplished by injecting pulses of known volume of hydrogen onto the clean catalyst surface or pulse chemisorption.

A known amount of catalyst is put in the chemisorption reactor tube and reduced in pure hydrogen (40 cc/min) for 2 hour during a temperature program of ramping to 250°C in 1 hour and a soak at 250°C for further 1 hour. This was done to reduce the metal particles and remove other impurities present on the surface. After reduction, the catalyst was flushed with helium gas (40 cc/min) at the same temperature for 1 hour. The catalyst was then allowed to cool down to room temperature in the helium flow. The flushing of the catalyst allows removal of adsorbed hydrogen from the surface.

Hydrogen (5%H₂/Ar mix) was introduced into the carrier gas stream (Argon) by means of a six-way Varian valve mechanism controlled by computer program. The volume of the sample loop used is 1cc. Hydrogen adsorption on platinum is dissociative and it is assumed that one hydrogen atom is adsorbed per surface atom of platinum. Upon addition of the fraction of the pulses adsorbed until a steady
state is achieved, it is possible to calculate the number of surface platinum atoms per gm. of catalyst. The dispersion can be calculated by dividing the number of surface atoms determined by the amount of Pt loading known from the catalyst synthesis.

2.4.6 Platinum absorption study

Platinum absorption studies were performed in Prof. Regalbuto's Laboratory at UIC. These measurements involved measurement of the so-called Point of Zero-Charge (PZC) of the SZ surface, followed by adsorption experiments with two different kinds of Pt precursor compounds – chloroplatinic acid (CPA) and tetra-ammonium platinum chloride (t-APCl) at varying pH's.

A set of pH shift measurements were conducted by equilibrating a constant amount (corresponding to a surface loading of 500 m²/L and 1000 m²/L) of the SZ catalyst (SZ₅₅₀ and SZ₆₅₀) in solutions of increasing pH from 1 to 13. pH of the solution was measured before adding SZ and after vigorous shaking for 1 hr. From the curve between initial pH versus final pH, PZC was estimated as described by Park and Regalbuto [108].

In a similar fashion, adsorption experiments were performed on SZ₅₅₀ and SZ₆₅₀. The surface loading, or oxide area per liter of solution used was kept constant at 1000m²/L for measurements using t-APCl as platinum source, and 500m²/L when using CPA as platinum source. Fifty milliliters of dilute solution of platinum compound i.e. approx. 200ppm (t-APCl, SL = 1000m²/L) and 300ppm (CPA, SL = 500m²/L), adjusted to various pH values using dilute HCl or dilute NaOH solution, was added to oxide powders previously weighed into polypropylene bottles. The bottles were then shaken vigorously for 1 hr in a rotary shaker. The final pH of the solutions was then measured. 3 - 4 ml portion of the well-mixed solution-oxide slurry
was removed from the bottles and the solid was filtered to permit measurement of Pt concentrations in the liquid phase by ICP analysis. Adsorption density is calculated as the different between initial and final concentration of Pt divided by the surface loading, and is expressed as micromoles of Pt adsorbed per square meter (Γ).

The experimental results of the pH shift measurements were used to extract parameters for use in Revised Physical Adsorption model proposed in [109]. A preliminary estimation of the adsorption curve was performed using the calculated parameters and the RPA model.

2.5 Spectroscopic characterization methods

There are many ways to obtain information on the physico-chemical properties of solid catalytic materials. Figure 2.3 presents a diagram from which most of the techniques can be derived. Spectroscopic techniques are based on some type of excitation, represented by the in-going arrow in Figure 2.3, to which the catalyst responds as symbolized by the outgoing arrow.

Characterization techniques become surface sensitive if the particles or radia-
Figure 2.4. The electro-magnetic spectrum, along with common photon sources and a number of characterization techniques based on photons.

The information to be detected comes from the outer surface layers of the sample. Photons that are scattered, adsorbed or emitted by a catalyst provide a versatile source of information. Figure 2.4 shows the electro-magnetic spectrum along with a number of techniques involving photons. In addition to common source of photons available for laboratory use (lamps, lasers, X-ray sources), synchrotrons offer a broad spectrum of highly intense, polarized radiation. Electro-magnetic radiation penetrates solids significantly. However, if the solid responds by emitting electrons, as in the photoelectric effect, one obtains surface specific information.

An approach that can be adopted to investigate fundamental relations between the state of the catalyst and its catalytic properties is to model the catalytic surface with that of a single crystal. Besides the fact that, not all catalysts can be modeled as a single crystal, the biggest disadvantage is that most of the characterization is necessarily carried out in ultra high vacuum and not under reaction conditions or in-operando. Another approach involves study of real catalysts with in-situ techniques such as infrared spectroscopy, EXAFS and XRD, either under reaction conditions, or as is more often done and repeated in this thesis, under a controlled environment after required treatments.
TABLE 2.1
POSSIBILITIES FOR SPECTROSCOPIC ANALYSIS IN CATALYSIS

<table>
<thead>
<tr>
<th>Environment</th>
<th>Real Catalyst</th>
<th>Single Crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction conditions</td>
<td>XRD, TP techniques, Infrared and Raman Spectroscopy, EXAFS, Mössbauer spectroscopy, ESR, NMR, AFM</td>
<td>Infrared spectroscopy, TP techniques, STM, AFM</td>
</tr>
<tr>
<td>Vacuum</td>
<td>XPS, SIMS, SNMS, LEIS, RBS, TEM, SEM</td>
<td>all surface science techniques</td>
</tr>
</tbody>
</table>

The *in-situ* techniques often only determine overall properties of the particles instead of the desired specific atomic scale characterization of the surface. The situation is schematically summarized in Table 2.1.

2.5.1 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) techniques attract wide interest for catalysis research, particularly because of their sensitivity to the top first layers of the solid materials and to the chemical state of all elements, namely the oxidation state and covalent or ionic types of bonding. XPS consists, in principle, of analysis of the energy of the photoelectrons emitted from a solid surface illuminated by X-rays. The technique requires that it must be carried out under a high vacuum.

The physical basis of the XPS technique is shown in Figure 2.5. The energy carried by an incoming X-ray photon is absorbed by the target atom, raising it into an excited state from which it relaxes by the emission of a photoelectron. Photoelectrons are emitted from the inner or core energy levels of the target atom and hence the electron energy spectrum is characteristic of the emitting atom type,
Figure 2.5. The electronic transition involved in the photoemission of a electron and Auger process. An incident X-ray photon is absorbed and a photoelectron emitted. Measurement of its kinetic energy allows one to calculate the binding energy of the photoelectron. The atom stays behind as an unstable ion with a hole in one of the core levels. In Auger process, the excited ion relaxes by filling the core hole with an electron from a higher shell. The energy released by this transition is taken up by another electron, the Auger electron, which leaves the sample with an elementspecific kinetic energy.

and may be thought of as its XPS fingerprint. Lines in the spectrum are labeled according to the energy level from which they originate. XPS spectra is usually presented in terms of kinetic energy of the emitted electrons ($E_{kin}$), as

$$E_{kin} = h\nu - E_b - \phi$$

where $h\nu$ is the X-ray photon energy, $E_b$ is binding energy of core level interest and $\phi$ is the work function of the target material.

Because a set of binding energies is characteristic of an element, XPS can be used to analyze the composition of samples. In addition, the binding energy also relates
to the chemical state of the element because the energy levels of the core electrons are affected by the number of electrons in the valance band. Thus, the binding energy experiences chemical shifts – positive with increasing oxidation state of the element, and for a fixed oxidation state with the electronegativity of the ligands.

All surfaces that have not been cleaned by sputtering or oxidation in the XPS spectrometer are contaminated by presence of carbon. This occurs due to optimum lowering of the surface free energy when a hydrocarbon fragment adsorbs on a surface [110]. Hence, the spectra of carbon was chosen as a reference spectra with a peak corresponding to C 1s electrons at 284.6 eV. This reference energy was also used to correct for the shift in spectra due to the charging effect on the sample. A spectra of gold foil was used to calibrate the work function of the instrument.

These experiments were done in the Surface Analysis Lab at the Dept. of Chemistry on a Kratos XSAM-800 spectrometer utilizing Mg-Kα radiation. The samples were mounted on brass flat mounts with a double-sided carbon sticky tape. Each sample was crushed to a fine powder and stuck on to the sticky tape such that all the powder is firmly glued. Gentle tapping of the sample mount with the sample ensured that all loose sample powder is removed from the sample mount. The samples were then loaded into the vacuum chamber to be degassed overnight in a vacuum of $10^{-8}$-$10^{-9}$ torr. This ensured that most of the adsorbed gases and/or hydrocarbon are removed from the surface. The data was collected with the help of Vision2™ software running on a computer interfaced to the spectrometer.

For each sample, spectra for O 1s (537-514 eV, 3 scans), C 1s (294-274 eV, 3 scans), S 2s (239-217 eV, 25 scans), Cl 2p (204-190 eV, 5 scans), Zr 3d (190-174 eV, 3 scans), S 2p (184-154 eV, 25 scans) and Pt 4f (85-65 eV, 150 scans) electron transitions were recorded in the decreasing order of binding energy. In many samples, it was noted that the shake-up satellite peaks of Zr 3d were overlapping the S
2p energy range. Hence, the surface compositions were evaluated from S 2s curves rather than S 2p ones.

After converting them to ASCII format, the data sets were processed using an XPS data analysis software package called CasaXPS \[111\] with a Kratos XSAM element library of relative sensitivity factors for normalizing the intensity for each element.

A *Shirley* type background was chosen as the background in analysis of the XPS spectrum. Peak identification and fitting was performed with 3 kinds of constraints put on the fittings \[112\]. For instance, for the degenerate peaks, appropriate area ratios were used to fit paired peaks (0.75 for Pt 4f\(_{7/2}\) and 4f\(_{5/2}\)); the energy between the doublets was kept constant at values as tabulated in XPS handbook \[113\], and the full width at half maximum (FWHM) was kept the same for all peaks in a fit. The CasaXPS package, allowed all these constraint-based peak deconvolutions in a fairly comprehensive manner.

### 2.5.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy (XAS) is an element-specific probe of the local structure (short range) of elements in a sample. Interpretation of XAS spectra commonly uses standards with known structures, but can also be accomplished using theory to derive the structure of a material. In either case, the species of the material is determined based on its unique local structure. An important advantage of XAS is its utility for analyzing heterogeneous samples – a wide variety of solid and liquids can all be examined directly. Other properties of XAS that make it so attractive for catalyst characterization include –

- A Long range order is not a necessity – non-crystalline as well as crystalline solids can be analyzed.
• Local atomic arrangement can be determined about almost all types of atom on the sample separately.

• The process of measurement is fairly easy and rapid provided intense and energy tunable source of X-rays is available.

• A sample can be analyzed non-destructively and in an in-situ or controlled atmosphere environment.

• The measurements can be made even for relatively small concentrations (as low as 10 ppm).

The disadvantage of the technique is that it is mainly a bulk technique and gives surface sensitive information only if very small crystallites are used since in such a case most of the atoms are surface atoms.

These spectroscopic techniques are useful in analysis of supported metal catalysts. The sharp and narrow absorption bands at both L\textsubscript{III} and L\textsubscript{II} X-ray absorption edges, which are called “white lines” \cite{114}, correspond to the electronic transitions from 2p\textsubscript{3/2} and 2p\textsubscript{1/2} core level states, respectively. Lytle et al. have reported that the magnitude (intensity) of the L\textsubscript{III} X-ray absorption edge of an element is related to its chemical environment \cite{115}.

As mentioned earlier, X-rays are absorbed by all matter through the photo electric effect. In this process, an x-ray photon is absorbed by an electron in a tightly bound quantum core level (such as 1s or 2p level) of an atom. In discussing X-ray absorption, one is concerned with the absorption coefficient, \( \mu \) which gives probability of absorption for a homogeneous sample of uniform thickness as per Beer’s Law:

\[
I = I_0 e^{-\mu t}
\]  \hspace{1cm} (2.7)
Figure 2.6. Various processes occur when an incoming x-ray beam strikes a solid where $I_0$ is the incident x-ray intensity on a sample, $t$ is the sample thickness, and $I$ is the intensity transmitted through the sample (Figure 2.6). For X-rays as for all radiation, the intensity is proportional to the number of X-ray photons.

At most X-ray energies, the absorption coefficient $\mu$ is a smooth function of energy, and is proportional to sample density, $\rho$, the atomic number $Z$, atomic mass $A$, and the x-ray energy $E$ roughly as

$$\mu \approx \frac{\rho Z^4}{AE^3}.$$  

Due to the $Z^4$ dependence, the absorption coefficient of different materials are very different – spanning several orders of magnitude – which results in good contrast between different materials for nearly any sample thickness and concentrations upon appropriate x-ray energy adjustments. Figure 2.7 shows the energy-dependence of the absorption cross-section ($\mu/\rho$) for O, Fe, Cd and Pb.

When the incident x-ray has an energy equal to that of the binding energy of a core electron, there is a sharp rise in absorption – an absorption edge corresponding to the promotion of this core level electron. For XAS, one is concerned with the intensity of $\mu$ as a function of the energy, near and at the energies close to these absorption edges. Since every atom has core-level electrons with well-defined binding
Figure 2.7. The absorption cross-section $\mu/\rho$ for several elements over the x-ray energy range of 1 to 100 keV

energies, a particular element can be probed by tuning the x-ray energy to an appropriate absorption edge, hence the *element-specificity*.

Following an absorption event, the atom is said to be in an *excited state*. The eventual decay of the excited state occurs either by the process of *fluorescence* or the Auger effect. Either of these processes can be used to measure the absorption coefficient $\mu$, however, fluorescence is more likely to occur in the hard x-ray regime (>2 keV).

XAS can be measured either in transmission or fluorescence geometries as shown in Figures 2.8, 2.9 and the energy dependence of the absorption coefficient $\mu(E)$ for transmission mode is expressed as

$$\mu(E) = \log \frac{I_0}{I}$$  \hspace{1cm} (2.9)

and in fluorescence mode, it can be expressed in rather simplified terms as

$$\mu(E) \propto \frac{I_f}{I_0}$$  \hspace{1cm} (2.10)

where $I_f$ is the monitored intensity of the fluorescence line associated with the absorption process. Typical absorption spectrum for transmission and fluorescence
Figure 2.8. Typical apparatus for transmission XFS experiment. $I_0$, $I_1$ and $I_2$ are ionization detectors. A minimal experiment requires $i_0$ and $I_1$. The addition of $I_2$ permits the XAS of a standard such as a metal foil to be measured. This standard XAS is used for accurate energy calibration.

Figure 2.9. Typical apparatus for a fluorescence XAS experiment. The fluorescence detector is usually an ionization detector or a solid-state detector. A minimal experiment requires only $I_0$ and the fluorescence detector.

measurements for Pt-L$_{III}$ edge in Pt/SZ are shown in Figure 2.10.

X-ray absorption spectrum is commonly divided into several spectral regions as shown in Figure 2.11. The region near the edge (white line), approx. 10 eV on either side, energy is termed XANES (X-ray absorption near-edge structure). The region beyond 50 eV till up to a 1000eV is called as EXAFS (Extended x-ray absorption fine structure). In the XANES region, the electronic transitions may occur to unfilled bound states, nearly-bound states (resonance) or continuum states of the appropriate symmetry. In the region from about 10eV up to 50eV higher than the edge energy – Near-edge absorption fine structure (NEXAFS), the ejected photoelectrons have low kinetic energy and experience stronger multiple scatter-
Figure 2.10. X-ray absorption spectra for (a) transmission mode and (b) fluorescence mode for Pt-L\textsubscript{III} edge (11.564 keV) in Pt/SZ

ing from the first and even higher co-ordination shells. In the EXAFS region, the transitions are to the continuum states, the electrons have high energy and scattering by neighboring atoms dominates. Thus there is no fundamental distinction between the physics of EXAFS and XANES. Their analysis, complexity and interpretation is what makes the distinction unique. XANES is strongly sensitive to the formal oxidation state and co-ordination chemistry (e.g. octahedral, tetrahedral co-ordination) of the absorbing atom, while EXAFS is used to determine the distances, co-ordination number and the species of neighbors of the absorbing atom. A brief background in the theory of EXAFS and XANES follows.

2.5.2.1 EXAFS

EXAFS is the oscillatory structure observed over a wide energy (typically up to \(\sim 1000\) eV) beyond the absorption edge, which can be described as a series of periodic sine waves that decay in intensity as the incident energy increases from the absorption edge.
Figure 2.11. Various regions in an X-ray absorption spectrum – usually referred by their acronyms

In an isolated atom, such as a mono-atomic gas, the continuum final state wavefunction consists of a spherical wave emerging from the central absorbing atom, and the spectrum shows no fine structure. However, when a neighboring atom is included (as in condensed matter), the final state wavefunction consists of both an outgoing part and a part that is scattered from neighboring atoms. The outgoing part and backscattered parts interfere either constructively or destructively, depending on the electron wavelength and the distance to backscattering element (Figure 2.12). This interference modulates the matrix element and the absorption probability, which gives rise to oscillations in the absorption coefficient $\mu$ which are periodic in the wavenumber $k$ (Figure 2.13).

Determination of the parameters in the classical EXAFS equation (described in appendix A) is achieved by resolving the data into individual waves corresponding to the different types of neighbors around the absorbing atom. This is commonly
Figure 2.12. EXAFS occurs because the photoelectron can scatter from a neighboring atom. The scattered photoelectron can return to the absorbing atom, modulating the amplitude of the photoelectron wavefunction at the absorbing atom. This in turn modulates the absorption coefficient $\mu(E)$.

Figure 2.13. Wiggles arise due to destructive and constructive interference between outgoing and backscattered wavefunctions resulting in the fine structure.
done by means of curve-fitting or Fourier-transform techniques. Curve fitting leads to determination of parameters using the “ratio method” or nonlinear least squares fitting of data using empirical or theoretical standards.

Fourier transform analysis provides a radial distribution scatter profile of the photoelectron. Intensity of the peaks in such a profile corresponds to number or the co-ordination of the absorber with the scattering neighbor atom. The peaks are related to types of neighboring atoms and the radial distance between the absorber and the scatterer, however, their positions do not equal the bond length. Additionally, the number of peaks does not imply multiple bond distances. The oscillatory component of the phase shift along with backscattering amplitude in EXAFS signal causes shifts in peak positions and results in multiple peaks for a single bond distance.

2.5.2.2 XANES

XANES is associated with the excitation process of a core electron to a bound and quasi-bound states. Although XANES is a much larger signal than EXAFS, the interpretation of XANES is complicated since the excitation process involves multi-electron and multi-scattering effects, which means there is no simple analytical (or physical) description of XANES. The EXAFS equation breaks down at low $k$ due to the $1/k$ term and increase in the mean-free-path at very low $k$ and hence there is not a useful “XANES equation”. There are typically two approaches to XANES analysis: (a) ab-initio MO theory, and (b) multiple scattering. Even though XANES can provide structural information, most catalyst applications of XANES seek detailed information about the electronic state of the element under investigation [116].

The structure in the pre-edge region and on the rising part of the edge often is rather sensitive to details of the local site symmetry, bond length, charge state
and orbital occupancy. This information can often be exploited, by application of XANES principles, to provide information on the chemical state of the sample, even in case where EXAFS spectra cannot be obtained with adequate signal to noise ratio.

2.5.2.3 XAS experimental setup

X-ray Absorption Spectroscopy measurements were made on the insertion-device beam line (10-ID) of the Materials Research Collaborative Access Team (MRCAT) of which the University of Notre Dame is a member, at the Advanced Photon Source of the Argonne National Laboratory. A cryogenically cooled double-crystal Si (111) monochromator with resolution better than 2.5eV at 11.564 keV (energy of Pt-\(\text{L}_{\text{III}}\) edge) was used in conjunction with a Rh-coated mirror to minimize the presence of harmonics \(^{[117]}\). Both the fluorescence and transmission modes were utilized as dictated by the intensity of the beam, sample and acquisition of a good spectrum.

The catalysts placed in the EXAFS cell, were pretreated in the laboratory by flowing gases at temperatures similar to those used during pretreatment prior to reaction. After the prescribed treatment, the sample was cooled to room temperature in the same gas as used for pretreatment. The cell was isolated by closing the valves fitted at both ends of the tube and then moved to the x-ray hutch for measurement (Figure 2.15). Consequently, the EXAFS analysis was conducted in an environment similar to the one as during a reaction, but at room temperature instead.

Standard procedures based on WINXAS97 software \(^{[118]}\) were used to analyze the EXAFS data \(^{[119]}\). Phase shifts and backscattering amplitudes were obtained from EXAFS data for the reference compounds: \(\text{Na}_2\text{Pt(OH)}_6\) for Pt-O, \(\text{H}_2\text{PtCl}_6\) for Pt-S and Pt foil for Pt-Pt.

For the fluorescence mode measurements were made with the detector set at
90° relative to the incident x-ray beam. The large area fluorescence ionization chamber was filled with argon gas and the intrinsic time constants of the fluorescence detector and the incident beam ionization chamber were matched to some extent by increasing the potential across the fluorescence detector electrodes. Matched time constants (0.1 seconds), longer than the detector intrinsic time constants, were set on the amplifiers. Data were collected with continuous scanning for a duration of 0.5 seconds per data point (ca. 0.6 eV). The sample was pressed as a thin wafer into a steel cylindrical sample holder at a 45° angle to the axis. A small hole in the side of the cylinder allowed x-rays to pass from the sample to the detector. The sample holder was centered in a continuous-flow in-situ EXAFS quartz tube (18 in. long, 0.75-in. dia.) fitted at both ends with polyimide windows and valves to isolate the reactor from the atmosphere (Figure 2.14). A cone off the side of the reactor aligned with the hole in the side of the sample holder, allowed fluorescence x-rays to leave the reactor.

Measurements were also made in the transmission mode with ionization chambers optimized for the maximum current with linear response (\(~ 10^{10}\) photons detected/sec). In this case, the samples were pressed into a cylindrical holder, such that the thin layer of the catalyst was perpendicular to the beam axis. The sample thickness chosen was such that it gave an absorbance of about 1.0 in the Pt-LIII edge region, corresponding to about 20 mg of fine sample powder. Figure 2.15 shows the setup when the reactor tube for transmission EXAFS was placed in the path of the beam.

### 2.5.3 Infrared vibrational spectroscopy

Vibrations in molecules or in solid lattices can be excited by the absorption of photons. As a vibrational spectroscopic technique, infrared is the most common.
Figure 2.14. Picture showing the EXAFS reactor tube and the sample holder

Figure 2.15. The EXAFS reactor tube placed in the measurement hutch in the path of the x-ray beam
Infrared radiation falls into three categories, as indicated in Table 2.2. It is the mid-infrared region that is of most interest to a catalyst scientist.

2.5.3.1 Molecular Vibrations

Molecules possess discrete levels of rotational and vibrational energy. Transitions between vibrational levels occur by absorption of photons with frequencies $\nu$ in the mid-infrared range (Table 2.2). The vibrational frequencies increase with increasing bond strength and with decreasing mass of the vibrating atoms. However, absorption of an infrared photon occurs only if a dipole moment of a molecule changes during vibration.

There are four types of vibrations, as illustrated in Figure 2.16, each with a characteristic symbol:

- stretching vibrations ($\nu$), changing the bond length,
- bending vibrations in one plane ($\delta$), changing bond angles but not the bond lengths,
Figure 2.16. Fundamental vibrations of several molecules

- bending vibrations out of plane ($\gamma$), in which one atom oscillates through a plane defined by at least three neighboring atoms,

- torsional vibrations ($\tau$), change in the angle between two planes through atoms.

Generally frequencies of these vibrations decrease in order $\nu > \delta > \gamma > \tau$. In addition, vibrations are divided into symmetric and asymmetric vibrations ($\nu_s$ and $\nu_{as}$).

The group frequency concept states that the functional groups in molecules may be treated as independent oscillators, irrespective of the larger structure to which they belong. As a consequence, infrared frequencies are characteristic for certain bonds in molecules and can also be used to identify species on the surfaces.
2.5.3.2 Diffuse Reflectance Infrared Spectroscopy

DRIFTS (Diffuse reflectance infrared Fourier transform spectroscopy) is a technique that was made possible with the advent of FT-IR and does not have as much history behind it as the more common transmission-absorption techniques. Transmission IR can be applied if the bulk of the catalyst absorbs weakly so that most of the energy is transmitted through the solid. In the case of dark samples or when the catalyst support particles are smaller than the wavelength of the infrared radiation, scattering losses become important. DRIFTS is then the indicated technique for strongly scattering samples or absorbing particles.

The advantage of DRIFTS as opposed to transmission infrared spectroscopy is that sample preparation is relatively easy and faster. As a downside, the intensity of the spectrum is highly dependent on the optical alignment. The usual sample preparation for DRIFTS involves grinding the sample powder and diluting it with ground KBr powder in an appropriate ratio.

As opposed to specular reflectance (where the reflected angle of incident radiation equals the angle of incidence), diffuse reflectance is the energy that is reflected in all directions when the infrared radiation is scattered by one or more particles. This diffusely scattered radiation is collected by an ellipsoidal mirror and focused on the detector (see Figure 2.17).

The expression used to relate concentration to peak heights (or areas) in a DRIFTS spectrum is called the Kubelka-Munk equation. The form of the Kubelka-Munk function is as follows:

\[
KM = \frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty} \quad (2.11)
\]

where \( k \) is absorption coefficient, a function of the frequency \( \nu \), \( s \) is the scattering coefficient, and \( R_\infty \) is the reflectivity of a sample of infinite thickness, measured as
a function of $\nu$. The Kubelka-Munk (or simply KM) function is equivalent to the absorbance although it has different units.

The scattering coefficient $s$ is a quantity dependent upon the particle size distribution, packing shape distribution and packing density of the sample in the sample holder. These variables are hard to control precisely. However, by following a consistent technique of sample preparation, one can keep the variability in scattering factors to a minimum. For qualitative analysis, it is of minor though also an important significance.

A very attractive feature of infrared spectroscopy, in general, is the possibility to perform \textit{in-situ} catalysis experiments, where in one can observe and follow the changes on a catalyst surface in suitable environments not affected by surrounding conditions\cite{120}, as in a reaction, surface probing etc.

It was observed that the sulfated zirconia prepared during the course of this work does not allow transmission infrared and the intensity of the signal detected through a translucent disc of SZ and KBr on the MCT (Mercury-Cadmium-Telluride) detector was not high enough. As a result, the methodology of analyzing SZ by means of DRIFTS spectroscopy was adopted.

These experiments were performed in a DRIFTS reaction cell (Harrick Scientific Corp.) placed in an FTIR spectrometer (Equinox 55, Bruker Gmbh). Infrared spectra were recorded either in $\%$ Transmission or Kubelka-Munk units and were taken using 256 scans at a resolution of 4 cm$^{-1}$. A diagram of the diffuse reflectance mirror alignment is shown in Figure \ref{fig:diffuse_reflectance_mirror_alignment}. The path of the infrared beam is as shown in the diagram, and follows mirrors M1 through M6. Mirrors M3 and M4 are elliptical mirrors used to focus the beam – mirror M3 focuses the beam onto the sample, while mirror M4 collects the reflected beam from the sample and focuses it onto mirror M5. A schematic diagram of the DRIFTS reaction cell is depicted in
The reaction cell allows control of the catalyst reaction environment since the catalyst is no longer exposed to air and humidity.

For these experiments, ca. 15 mg of the sample was mixed with 1 gm of pre-ground KBr powder. The mixture is ground again to attain uniformity. The resultant powder was then placed in the sample cup located in the DRIFTS reaction cell. The upper surface of the powder was made level and flush with the top of the sample cup by drawing a flat spatula across the top of the sample cup. This ensured proper alignment with the elliptical mirrors. Appropriate gases (He, H₂, dry air) at a flow rate of 50 cc/min were used during the activation and drying of the sample and traveled up through the sample bed. The DRIFTS reaction cell includes a heating element and a thermocouple which were interfaced with a temperature controller (Omega). This allowed heating of the sample up to 300 °C under precise temperature control. The DRIFTS reactor featured ZnSe crystal windows, which allows transmission of infrared radiation from 650 to 4000 cm⁻¹. Pictures of the in-situ reaction chamber and the DRIFTS setup are included (Figure 2.19).
Figure 2.17. Schematic of Diffuse reflectance mirror setup with IR beam path (courtesy Harrick Sci. Corp.)
Figure 2.18. Schematic of the reaction cell for in-situ DRIFTS
Figure 2.19. Pictures of DRIFTS setup and the reactor chamber
CHAPTER 3

CHARACTERIZATION AND n-PENTANE ISOMERIZATION ACTIVITY STUDIES

3.1 Introduction

This chapter deals with the physical characterization of SZ catalysts prepared with the 3-step method described in Chapter 2 and activity measurements with such catalysts during n-pentane isomerization carried out at atmospheric pressure.

The section on evaluation of activity discusses the isomerization of n-pentane over SZ-based catalysts, prepared by different methodology. A brief discussion of n-butane isomerization over some selected catalysts is also included.

3.2 Physical characterization

The following physical characterization was carried out for SZ-based catalyst samples:

1. BET surface area measurement

2. TGA/DTA analysis

3. X-ray diffraction

4. Elemental analysis

5. Pulse chemisorption with H₂ and CO
3.2.1 BET surface area measurements by nitrogen adsorption

Table 3.1 shows the BET surface area of selected samples before and after calcination at different temperatures. The freshly made zirconium hydroxide has a specific surface area of over 200-300 m²/g, which is in agreement with the literature data [45, 121]. After calcination at a temperature of 650 °C, SZ₆₅₀ exhibits a specific surface area of ca. 120 m²/g. Upon calcination to a temperature higher than 650 °C, there is further decline in the specific surface area to a value of ca. 60-80 m²/g.

Thus, even if the area of the hydroxide precursor was large as in the case of Zr hydroxide (MEI) which had a high surface area of over 300 m²/g, the calcination led to reduction in surface area of the samples to almost similar values corresponding the calcination temperature used, i.e., around 125-130 m²/g for samples calcined at 650 °C. For the Zr(OH)ₓ (Aldrich), the initial area was much lesser and after calcination at 650 °C was even lesser at 25 m²/g. Calcining the zirconium hydroxide without addition of sulfur from sulfuric acid led to a much higher loss in surface area to 76 from ca. 230-240 m²/g. Adding platinum to the SZ (whether SZ₅₅₀ or SZ₆₅₀) did not lead to any significant change in the surface area.

It is evident that presence of sulfur interacts with ZrO₂ and stabilizes the surface area of the calcined samples. Calcination beyond 700 °C, however, leads to loss of sulfur from the hydroxide as will be seen in a later section on DTA/TGA and higher reduction in surface area to 76 m²/g. These values match the values reported in literature [8].

3.2.2 TGA-DTA

TGA-DTA studies were performed on selected samples in order to evaluate the weight loss and any thermal effects as observed [58].
TABLE 3.1
BET SURFACE AREA OF SELECTED SAMPLES

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination Conditions</th>
<th>$SA_{BET}$ m²/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr hydroxide</td>
<td>–</td>
<td>232</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>650 °C, 3 hr.</td>
<td>55</td>
</tr>
<tr>
<td>SZ</td>
<td>550 °C, 3 hr.</td>
<td>146</td>
</tr>
<tr>
<td>SZ</td>
<td>650 °C, 3 hr.</td>
<td>120</td>
</tr>
<tr>
<td>SZ</td>
<td>750 °C, 3 hr.</td>
<td>76</td>
</tr>
<tr>
<td>SZ-Na</td>
<td>NaOH ppt., 650 °C, 3 hr.</td>
<td>57</td>
</tr>
<tr>
<td>Zr hydroxide (Aldrich)</td>
<td>–</td>
<td>102</td>
</tr>
<tr>
<td>SZ (Aldrich)</td>
<td>650 °C, 3 hr.</td>
<td>25</td>
</tr>
<tr>
<td>Zr hydroxide (MEI)</td>
<td>–</td>
<td>334</td>
</tr>
<tr>
<td>SZ (MEI)</td>
<td>650 °C, 3 hr.</td>
<td>115</td>
</tr>
<tr>
<td>Zr hydroxide (MEI)</td>
<td>Na reflux</td>
<td>371</td>
</tr>
<tr>
<td>SZ (MEI)</td>
<td>Na, 650 °C, 3 hr.</td>
<td>159</td>
</tr>
<tr>
<td>Zr hydroxide (MEI)</td>
<td>Na reflux, leaching</td>
<td>362</td>
</tr>
<tr>
<td>SZ (MEI)</td>
<td>Na; leached, 650 °C, 3 hr.</td>
<td>147</td>
</tr>
</tbody>
</table>
Figure 3.1. Thermogravimetric analysis of SZ$_{550}$ and SZ$_{650}$. The numbers along the length of the curves indicate the temperature in °C.

Figure 3.1 shows typical profiles of sulfated Zr hydroxide samples heated to 550 °C and 650 °C. Although the weight loss occurs continuously over the entire range, two separate regions of weight loss can be identified. The first region of weight loss, until a temperature of 200-250 °C can be considered to be due to loss of the absorbed water and loose bound water of hydration. The second region lies beyond the temperature of 500 °C. It is important to recall that the onset of the crystallization of zirconium hydroxide is reported to occur near 400 °C [45]. The continuous loss in weight is due to gradual loss of OH groups from the Zr(OH)$_x$ as it begins to crystallize from an amorphous phase into a tetragonal phase.

Figure 3.2 shows the rate of weight loss for each sample. For both samples, the rate of weight loss is moderately high until 190 °C, and there is some loss even when the temperature is maintained at 200 °C. Once heated beyond 200 °C, a gradual
Figure 3.2. Rate of weight loss for samples of sulfated Zr hydroxide at 550 °C and 650 °C
weight loss continues till about 400 °C and thereafter the rate of loss more or less becomes constant at ca. 0.005 mg/min for the samples that is heated until 550 °C. However, for the the sample that is heated until 650 °C, there is a sudden and rapid increase in the rate of weight loss beginning at near 565 °C and the rate attains a maximum at 0.14 mg/min. This period of weight loss continues for ca. 20 minutes after which the rate starts falling again and reaches a level that is similar to that obtained for the sample heated to 550 °C. Thus for the sample heated to 550 °C, the total % weight loss during the heating period that mimics the actual calcination temperature program used for calcining sulfated Zr(OH)$_x$, is ca. 8%. In contrast, the weight loss for the sample heated up to 650 °C, is exceeding 16%.

A similar TGA study was performed for samples where the final temperature was increased up to 750 °C (Figure 3.3, top). The plot indicates further weight loss as the temperature of the sample was raised beyond 650 °C. As the temperature was maintained steady after heating till the final temperature of 650 °C or 750 °C, the rate of weight loss became stabilized at very low values. Another series of experiments was carried out in order to evaluate the effect of the heating rate on the weight loss. The same quantity of sample was heated at a rate of 5 °C/min and 10 °C/min monotonically. The results are shown in Figure 3.3. If the heating rate was fast (as is in the case of actual calcination for the preparation of the catalyst), there was a steep increase in weight loss in the first few minutes of the heating program and it reached as high as 0.15 mg/min. The rate of fall in weight then decreased steadily till a temperature of ca. 590 °C, beyond which it increased again rapidly to reach a maximum at 13 mg/min. As the temperature of the oven became steady at 650 °C, the fall in weight became steady at very low value. In the case of the sample heated at a lower rate of 5 °C/min, the rate of weight loss did not rise to high values during the period the loss of weight from the hydroxide corresponds to
Figure 3.3. Effect of heating rate on the profile of loss in weight in SZ samples.

Loss due to absorbed water and the water of hydration. It is likely that the structural changes happening during this period play some role in the properties of the final catalyst.

Recently, Stichert et al. [27] also reported similar TGA profiles during their preparation of monoclinic SZ catalysts from aged zirconia gels (Figure 1.6). The temperature at which they observed the onset of rapid weight loss is slightly higher (ca. 650 °C) than what is observed in the course of this work.

Differential thermal analysis (DTA) was simultaneously performed and revealed no sudden exothermicity during heating in the temperature range of 200 °C to 750 °C as seen in the Figure 3.4. This effect is most likely due to the incipient wetness.
Figure 3.4. DTA profile for sulfated zirconium hydroxide when heated till 750 °C sulfation method used in the preparation of the sulfated-Zr(OH)$_x$ as a result of which the amount of sulfur on the hydroxide is more than that for a monolayer coverage. Davis et al. also reported similar results when their sample contained up to 13 wt% sulfur [121]. At 4 wt% (the initial sulfur loading used in this work), however, they observed an exotherm at 460 °C.

To further ascertain the effect of the amount of the sample on the detection of exothermicity during the calcination of sulfated Zr hydroxide, the bed temperature was monitored as the heating progressed. The results are shown graphically in Figure 3.5. The results confirm that there is no exothermic reaction occurring during the crystallization of SZ irrespective of the amount of sulfated Zr hydroxide used in the calcination step.
Figure 3.5. The temperature profile of the powder bed during the calcination of sulfated zirconium hydroxide till 650 °C. The bed height was 4 cm (φ = 2 cm).
3.2.3 X-ray diffraction studies

As described earlier, sulfated zirconium hydroxide is predominantly amorphous in nature and has very broad trends indicating short range crystallinity in the sample (Figure 3.6). In the following discussion, the figures include samples from different batches of preparation and as such have slight variations.

X-ray diffraction analysis shows the effect of calcination temperature on the crystallinity of the sulfated zirconia. From the diffractograms in Figure 3.7 and 3.8, one can easily observe that calcination at higher temperature increases the crystallinity of the SZ. This is evident from the increased intensity of the diffraction peaks. In Figure 3.7, both the samples are predominantly in the tetragonal phase as deduced from the 2θ peak at 30.3°. The other peaks also match those observed and reported as standards (ICDD-PDF #88-1007). The peak at 2θ of 28.1° corresponds to pres-
ence of some monoclinic phase in the sample. The percentage of the monoclinic phase that can be calculated as

\[
\text{fraction of monoclinic phase} = \frac{A_{28}}{A_{28} + A_{31}} \quad (3.1)
\]

was found to be within a range of 0 - 14% in different samples. In the above equation, \(A_{28}\) and \(A_{31}\) correspond to area of the peak corresponding to monoclinic and area of the peak at 31 °, corresponding to that of the tetragonal phase respectively. The crystallite size of the calcined SZ samples calculated according to Equation (2.5) is between 8-14 nm. In general, the SZ\(_{550}\)-based samples had a slightly larger crystallite size than the samples calcined at the higher temperature of 650 °C (SZ\(_{650}\)). This is consistent with the reported literature [41].

To rule out any influence of the addition of platinum and the pretreatments on the phase of the catalyst, similar analysis was performed on the unmodified and modified catalysts. The result demonstrates that there is no or little change in the phase structure of SZ upon addition of the Pt metal and pretreatments (Figure 3.9). Similar results were obtained for catalysts prepared from different batches of SZ catalyst. Figure 3.10 shows an XRD pattern that is similar to that of the Pt(r)/SZ\(_{650}\) catalyst as that for Pt(o)/SZ\(_{650}\) in Figure 3.9.

Reduction of a calcined SZ sample yields an interesting result as well. Figure 3.10 shows that an reduced and re-calcined SZ\(_{650}\) undergoes a phase transformation to a multiphase crystalline solid with tetragonal, monoclinic and cubic phases present. The reduction was carried out in the same fashion as it is carried for reducing the platinum i.e. heating up to 300 °C in hydrogen flow for 4 hrs.

One may notice that the peak corresponding to monoclinic phase of the crystalline zirconia appears in a few samples where it is not present in others. Since the samples were ground to a powder of uniform size before analysis in the diffraction...
Figure 3.7. X-ray diffractograms for $\text{SZ}_{550}$ and $\text{SZ}_{650}$: Increased crystallinity due to higher calcination temperature
Figure 3.8. X-ray diffraction plots for Pt(r)/SZ prepared from SZ calcined at different temperatures – 550 °C, 605 °C and 650 °C
Jentoft and co-workers have recently reported on the effect of grinding and milling on the partial change in phase of the Mn-promoted SZ catalysts from tetragonal to monoclinic [122]. Non-uniformity in the grinding and preparation of different samples for the XRD analysis at different times may also be a reason for the slight variations on the XRD plots of the samples.

3.2.4 Elemental analysis – sulfur and platinum

The results of sulfur analysis of unmodified SZ and Pt-modified SZ catalysts are tabulated in Table 3.2. The analysis was performed on fresh versus used Pt-containing sample i.e. samples that have been exposed to reaction conditions. The values of sulfur content in unmodified SZ indicate that there is almost no loss in sulfur from this sample. However, there is a small loss in sulfur content (ca. 10%)
Figure 3.10. Comparison of the diffraction patterns of amorphous S-Zr(OH)$_x$, SZ$_{650}$ which was reduced and re-oxidized and Pt(r)/SZ$_{650}$ during the Pt addition and reduction steps, and a further 5% loss is observed in the sample analysed after carrying out n-pentane isomerization with it. The sulfur content of the sample calcined at 650 °C is almost 50% lesser than that in the SZ$_{550}$ even though both the samples were prepared from the same batch of sulfated Zr hydroxide. As reported in the section on TGA/DTA studies, there was a rapid loss beginning at a temperature of 580 °C, that loss would correspond to loss of sulfur from the surface in the form of SO$_2$ and SO$_3$ along with loss of water.

When sulfated Zr hydroxide is reduced after oxidation at 650 °C, there is almost complete loss of S from the surface. This sample had a sulfur content of less than 0.2%.

By determining the sulfur content on other samples, it was found that most of the samples in which high activity was obtained, had lower sulfur contents of
TABLE 3.2
SULFUR CONTENT (wt%) OF SZ SAMPLES CALCINED AT 550 °C AND 650 °C

<table>
<thead>
<tr>
<th>Sample</th>
<th>550 °C</th>
<th>650 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>unmodified SZ</td>
<td>4.40</td>
<td>2.08</td>
</tr>
<tr>
<td>Pt(r), before reaction</td>
<td>3.96</td>
<td>1.65</td>
</tr>
<tr>
<td>Pt(r), after reaction</td>
<td>3.75</td>
<td>1.56</td>
</tr>
</tbody>
</table>

approximately 1.3 to 15% by weight.

By carrying out ICP-MS analysis to determine Pt content of the catalyst samples, it was confirmed that there is no loss of platinum from the catalyst during any of the preparatory stages and the wt% of platinum remains equal to the loaded amount of 1%.

3.2.5 Pulse chemisorption

To measure the active surface area of Pt in the catalyst samples, pulse chemisorption was conducted on selected samples (see details in Chapter 2).

The platinum on the SZ-based catalysts does not show appreciable chemisorption of either H₂ or CO gases [123]. This result was also observed during the course of this work. However, carefully performed chemisorption measurements with hydrogen revealed an interesting trend.

For the purpose of these studies, unmodified SZ calcined at two different temperatures – 550 and 650 °C and Pt-modified counterparts of the unmodified SZ catalysts were used. Over \( \text{SZ}_{550} \), neither hydrogen nor CO show any measurable adsorption at room temperature (RT) and almost all the H₂ and CO in the injected pulse was detected by a thermal conductivity detector (TCD). Similar result was
obtained in the case of SZ_{650} for H_2 pulse experiments, however, in case of CO, a reaction over the SZ_{650} seems to occur and the pulse measurements were not at all indicative of adsorption on the platinum.

The results for CO chemisorption over Pt(r)/SZ_{650} were also similar and the output signal of the TCD indicated imbalance in the bridge resistance corresponding to a presence of other gas(es) besides CO and He (carrier) in the chemisorption reactor. Pt(r)/SZ_{550} showed no detectable adsorption of CO or H_2 similar to that over SZ_{550}.

All the above measurements were carried out at room temperature after reducing the catalyst at 200 °C for 2 hrs and flushing with appropriate carrier gas (helium in case CO chemisorption or argon in case of H_2 chemisorption) and cooling during the flush-gas flow.

Carbon monoxide (CO) is a weak base frequently used in titration experiments to assess acidity of the strong acids. As SZ-based catalysts have strong acidity, it is very likely that CO is interacting in a very strong fashion with the acid sites and thus is not a suitable probe molecule for evaluating metal area and dispersion on Pt-modified SZ-based catalysts. The results with CO chemisorption mentioned above confirm this assertion and only hydrogen was used in further experiments.

Although there was little indication of hydrogen chemisorption over the Pt-containing catalysts, hydrogen was present during the isomerization reaction that were considerably different than chemisorption experiment. It should be noted that reduced platinum supported on silica or alumina exhibits significant chemisorption capacity even at RT [124] [126].

Under the assumption that platinum on SZ might not be active for chemisorption of hydrogen at room temperature, the hydrogen chemisorption measurements were then attempted over catalysts maintained at temperatures higher than room
temperature. Similar measurements were also performed for unmodified SZ catalysts as well. At higher temperatures (150 °C, 200 °C and 250 °C, both SZ$_{550}$ and SZ$_{650}$ adsorbed undetectable quantities of hydrogen, if any.

On the platinum modified catalysts i.e. Pt(r)/SZ$_{550}$ and Pt(r)/SZ$_{650}$, however, it was found that temperature of the sample during adsorption had a significant effect on the adsorption capacity of the catalyst. It was noticed that a definite amount of hydrogen was uptaken by the catalyst from each pulse sent to the catalyst in the chemisorption reactor. Moreover, the height of the hydrogen peaks as detected in the TCD assumed an *apparent* steady value which gave a false impression that the surface has become saturated with the adsorbing molecule. This was confirmed by measuring the response of the empty reactor, i.e., without any catalyst or with plain silica. As the temperature of the catalyst was increased in following measurements, the amount of uptake of hydrogen increased. The results are shown graphically in Figures 3.11 and 3.12 as percent uptake of hydrogen per pulse for Pt(r)/SZ$_{550}$ and Pt(r)/SZ$_{650}$ samples, respectively.

For the Pt(r)/SZ$_{550}$ and the Pt(r)/SZ$_{650}$ samples, the room temperature adsorption or uptake remains constant at a level of 5% and 10%, respectively. With increase in temperature, the *apparent* saturation level increases to higher values. The uptake of hydrogen from a pulse is higher in the first few pulses and the SZ$_{650}$ sample shows progressively higher first-pulse uptake than the SZ$_{550}$ sample. With the rise in temperature, the uptake in the first few pulses increases rapidly and almost 85% hydrogen is uptaken in the SZ$_{550}$-based sample and 95% in the SZ$_{650}$-based sample.

Morterra and coworkers \[127\] also found similar results for hydrogen and CO chemisorption experiments performed at room temperature, however, they attributed the decrease in adsorption capacity to reversible reduction of surface sulfates.

In 2000, Satoh et al. \[128\] published their results of adsorption of hydrogen on
Figure 3.11. Hydrogen uptake in Pt(r)/SZ$_{550}$ as function of temperature
Figure 3.12. Hydrogen uptake in Pt(r)/SZ$_{650}$ as function of temperature
the sulfated zirconia-supported platinum (Pt/SO₄²⁻/ZrO₂) catalysts. They found that at temperatures higher than 150 °C, the Pt-containing SZ sample continued to uptake hydrogen in a constant pressure system for up to 24 hours and the hydrogen-to-metal ratio exceeded unity, indicating a possibility of *spillover* phenomenon as part of hydrogen adsorption process. The results presented above are in agreement with their finding and that continued hydrogen uptake occurs at higher temperatures. Indeed, Tanaka et al. have suggested use of Pt/SZ materials as a possible hydrogen storage materials which release hydrogen by adsorption of water [129]. More recently, Wang et al. also presented evidence for hydrogen spillover on Pt/SZ catalyst based on their results using FT-IR spectroscopy and TPD [130].

3.2.6 Summary

The main results of the characterization studies of SZ and Pt/SZ mentioned above can be summarized as:

- the surface area of SZ decreases with increase in the temperature of calcination. On an average, the BET surface area of Pt/SZ₆₅₀ (prepared by the 3-step method) lies in the range of 110-140 m²/g.

- calcination of S-Zr(OH)ₓ at the higher temperature of 650 °C results in a weight loss (above 15%) due to evolved sulfur that occurs at a temperature of ca. 585 °C. During the calcination step, no exothermicity near 460 °C is noticed.

- calcination also results in crystallization of S-Zr(OH)ₓ and the extent of which increases with the temperature. The samples (without or with Pt) do not undergo a phase change to monoclinic but remain predominantly in a tetragonal phase.
• Only 2 wt% sulfur remains in the SZ_{650} sample as compared to ca. 4 wt% in the SZ_{550} sample. During the pretreatments and reaction, there is further decrease in the sulfur content the catalyst, but the percent loss is same in both samples.

• The Pt/SZ_{550} or the Pt/SZ_{650} samples showed no hydrogen or CO chemisorption activity at room temperature. At higher temperature, CO reacted with the sample, but hydrogen showed an increasing uptake with increasing temperature. The results indicate a possibility of hydrogen spillover phenomenon at the reaction temperature.

3.3 Evaluation of catalytic activity

As described earlier, acid catalyzed skeletal isomerization of n-alkanes is a very important reaction in current reformulation of gasoline.

Sulfate zirconia-based solid acid catalysts are very active for hydrocarbon isomerization, in particular, the rearrangement of C_{4}-C_{6} molecules. Promoted or modified SZ catalysts exhibit several orders of magnitude higher activity for these reactions over unmodified SZ catalysts. It will be shown that several factors such as preparation parameters, pretreatment, activation and reaction conditions have considerable effect on the catalyst activity. Pretreatment conditions have a direct impact on the catalyst performance, texture and crystalline structure, sulfur content and state of active sites, that affect the catalytic activity. Calcination is a necessary step in order to generate catalytically active SZ structures.

A common issue for unmodified and modified SZ-based catalysts is their fast deactivation during isomerization reactions, which limits their actual use on the large-scale industrial process except under high pressure conditions. Addition of Pt helps improve the stability and in arresting deactivation at higher temperatures as
is the case in many hydrocarbon reactions\cite{8,106}. While there are plenty of studies on the acidity of sulfated zirconia catalysts, there is no systematic study yet on the effect of preparation and pretreatments on the Pt-promoted SZ catalysts or on arresting deactivation and attaining a sustained high activity during isomerization reaction.

Thermodynamically, the formation of isopentane is favored at a lower temperature. Figure 3.13 shows the equilibrium fractions of each of the alkanes isomer of n-pentane at atmospheric pressure as a function of temperature. The equilibrium calculations were performed assuming all gases to be ideal, following the method explained by Stull \cite{131}. The isomerization of n-pentane is best carried out in the range of temperature between 150 °C and 250 °C in order to get higher selectivity towards isopentane. At temperatures lower than ca. 150 °C, selectivity towards tert-pentane (2,2-dimethyl propane) will increase at the cost of isopentane. Above 250 °C, the conversion to isopentane decreases and hence the overall yield is lower. Moreover, at higher reaction temperatures, the n-pentane is more susceptible to cracking, resulting in wide distribution of products and lower selectivity towards isopentane.

3.3.1 Catalysts prepared with 2-step method

The 2-step method, also referred as the conventional method, has been described earlier in Chapter 1 (Figure 1.3). The essence of this method is addition of platinum and sulfur as their precursors prior to the calcination. The calcination step is expected to both crystallize as well as reduce the platinum into metallic. As demonstrated later in this thesis, this does not lead to metallic platinum at all.

The catalysts that were prepared according to the two step conventional method will be referred to as SZ or PtSZ catalysts. Appropriate suffix will be used to
Figure 3.13. Equilibrium fractions of alkanes isomers of n-pentane as a function of temperature (P = 1 atm.)
distinguish between various samples. Most of the catalysts used in this study were prepared without any modification of the zirconia support i.e. unmodified SZ-based catalysts. In some cases, Al was added as a promoter following the recent report by Gao et al. [132] who reported preparation of an Al-promoted SZ catalyst with high activity for n-butane isomerization. All catalysts were prepared with an initial loading of 4 wt% sulfur by the incipient wetness method from a 0.5M sulfuric acid solution.

For catalysts prepared by the two step conventional method, pretreatment consisted of flowing nitrogen (dry) at 250 °C for 30 min through the catalyst bed prior to the reaction to eliminate adsorbed water. The reaction was carried out at 250 °C, in most cases and at atmospheric pressure conditions.

Figure 3.14 shows the profile of n-pentane conversion versus time-on-stream on (a) a conventional SZ550 catalyst prepared as described in [106] and (b) another SZ550 catalyst that was tested under varying flow of n-pentane. The flow rate of n-pentane was changed by varying the flow rate of hydrogen through the bubbler. The activation procedure used for both catalyst was – (a) N2 flow at the rate of 20 cc/min for 2 hrs at 500 °C and (b) flowing hydrogen (20 cc/min) at 250 °C for 6 hrs.

In each case, during the initial startup of the reaction, the formation of dark droplets below the heating zone on the walls of the reactor tube was observed. These formed due to the heavy hydrocarbon residue that forms during the first few minutes of TOS (time on stream). This residue does not adsorb on the surface but breakthroughs the bed and condense on the reactor exit tube wall. For the catalyst (a), initial conversion is about 45% but the conversion then starts to fall due to deactivation of the catalyst to almost 5% in 20 minutes TOS. The selectivity towards isopentane was nearly constant at a value of 75% after first few minutes TOS, but
Figure 3.14. Conversion vs. TOS profile for $SZ_{550}$ sample (a) constant $P_{nC_5}$ (b) varying partial pressure of n-pentane

it was lower at a value of 40% when the conversion was high, which is expected. For the test of $SZ_{550}$ with varying n-pentane flow, the deactivation was high and the conversion of n-pentane fell to a level of nearly 5% in 25-30 minutes. This result suggests that n-pentane undergoes a significant rearrangement upon contact with the fresh catalyst forming hydrocarbon fragments. Some of such fragments recombine and for the observed dark liquid but other polymerize on the catalyst surface forming the residues generally referred to as “coke”. The coke fragments eventually block the active acid sites thus leading to deactivation.

An alumina containing catalyst was prepared by co-precipitation from $\text{ZrOCl}_2$ and $\text{Al(NO}_3)_2$, calcining the dried and sulfated precipitate at 600 °C and 650 °C according to the procedure reported by Gao et al. [132]. The catalyst was pretreated in flow of dry air instead, at a temperature of 450 °C for 3.5 hours prior to reaction.
The activity of the catalyst is shown in Figure 3.15. The initial activity was very high for both samples but deactivation rate was high as well. The conversion increased when the reaction temperature was increased to 300 °C during the reaction, however the deactivation was still prevalent. For the SZA650 catalyst, the overall activity seemed higher due to lesser deactivation. The conversion after 40 min TOS was still over 10 %.

For the above mentioned catalyst samples, a regeneration treatment in the form of oxidation in flowing air at a temperature of 550 °C was performed in order to remove carbonaceous coke deposits from the surface of the catalyst. There was little change in the activity of the catalyst as indicated by the conversion versus TOS data and within the range of experimental error, the activity could be assumed to be same. Thus, a regeneration was able to burn off any coke deposits which may have poisoned the active acid sites and reactivate them for isomerization.

Similarly, platinum containing catalysts were prepared to evaluate their activity in the n-pentane isomerization at atmospheric conditions. After adding the platinum, a part of the sample was reduced (PtSZ650(r)) whereas the other was oxidized in air (PtSZ650(o)). Figure 3.16 presents the activity results for these catalysts. The initial conversion for PtSZ650(o), i.e. a catalyst that was calcined at 650 °C after adding platinum and sulfur in one step, seems to be lower than that for PtSZ650(r). However, the deactivation is rapid in the case of the latter sample, with the conversion decreasing to as low as 10 %. For the oxidized catalyst, a trend in activity recovery is observed and the conversion becomes stable at a value of around 25 % after the initial decrease.

Regenerating the catalyst in flowing air at 500-550 °C after the reaction in order to reactivate the catalyst results in an increase in activity (and stability) in both the samples. For the oxidized catalyst, the steady conversion attains a higher value.
Figure 3.15. Conversion vs. TOS for SZA\textsubscript{600} and SZA\textsubscript{650} samples
of approx. 35 %. In the case of the reduced catalyst, the regeneration led to only a slight increase in the n-pentane conversion at large TOS. With increasing TOS, the activity seems to increase and attains an equilibrium value corresponding to a conversion of ca. 25 %.

The steady state catalytic activity of the oxidized sample is higher than that of the reduced sample since the latter deactivates fast as well. This is probably due to poisoning of the platinum in the PtSZ$_{650}$($r$) due to reduction of sulfates groups on SZ to H$_2$S in presence of hydrogen, which causes irreversible poisoning of the Pt. At the same time, the presence of hydrogen inhibits the formation of strong acid sites that are responsible for the isomerization activity.
3.3.2 Catalysts prepared with 3-step method

The extra step involved in preparation of metal-modified SZ catalysts is an important one. The activity results presented in this section emphasize this significant aspect of SZ-based catalyst synthesis.

Figure 3.17 presents the conversion versus TOS plots for Pt(o)/SZ\textsubscript{550} samples prepared according to the 3-step method. The effect of addition of platinum to precalcined SZ\textsubscript{550} was clearly seen and the activity of the catalyst seemed to be stabilized at a higher conversion level as compared to the unmodified SZ\textsubscript{550} catalyst (Figure 3.14). The shape of the conversion vs. TOS curve was also different than that for the catalysts prepared by the conventional method. The conversion after 50 minutes was lower but the deactivation rate also seemed less pronounced. The selectivity towards isopentane (also shown in the same plot) remained fairly constant at a value of ca. 80%. Upon a regeneration of the catalyst after one reaction run, the conversion stabilizes at a higher value of about 30%. For n-pentane isomerization over the SZ\textsubscript{550}-based catalysts, this is a significant improvement in yield from 3.5% (in SZ\textsubscript{550}) to 20-22%.

An improvement in the catalytic activity was also observed when the sample prepared from SZ\textsubscript{550} was pretreated at 300 °C in increased hydrogen flow, instead. Figure 3.18 shows the results of isomerization reaction for Pt(r)/SZ\textsubscript{550} sample. The conversion with the fresh sample is low and shows the typical profile, which shows stabilized value near 5-7% but after a regeneration the deactivation is not that severe and the value of the conversion becomes stable around a slightly lower value of 20%. The conversion obtained with this sample is similar to that obtained with Pt/SZ\textsubscript{550}(r) (Figure 3.16). The profile for the conversion curve remained almost the same after further regeneration.

The activity of the fresh and regenerated Pt(o)/SZ\textsubscript{650} samples is presented in
Figure 3.17. Conversion and isopentane selectivity vs. TOS for Pt(o)/SZ550: Effect of regeneration
Figure 3.18. Conversion vs. TOS for Pt(r)/SZ$_{550}$: pretreatment at 300 °C and high hydrogen flow rate
The conversion achieved over a fresh sample showed a trend that indicated high initial activity followed by deactivation in 10 minutes and then a recovery of conversion values that stabilized at ca. 35%. After carrying out a regeneration after the reaction runs, it can be seen that the initial deactivation profile was diminished and the conversion became stable at a much higher value of ca. 50%. The conversion stayed at this stable value for over 4 hours. The selectivity towards isopentane for the same samples is shown in Figure 3.20. With the increase in the conversion upon regeneration, the selectivity had an opposite effect. The steady selectivity of the regenerated catalyst attained a lower value than a value of over 85% achieved for the fresh catalyst. It should be noted that even though the catalyst was prepared by an oxidation pretreatment, the reaction environment is that of a reducing type – presence of hydrogen in the feed stream will cause reduction of the catalyst since the catalyst is heated to the reaction temperature in the presence of hydrogen in the feed stream.

Similar tests were also performed with palladium as the active metal over $SZ_{650}$ and $SZA_{650}$ samples (Figure 3.21). As seen for the unmodified SZ and SZA catalysts in an earlier section, there was little benefit of adding aluminum to the SZ catalyst. The conversion for both the catalyst samples was essentially the same with a gradually decreasing trend with TOS. The conversion obtained over both the samples decreased to about 30% in 50 minutes TOS. Presence of palladium also seemed beneficial in preventing the deactivation as compared to that for the unmodified catalysts. However, the results obtained with platinum were better than that obtained over palladium, and Pd was not used further on for preparing the modified catalysts.

Figure 3.22 and 3.23 show results for the sample reduced after addition of platinum to $SZ_{650}$ (Pt(r)/$SZ_{650}$). As seen earlier, for the reduced sample, the conversion
Figure 3.19. Conversion vs. TOS for Pt(o)/SZ$_{650}$ sample: Effect of regeneration

Figure 3.20. Selectivity towards isopentane vs. TOS for Pt(o)/SZ$_{650}$ sample: Effect of regeneration
Figure 3.21. Conversion vs. TOS for Pd-modified $SZ_{650}$ and $SZ\alpha_{650}$ samples
increased to a steady value of ca. 35% after a low initial value. The steady value of conversion increased further upon a regeneration and even more after 2 regenerations of the catalyst. The conversion vs. TOS did not show the low initial conversion followed by a recovery but a gradual decay in conversion which became almost constant at a value of near 50%. The values of conversion obtained with this catalyst showed an improvement of over 250% in comparison to the catalyst prepared by the 2-step method (Figure 3.16) which only showed a conversion up to 20%. Although the values of conversion obtained for this sample after 2 regenerations were similar to those obtained for Pt(o)/SZ\textsubscript{650} after 2 regenerations (Figure 3.19), the selectivity of this sample was slightly better than that of the latter. The selectivity towards isopentane (Figure 3.23) remained at a level of 80% on an average and did not seem to depend on regeneration. All the samples described above were pretreated with \textit{N}_2 followed by \textit{H}_2 at 250 °C at flow rate of 40 cc/min.

When the pretreatment was changed to flowing hydrogen at a high flow rate and a higher temperature of 300 °C, the conversion versus TOS for Pt(r)/SZ\textsubscript{650} curve showed no valley-like feature in the initial few minutes of TOS (Figure 3.24). Instead the conversion curve for the fresh catalyst became stable at a value close to 45% conversion. The real difference in the activity of the catalyst came after regeneration. After carrying out a regeneration on the catalyst, the conversion showed a high initial value of near 75% and then decreased to a steady value of above 55% after few minutes TOS. Another regeneration did not cause further increase in the values of conversion as opposed to those seen in the preparations above. In this sample, the selectivity in each test remained at an average value of 70% which was slightly lower than for the sample pretreated at a lower temperature and lesser flow rate of H\textsubscript{2}.

Figure 3.25 shows the result of carrying out the isomerization reaction over Pt(r)/
Figure 3.22. Conversion vs. TOS for Pt(r)/SZ_{650}

Figure 3.23. Selectivity towards isopentane vs. TOS for Pt(r)/SZ_{650}
Figure 3.24. Conversion vs. TOS for Pt(r)/SZ$_{650}$: pretreated at 300 °C and high hydrogen flow
Figure 3.25. Conversion vs. TOS for Pt(r)/SZ_{650} at 150 °C, 200 °C and 250 °C

SZ_{650} at three different temperatures of 150 °C, 200 °C and 250 °C. The conversion obtained at each temperature increases with temperature with the highest being 70%. The increase in the stable conversion obtained at 250 °C is higher than that obtained at 200 °C. A similar effect was also seen for other samples and the percent increase in conversion between that obtained at 200 °C and 250 °C was more than the percent increase between that at 150 °C and 200 °C.

The activation energy for these catalyst could not be calculated since the conversion of n-pentane observed was very high. In order to obtain an Arrhenius plot of rate versus time inversed, it is necessary to operate at fully mixed reactor (CSTR) conditions and with low conversion values. Significant modifications to the reaction system were required in order to attain such conditions. As such these studies were not attempted.
The results presented in this section show that addition of platinum after calcination of sulfated Zr(OH)$_x$ lead to a catalyst which suffers to a much lesser extent from deactivation and has a high stable conversion that lasts up to 4 hrs. The key steps in obtaining high activity is the addition of platinum to precalcined SZ and subsequent reduction-oxidation procedure.

It is important to emphasize that the values of conversion and the activity obtained for the Pt/SZ catalysts mentioned above was the highest reported for the conditions used in this work. Although non-deactivating catalysts with equivalent conversion have been reported by Liu and Sachtler [80] for n-pentane isomerization catalysts, the reaction was carried out at much higher pressure.

3.3.3 Effect of pretreatment on SZ$_{650}$-based catalysts

Having identified that (a) a catalyst prepared from sulfated Zr(OH)$_x$ after calcining it at 650 $^\circ$C yields higher activity and that (b) modification with platinum followed by reduction followed by oxidation lends stability to catalyst activity, further work was carried out to study the effect of various pretreatments applied to platinum-impregnated SZ$_{650}$ samples on the activity and conversion. The different pretreatments consisted of reduction carried out for a short time (2 hrs.) versus long (4 hrs.) and their combination. Other samples were subjected to oxidative treatment (same as regeneration but prior to any reaction) and still others were further reduced after the oxidation pretreatment.

The results with oxidation pretreatment (Pt(o)/SZ$_{650}$, Figure 3.19) and the shorter reduction pretreatment (Pt(r)/SZ$_{650}$, Figure 3.24) have already been discussed in the previous sections. The activity of the sample that was reduced for a longer time is shown in Figure 3.26 as conversion versus TOS. The conversion obtained for the fresh sample was stable at a value of near 55%. In these samples,
there was no indication of the initial deactivation profile as had been observed in the case of the Pt(o)/SZ\textsubscript{650} samples. In this case as well, the regeneration resulted in the catalyst having a higher activity. The conversion after the regeneration was higher than for the fresh sample at all sampling points and stabilized near a value of 60%.

Figure 3.26. Conversion vs. TOS for Pt(r\textsubscript{i})/SZ\textsubscript{650}: effect of regeneration

Figure 3.27 presents the results for the isomerization reaction for the catalysts that were oxidized after the shorter and longer reduction – i.e. Pt(r\textsubscript{s},o)/SZ\textsubscript{650} and Pt(r\textsubscript{l},o)/SZ\textsubscript{650}. The Pt(r\textsubscript{l},o)/SZ\textsubscript{650} sample that was reduced for 4 hours showed a conversion that was lower than that for the Pt(r\textsubscript{s},o)/SZ\textsubscript{650} sample, which was reduced for 2 hours. The Pt(r\textsubscript{l},o)/SZ\textsubscript{650} sample shows a gradual decrease in the conversion but remains in the average range of 65-70% for over 70 minutes of TOS. For the Pt(r\textsubscript{s},o)/SZ\textsubscript{650} sample, the initial conversion was lower at about 65% but
increased to a stable value of ca. 75%. The effect of reducing for longer times seems to be reduction of the sulfur species on the SZ surface. However, the activity remains high, which implies that those species are not removed from the SZ but are rearranged in some manner.

The results for Pt(r_s,o,r_s)/SZ_{650} and Pt(r_s,o,r_1)/SZ_{650} are also shown in Figure 3.27. In this case as well, the catalyst for which the final pretreatment was reduction for a longer time had a relatively lower conversion than the catalyst that was pretreated for shorter time. The Pt(r_s,o,r_1)/SZ_{650} sample, however, showed a high and stable conversion of 75% which is the highest reported conversion for a Pt-modified SZ catalyst in the available literature! On the other hand, the conversion obtained for the Pt(r_s,o,r_s)/SZ_{650} sample exceed that value, remaining stable at a value of over 85%. While the conversion values obtained for these set of catalysts are high, the selectivity towards isopentane decreased. These catalyst samples were so active that they caused cracking of n-pentane which resulted in fractions C_3 to C_8 being detected in the reactor exit stream. The selectivity obtained was in the range of 35–40% for these samples. The result presented in Figure 3.27 clearly identifies the pretreatment steps that will result in a catalyst with exceptionally high activity for n-pentane isomerization activity. These pretreatments include short reduction followed by oxidation and then repeat reduction.

Similar experiments for \textit{n-butane isomerization} over the active Pt(r_s)/SZ_{650} and Pt(r_s,o,r_s)/SZ_{650} and other samples in the presence of hydrogen did not result in considerable activity and the maximum conversion obtained was 4–5%. The mechanism for n-butane isomerization, as explained in Chapter I, is a bimolecular mechanism, in which dehydrogenation of n-butane is the first step. In the presence of hydrogen, the equilibrium for this reaction is shifted towards left leading to decrease in formation of n-butene, which results in a decrease in the overall isomerization rate. A similar
Figure 3.27. Conversion vs. TOS for Pt(rₐ,o), Pt(r₁,o), Pt(rₐ,o,rₙ), Pt(rₐ,o,r₁)SZ₆₅₀⁻ based catalysts
result was also obtained by Tomishige et al. who suggested that this inhibition of activity is caused by hydride formation due to hydrogen spillover mechanism [133]. Another explanation would be that the dehydrogenated oligomers formed from n-butene residues are increasingly resistant to hydrogenation than during n-pentane isomerization. Due to decreased hydrogenation, these oligomers could eventually block the acid sites completely by deposition as coke. It could also be that different kind of active acid sites are taking part in the n-butane isomerization as compared to those taking part in the n-pentane isomerization. The n-butane isomerization in the presence of an inert gas such as helium was not attempted.

3.3.4 Effect of the Zr(OH)$_x$ support

Since the surface area of the catalyst varies with the Zr(OH)$_x$ support used, SZ prepared from various sources (with varying surface area and properties) were used to prepare Pt(r$_s$)/SZ$_{650}$ catalyst samples.

Some of the samples were prepared from the as-received zirconium hydroxide from either Aldrich or MEI, whereas others were prepared from the Zr(OH)$_x$ refluxed in NaOH solution. The results of the active samples are presented in Figure 3.28. The sample prepared from SZ$_{650}$(Aldrich) showed an initial conversion of ca. 30% that increased with TOS to reach a nearly stable value of 40-45%. The sample prepared from SZ$_{650}$(MEI) showed a much higher activity compared to that SZ$_{650}$(Aldrich) with almost a steady value near 80% conversion. It also had a much lower selectivity (nearly 35%) towards isopentane.

Refluxing with sodium hydroxide solution increases the surface area of zirconium hydroxide [45]. Samples of Zr hydroxide (Aldrich) and Zr hydroxide (MEI) were refluxed with a NaOH solution at 100 °C for 12 hours. A part of the refluxed sample was leached by boiling in ammonium nitrate solution thrice for 3 hrs. The rest of the
steps for the preparation were the same as for Pt(r$_s$)/SZ$_{650}$ from the precipitated Zr hydroxide. The NaOH refluxed samples (Pt(r$_s$)/SZ$_{650}$-Na) did not show any appreciable activity for n-pentane isomerization. This was true for both the Aldrich and the MEI sample. However, the leached sample from Zr hydroxide (Aldrich) (Pt(r$_s$)/SZ$_{650}$-Na-l (Aldrich)) had much higher activity than even the leached sample from Zr hydroxide (MEI), which showed conversion less than 5% over a period of 30 minutes TOS. The conversion versus TOS for Pt(r$_s$)/SZ$_{650}$-Na-l (Aldrich) is shown in the Figure 3.28. The refluxed-leached SZ$_{650}$ sample shows a higher conversion than the sample prepared from plain Zr hydroxide (Aldrich).

Similarly, samples of Zr hydroxide were prepared from the high surface area MEI sample, by refluxing in solutions with different pH – ammonium hydroxide (SZ$_{650}$-
R₁₂), DD water (SZ₆₅₀-R₇) and zirconyl nitrate (SZ₆₅₀-R₁₈₅). This was done in order to identify if pH of the refluxing solution affected the properties of the final Zr(OH)$_x$ which would, in turn, alter the properties of the final catalyst. There was little affect of the pH of the refluxing solution on the activity of these catalyst samples and all showed very less (∼ 5-7%) conversion. Since the refluxing was carried out in absence of alkali metal, there was little change in the surface area of Zr(OH)$_x$ and hence there was not effect of the activity. The results of the activity experiments indicated that instead of the pH of the refluxing solution, it is the refluxing itself that affects the activity of the catalyst.

Amongst all the samples that were refluxed or refluxed-leached, only the samples prepared by using Zr(OH)$_x$(Aldrich) showed substantial activity. A possible explanation for this apparent anomaly could be due to the low surface area of the Aldrich hydroxide sample (Table 3.1). The Zr(OH)$_x$(MEI) sample had high a surface area of over 300 m$^2$/g where as the Zr(OH)$_x$(Aldrich) sample had a low surface area of only 100 m$^2$/g. The Zr(OH)$_x$(MEI) sample incorporated Na into the matrix structure to a higher extent so that it did not get removed from the hydroxide when it was leached. Chuah and Jaenicke [45, 46] have also indicated the possibility of presence of Na in the Zr(OH)$_x$ matrix structure. If the Na remained within the matrix after the leaching process, it would have reacted preferably with the sulfate species in SZ catalyst and would not allow formation of the active acid sites, thus rendering the prepared SZ with no or very few active acid sites.

3.3.5 Summary

The activity studies clearly lay out the effect of the preparation steps such as the calcination temperature and the pretreatment on the activity and conversion obtained with the Pt/SZ catalysts. Addition of alumina in the preparation did
not lead to an improvement in the performance as was shown by Gao et al. [132] for n-butane isomerization. It is shown that addition of platinum after calcination of S-Zr(OH)$_x$ at the higher temperature leads to a catalyst with improved performance over those reported by Risch [106]. A reduction pretreatment instead of the usual oxidation step proves much more beneficial to the activity of the catalyst. In each case, there was increase in the conversion of n-pentane after carrying out a regenerative oxidation step.

The beneficial effects of reduction and regeneration led to the preparation of a catalyst that was pretreated with a combination of reduction and oxidation steps prior to the reaction. This modification made it possible to achieve conversion levels that are the highest yet available in any published report. The activity of the catalyst is very high and it results in cracking of n-pentane and hence a decrease in the selectivity towards isopentane is observed.

3.4 Discussion

By carrying out activity tests for a series of catalysts prepared from SZ$_{550}$ and SZ$_{650}$, it is clear that for the catalyst to attain a good activity, each step in the preparation procedure is important. The catalysts prepared by the 3-step method described in Chapter [2] are more active and undergo apparent deactivation to a small extent during a typical experiment.

The catalysts prepared by calcining S-Zr(OH)$_x$ at a higher temperature of 650 °C had more activity that the one prepared by calcining at 550 °C but they deactivated fast as well because of the higher rate of the active site coverage by the carbonaceous deposits. Similar results have been obtained by various authors as well [8, 63]. It is the Pt-containing SZ catalysts that provide even better results in the activity studies.
The catalysts that were reduced after addition of platinum, had lesser deactivation and relatively higher activity than those oxidized. However, by carrying further pretreatment of oxidation and re-reduction, it is possible to attain even higher activity over the same catalyst. In effect, by using these steps, the usual deactivation in SZ-based catalyst as a whole has been arrested and this catalyst displays activity so high along with sustained stability as yet reported in available literature for the atmospheric reaction conditions used in this work.

The reasons for this enhancement in the activity by the oxidation-reduction procedure are partly understood by results of the physical characterization. The samples that were calcined at a higher temperature of 650 °C were more crystalline and all had lesser sulfur content in it. Most of the sulfur that remained in the sample is strongly bound to the catalyst. Removal of the labile sulfur species from the surface is important since its presence would prevent the formation of active metallic platinum sites due to poisoning.

Chemisorption results point towards the role of platinum in the reaction. The amount of hydrogen adsorbed increased with the temperature of adsorption. The conversion obtained with Pt(r)/SZ650 catalyst also increased with increasing temperature of reaction. There are two ways in which this result can be interpreted. It could be the simple effect of a higher reaction rate at higher temperature. A higher reaction rate would mean that the deactivation rate would also increase. The catalyst did not suffer from deactivation within the 90 minutes of TOS indicating that it is not so. Alternatively, it could be a direct consequence of the enhanced availability of hydrogen due to higher extent of hydrogen adsorption at higher temperature, besides an increase in reaction due to higher temperature. In such a case, the activity would be higher and the usual deactivation would be suppressed. The results presented in this chapter hint towards a higher likelihood for this phenomenon.
The Pt in the Pt(r)/SZ\textsubscript{650} sample acts as a facilitator for rapid transfer of hydrogen from the feed stream to the active sites on the sulfated zirconia surface. The presence of metallic platinum would be a requirement for this to happen. Results presented later in Chapter 4 show that this is the case and most of the platinum in the more active catalysts is present in the metallic form.

There is a possibility of rearrangement of the acid sites on the surface during the regeneration or the oxidation step, which would lead to a situation where the acid sites receive the hydrogen readily supplied from the platinum sites thereby preventing their deactivation and sustaining high activity. Another likelihood is that in the final catalyst, the platinum is covered with a thin layer of sulfide even in the Pt(r)/SZ\textsubscript{650} samples. Presence of this thin layer of sulfide would hinder the hydrogen transfer capacity of the platinum crystallites. The reduction-oxidation steps cause this layer of sulfide to get depleted in certain facets of the crystallite and hence the phenomenon of hydrogen adsorption and transfer to the support (spillover) is increased. In this scenario, there may not be any rearrangement of sites and it is the hydrogen transfer process that governs the deactivation suppression. However, in either case, the role of platinum is the same and as such it does not take part in the n-pentane isomerization.
This chapter presents the results of the study performed with the aim of investigating the effect of (a) the preparation of the SZ, (b) the pretreatments used prior to reaction and (c) the support used to prepare the SZ catalysts, on the state of platinum in the final as well as used catalysts. Similar study was also performed on a set of inactive catalysts. The tools most suited for probing the metal on SZ support, used during this work include an ex-situ technique (XPS) and a controlled-atmosphere spectroscopy (XAS).

In order to elucidate the effect of method of addition of platinum, platinum adsorption studies were also performed. The adsorption results would clarify how the usual method of adding platinum via wet impregnation compared with the addition via incipient wetness method.

4.1 Literature review on the state of platinum

As has been reported [53, 134] and shown in previous chapter, addition of platinum to SZ catalysts enhances the apparent catalytic activity in the skeletal isomerization of alkanes without deactivation when the reaction is carried out in the presence of hydrogen. The platinum species in Pt/SZ catalysts is rather different than a metallic platinum and does not show appreciable activity in hydrogenation or
hydrogenolysis \[135\], nor does it adsorb CO. The state of platinum is thus a subject of many investigations, however, it is unclear and is still a matter of controversy.

Hattori and co-workers \[104, 136\] used XPS, IR of adsorbed CO and TPR techniques and concluded that platinum is mainly in an oxidized state with some metallic phase inside. On the basis of XPS, XRD and TPR, Dicko and Sayari \[98, 137\] suggested that Pt is metallic in nature, even after calcination in air at 600°C. In contrast, Iglesia et al. \[138\] proposed that the platinum is present as metal sulfide and provides hydrogenation/dehydrogenation activity as well as a site for spillover of hydrogen. Paal and co-workers performed extensive studies using XPS and ISS on Pt/SZ catalysts \[103, 105, 139\] and suggested that Pt is sulfided (i.e. co-ordinated with S) and not in a metallic form.

Zhao et al. \[140\] as well as Tabora and Davis \[76\] used EXAFS spectroscopy to probe the oxidation state of platinum and reported a metallic state similar to PtO\(_2\) for Pt on SZ. Ebitani et al. also used EXAFS but concluded that Pt exists as metallic phase with a co-ordination of 4.9 \[141\] after hydrogen treatment at 350°C. They also reported that Pt particles on SO\(_4^{2-}\)/ZrO\(_2\) were more difficult to reduce than those on plain ZrO\(_2\). Using Pt L-edge XAFS, Shishido et al. \[142\] reported a Pt-Pt coordination of near 7.5 in a catalyst reduced in H\(_2\). Since a considerable Pt-O coordination was also present after H\(_2\) treatment, they proposed a model of platinum on sulfated zirconia where the metallic metal is encapsulated with a layer of platinum oxide (Figure 4.1).

On the basis of the state of the art, it is clear that there is a considerable debate on the state of Pt on sulfated zirconia. This is partly due to the fact that different research groups have used different preparation methods, pretreatments and reactions environments for their analysis. Shishido et al. \[142\] prepared the catalysts with H\(_2\)PtCl\(_6\) where as Paal et al. \[105\] used PtCl\(_4\). Both the catalysts
Figure 4.1. Proposed model of platinum on $\text{SO}_4^{2-}/\text{ZrO}_2$ [142]. The model explains well the contradictory results that Pt is metallic by XRD analysis and is in a cationic state by XPS analysis.

were prepared as per the 2-step method mentioned in Chapter 1. While not clear from the papers, it is suspected that the preparation of Zr hydroxide was not same in both the cases.

For the sake of clarity, the following sections present the results of a particular spectroscopic method each. Within each section, the subsections include the results obtained for a specific study e.g. effect of pretreatment etc.

4.2 X-ray photoelectron spectroscopy results

XPS was performed over select catalysts in order to obtain information on the state of the surface of the catalysts. In particular, the effect of the SZ calcination temperature and the effect of various pretreatments on the state of the surface was studied.

4.2.1 Effect of SZ calcination temperature

Calcination of sulfur-loaded Zr hydroxide is an important step in the preparation of an active and stable Pt-containing SZ catalyst. Catalysts used in this study were prepared from two kinds of sulfated zirconia support – $\text{SZ}_{550}$ and $\text{SZ}_{650}$.

Typical XPS spectra of O 1s, S 2s, Zr 3d and Pt 4f recorded for Pt(r)/$\text{SZ}_{650}$
sample are shown in Figure 4.2. Oxygen 1s spectra could be resolved as a contribution due to 2 different species present on the surface. A shake-up satellite peak is also seen even in the XPS spectra of O 1s. Higher BE peak at ca. 532 eV can be attributed to oxygen in sulfate groups or as hydroxides. The peak near 530 eV is associated with oxygen in metal oxides such as ZrO₂. XPS spectrum of Sulfur 2s seems to indicate presence of 3 kinds of species (Figure 4.3). The sulfur peak appearing at ca. 232.5 eV is typical of sulfates or sulfites (sulfur in +4 or +6 state) where as the peak at ca. 228 eV could correspond to sulfide-like species on Pt or H₂S adsorbed on Pt. The peak at near 225 eV is assigned to sulfidic sulfur (S²⁻).

Since Hafnium is present as an impurity in the stock Zr compounds, it could be present on the surface of the final catalyst as well. If present, a Hf 4d₃/₂ peak would appear at a BE value of 221.3 eV. The peak corresponding to the presence of sulfates decreased when the catalyst was prepared from SZ₆₅₀ indicating lesser formation of surface sulfates. Spectra for Pt 4f could be resolved as 2 kinds of Pt species present in the SZ₅₅₀-based samples and as a single species in the SZ₆₅₀-based samples (Figure 4.4). The 4f₇/₂ peak at near 71 eV for metallic platinum shifts towards higher BE values in the case of SZ₆₅₀ samples. The peak which appears at ca. 72.5 eV could correspond to Pt bonded with S as Pt sulfide or Pt(II).

The surface concentrations as derived from the XPS analysis for a set of catalysts consisting of Pt(r)/SZ₅₅₀ and Pt(r)/SZ₆₅₀, both before and after reaction are presented in Table 4.1. Although spectra for carbon was collected and used for calibration as well as charge shift correction, the calculations for surface concentrations exclude its presence. An XPS survey spectrum indicated presence of Cl in the sample, which is thought to be due to ZrOCl₂ that was used to prepare the Zr hydroxide precursor. While there is an increased presence of Cl on the Pt(r)/SZ₆₅₀ compared to Pt(r)/SZ₅₅₀, the surface Cl concentration essentially remains unchanged within
Figure 4.2. XPS spectra for O 1s, S 2s, Zr 3d and Pt 4f region for Pt(r)/SZ$_{650}$
Figure 4.3. XPS spectra for S 2s for SZ\textsubscript{550} and SZ\textsubscript{650}-based samples
Figure 4.4. XPS spectra for Pt 4f for $\text{SZ}_{550}^-$ and $\text{SZ}_{650}^-$-based samples
TABLE 4.1
SURFACE COMPOSITION FOR Pt(r)/SZ\textsubscript{550} AND Pt(r)/SZ\textsubscript{650} SAMPLES, BEFORE AND AFTER A REACTION (-T), ON A CARBON-FREE BASIS

<table>
<thead>
<tr>
<th>Sample</th>
<th>O</th>
<th>Cl</th>
<th>S</th>
<th>Zr</th>
<th>Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(r)/SZ\textsubscript{550}</td>
<td>71.97</td>
<td>6.11</td>
<td>8.19</td>
<td>13.20</td>
<td>0.52</td>
</tr>
<tr>
<td>Pt(r)/SZ\textsubscript{550} -T</td>
<td>71.68</td>
<td>5.52</td>
<td>7.65</td>
<td>14.89</td>
<td>0.27</td>
</tr>
<tr>
<td>Pt(r)/SZ\textsubscript{650}</td>
<td>66.83</td>
<td>8.34</td>
<td>7.06</td>
<td>17.64</td>
<td>0.13</td>
</tr>
<tr>
<td>Pt(r)/SZ\textsubscript{650} -T</td>
<td>65.30</td>
<td>8.56</td>
<td>7.5</td>
<td>18.44</td>
<td>0.19</td>
</tr>
</tbody>
</table>

The limits of errors in both the fresh and the used SZ\textsubscript{550} or SZ\textsubscript{650} catalyst. Oxygen is the most abundant element present on the surface including the oxygen adsorbed from atmosphere or from absorption of water, besides being present in the form of hydroxide, sulfate or oxide.

The Pt/SZ\textsubscript{550} sample has more surface platinum, which decreases in content when analyzed after reaction and a regeneration. The percent values for sulfur on the surface remain almost the same even though SZ\textsubscript{650} contains almost half the amount of sulfur as on SZ\textsubscript{550}.

Concentrations on the surface of the catalyst can be expressed as a ratio as well. It is expected that the amount of Zr on the surface remained unchanged, since zirconia in tetragonal form is stable. Hence, elemental ratio is a more accurate representation of the surface concentration than expressing it in terms of %. The relevant ratios of elements (S, Pt, O and Zr) are presented as plots in Figure 4.5. The S/Zr ratio in the SZ\textsubscript{650}-based catalyst is lower than in the SZ\textsubscript{550}-based one, which implies that there is more S present in SZ\textsubscript{550} sample than can be implied.
from the surface concentration value alone. There is an indication that there is a change in the sulfur concentration during the reaction and regeneration as the S/Zr decreases to 0.5 for a Pt(r)/SZ\textsubscript{550}-T sample. Similar change is also seen for Pt from the Pt/Zr ratio. More Pt seems to be near the surface in SZ\textsubscript{550} sample than in the SZ\textsubscript{650} sample as well. Changes in the Pt/S ratios in each sample gives a strong indication that the surface is undergoing changes and rearrangement during the reaction and regeneration steps in the life of the catalyst.

From the ratio of O 1s peak area near 532 eV with respect to S, it is evident that in Pt(r)/SZ\textsubscript{550}, most of this sulfur is present as a sulfate since their ratio is close to 4. In the SZ\textsubscript{650} samples, this ratio is lower implying that some of the sulfur is present in forms other than sulfate. It is important to keep in mind that these values are indicative of the elements on or near the surface, i.e. a few Å depth, only.

4.2.2 Effect of pretreatment on Pt in SZ\textsubscript{650}-based catalyst

The previous section clearly shows that the temperature chosen for calcination of sulfated zirconium hydroxide has a dramatic effect on the state of Pt in the SZ-based catalysts. In order to evaluate the effect of pretreatment such as oxidation, reduction on the state of platinum on a SZ\textsubscript{650} catalyst, different series of samples were prepared. The catalysts were prepared from the same batch of SZ\textsubscript{650} since SZ\textsubscript{650} has been shown to result in presence of large metallic platinum crystallites on the SZ catalyst. It is also known from the activity studies that SZ\textsubscript{650} results in catalysts with higher activity and stability than SZ\textsubscript{550}.

PtSZ\textsubscript{650}(o) and PtSZ\textsubscript{650}(r) were prepared as per the 2-step procedure. After impregnating the Zr hydroxide with sulfuric acid, the dried sample was impregnated with Pt from t-AP Nitrate. A part of the sample was then either reduced (PtSZ\textsubscript{650}(r)) or oxidized (PtSZ\textsubscript{650}(o)).
Figure 4.5. Component ratio of elements in Pt/SZ$_{550}$ and Pt/SZ$_{650}$ catalysts
TABLE 4.2
NOMENCLATURE AND CONDITIONS FOR PREPARATION OF Pt/SZ<sub>650</sub> CATALYSTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment used after loading Pt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(o)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>oxidation at 550°C</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;s&lt;/sub&gt;)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 2 hours (short)</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;l&lt;/sub&gt;)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 4 hours (long)</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;s&lt;/sub&gt;,o)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 2 hours, oxidation at 300°C</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;l&lt;/sub&gt;,o)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 4 hours, oxidation at 300°C</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;s&lt;/sub&gt;,o,r&lt;sub&gt;s&lt;/sub&gt;)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 2 hours, oxidation at 300°C, reduction for 2 hours</td>
</tr>
<tr>
<td>Pt(r&lt;sub&gt;s&lt;/sub&gt;,o,r&lt;sub&gt;l&lt;/sub&gt;)/SZ&lt;sub&gt;650&lt;/sub&gt;</td>
<td>reduction at 300°C for 2 hours, oxidation at 300°C, reduction for 4 hours</td>
</tr>
</tbody>
</table>

Similar set of catalysts was also made with the 3-step procedure in which Pt was added to SZ<sub>650</sub>. The pretreatment used for this set of catalysts is explained in Table 4.2. Although the sample has been reduced, during the sample preparation for XPS analysis, they were exposed to air.

Spectra for PtSZ<sub>650</sub>(r) and PtSZ<sub>650</sub>(o) samples are shown in Figure 4.6. The profile for the O 1s, S 2s and the Pt 4f spectra is similar to that of the Pt(r)/SZ<sub>650</sub> samples described in the previous subsection. Oxygen 1s spectra can be resolved into 2 separate peaks corresponding to presence as sulfates or hydroxides and metal oxides (ZrO<sub>2</sub>). Sulfur 2s peak resolves into 3 separate, well defined peaks of which the peak near 224 eV is assigned to sulfur in the form of sulfides. A similar state of adsorbed S or H<sub>2</sub>S on Pt gives rise to a peak near 227 eV. The % concentration of sulfates, as indicated by the area for peak at 232.5 eV, is higher than for sulfides.
Figure 4.6. XPS spectra for O 1s, S 2s and Pt 4f region for catalysts prepared by 2-step method

(peaks at 227-226 eV and 225-224 eV). In the Pt 4f spectral region, there is a considerable difference between the 2 samples. The curve for the oxidized sample resolves into 2 separate Pt species – 72.2 eV and 74.2 eV. The BE of 74.2 eV corresponds to platinum in +4 oxidation state. Approximately 20% of the platinum near the analyzed surface of the catalyst is in this state. In the other sample (reduced), almost all the platinum is in Pt(II) state.

The above result suggests that most of the sulfur in the surface is present in the form of S^{+6} species with some amount also present as sulfide or as adsorbed sulfur.
Pt in the samples is not present as a metallic species instead as Pt(II) or Pt(IV) oxidation state.

Similar set of data is presented (Figure 4.7) for oxidized samples prepared with $SZ_{650}$ according to the 3-step method. A clear difference is seen in the spectra for the S 2s region between the samples made with the 2-step method (Figure 4.6) and the 3-step method. The resolved peak corresponding to sulfates is of lesser intensity in the latter samples. There are a few variations in the BE shift of the platinum 4f$_{7/2}$ peaks from that of Pt(II) state, however they do not correspond to either metallic platinum or platinum with +4 oxidation state by itself. Except for Pt$SZ_{650}$ and the Pt(o)/$SZ_{650}$ samples, all the samples have the Pt 4f$_{7/2}$ peak near 71.8 eV. For the two samples, the Pt peak could be found at 72.25 and 72.42 eV, respectively. This implies that in the rest of the samples, the oxidation state of Pt is slightly lesser than that of a Pt(II). One of the reason for this anomaly could be the effect of the ligand in the Pt(II) compound. More electronegative ligand such as sulfur would cause higher +ve BE shift than oxygen. Based on the above argument, it could be stated emphatically that PtS species is present on the surface.

The concentration of O, Zr, S and Pt present in the near surface region with carbon-free basis, is presented as in Table 4.3. While there are no clear trends, it is evident that most of the surface is covered with oxygen and zirconia with some difference between the samples made as per the 2-step method versus samples with the 3-step method. The % values for S are similar on all samples.

A more clearer observation can be made from the ratios of the components on the surface of these samples presented graphically in Figure 4.8. The difference between the catalysts prepared from the two different methods is clearly noticeable from the O/Zr and S/Zr plots. It implies that per amount of Zr, there is more oxygen and sulfur on the surface when the catalyst is prepared with the 2-step method. These
Figure 4.7. XPS spectra in O 1s, S 2s and Pt 4f region for catalysts prepared as per the 3-step method
<table>
<thead>
<tr>
<th>Sample</th>
<th>Element</th>
<th>O 1s</th>
<th>Zr 3d</th>
<th>S 2s</th>
<th>Pt 4f</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSZ_{650}(r)</td>
<td></td>
<td>72.03</td>
<td>15.91</td>
<td>11.94</td>
<td>0.11</td>
</tr>
<tr>
<td>PtSZ_{650}(o)</td>
<td></td>
<td>71.58</td>
<td>15.70</td>
<td>12.37</td>
<td>0.29</td>
</tr>
<tr>
<td>Pt(o)/SZ_{650}</td>
<td></td>
<td>68.54</td>
<td>18.74</td>
<td>12.51</td>
<td>0.21</td>
</tr>
<tr>
<td>Pt(r_s,o)/SZ_{650}</td>
<td></td>
<td>68.02</td>
<td>18.86</td>
<td>13.0</td>
<td>0.12</td>
</tr>
<tr>
<td>Pt(r_s,o,r_1)/SZ_{650}</td>
<td></td>
<td>67.63</td>
<td>19.65</td>
<td>12.75</td>
<td>0.15</td>
</tr>
<tr>
<td>Pt(r_s,o,r_s)/SZ_{650}</td>
<td></td>
<td>67.81</td>
<td>19.47</td>
<td>12.68</td>
<td>0.12</td>
</tr>
<tr>
<td>Pt(r_1)/SZ_{650}</td>
<td></td>
<td>67.26</td>
<td>19.38</td>
<td>12.34</td>
<td>0.27</td>
</tr>
<tr>
<td>Pt(r_1,o)/SZ_{650}</td>
<td></td>
<td>67.16</td>
<td>19.98</td>
<td>12.70</td>
<td>0.15</td>
</tr>
</tbody>
</table>
ratios do not differ considerably in the samples prepared by the 3-step method. A noteworthy feature is the variation in the O(532)/S ratio. In the 3-step method samples, the ratio lies in the range 1.0 to 1.5 as compared to 3.0 to 3.5 for PtSZ$_{650}$ (r) and PtSZ$_{650}$ (o) samples. This is a clear indication that sulfur is not present on the surface in the form of sulfates.

4.2.3 Summary

The XPS results presented above relate to the state of the surface and surface concentration of different elemental species in the SZ samples. Most important result from the analysis of various samples is that majority of the sulfur is present in +6 to +4 oxidation state but it is not in the form of sulfates. Even though the SZ$_{550}$ and SZ$_{650}$ samples had differing amounts of sulfur content (SZ$_{550}$ had almost 50% more wt% S than SZ$_{650}$), the amount of sulfur present on the surface was similar. There is a variation in the ratios of Pt/Zr and Pt/S between the SZ$_{550}$ and SZ$_{650}$ samples that hints at surface reconstruction or arrangement during the reaction and pretreatments.

4.3 X-ray absorption spectroscopy results

The use of XAS could help understand the effect of the SZ calcination temperature, of pretreatments on the SZ$_{650}$ samples, and the state of platinum in the active catalysts. This spectroscopic method allows analysis of the samples in conditions close to the actual reaction environment as opposed to XPS technique.

4.3.1 Effect of SZ calcination temperature

As mentioned earlier, calcination of sulfur-loaded Zr hydroxide is an important step in the preparation of an active and stable Pt-containing SZ catalyst. Two kinds of sulfated zirconia support – SZ$_{550}$ and SZ$_{650}$ were used to prepare the catalysts.
Figure 4.8. Surface concentration ratios (XPS) of sample components
used in this study. Another sample (Pt/SZ$_{550}$) from a previous study\cite{106} was also used in order to compare with the prepared samples. This sample was prepared by calcining the Pt-impregnated SZ$_{550}$ at 550$^\circ$C. Hence, it will be referred to as Pt(o)/SZ$_{550}$. The samples are referred to with their treatment used before the measurements, suffixed in square (box) brackets e.g. [r] corresponding to a reduction in H$_2$. The reduction pretreatment was considered necessary so as to reverse the oxidation of the catalyst when it had been exposed to air while performing sample preparation, prior to measurements. Recall that the XAS measurements were carried out in a controlled atmosphere conditions in a sealed quartz measurement tube.

Figure 4.9 includes the magnitude of the Fourier transforms of EXAFS of the used Pt(o)/SZ$_{550}$ and Pt(r)/SZ$_{550}$. The magnitude of the Fourier transform for Pt(o)/SZ$_{550}$ catalyst shows a strong peak at $R = 1.65$ Å which is related to Pt-O scatter whereas another strong peak ($R = 2.1$ Å) corresponding to Pt-S is the only peak seen in the Fourier transform for the Pt(r)/SZ$_{550}$ catalyst. This indicates that in the Pt(r)/SZ$_{550}$ catalyst, almost all the platinum is bonded to sulfur.

The magnitude of the Fourier transforms of EXAFS of the reduced Pt(r)/SZ$_{550}$ (Pt(r)/SZ$_{550}$[r]), Pt(r)/SZ$_{650}$[r] and Pt(r)/SZ$_{650}$[r,o] catalysts is shown in Fig. 4.10. Since the isomerization reaction involved excess hydrogen flow, reducing the catalyst prior to EXAFS measurement makes the state of metal on the catalyst similar to that in the reaction environment. The transform for Pt(r)/SZ$_{650}$[r] (dotted line) exhibits peaks at 2.1 and 2.55 Å characteristic of presence of Pt-Pt and Pt-S bond distances. The transform for Pt(r)/SZ$_{550}$[r] (solid line) exhibits features characteristic of Pt-S alone. This indicates that in the catalyst sample calcined at 550$^\circ$C, Pt is mostly bonded to S whereas calcination at 650$^\circ$C eliminates some of the S from the Pt which is consistent with the higher activity observed in this sample (page 119).
When the Pt(r)/SZ$_{650}$[r] is further oxidized (Pt(r)/SZ$_{650}$[r,o]), the peaks due to Pt-Pt and Pt-S decrease and a new peak due to Pt-O is observed. This Pt-O peak is also observed in the case of used Pt(r)/SZ$_{650}$ catalyst. It is evident, due to absence of the Pt-S scatter peak on the used Pt(r)/SZ$_{650}$ catalyst, that during the reaction-regeneration cycles, the sulfur species are removed from the catalyst.

The best fit EXAFS parameters (CN = coordination number, R = bond distance, Debye Waller factor (DWF), $E_0$ = Energy origin) of multiple shells (Pt-Pt, Pt-S and Pt-O) are summarized in Table 4.4. The real and imaginary parts of the Fourier transform of Pt-L$_3$-edge $k^2$-weighted EXAFS and fitted spectra of two reduced catalysts – Pt(r)/SZ$_{550}$[r] and Pt(r)/SZ$_{650}$[r] – reproduced by using the parameters in Table 4.4 are shown in Fig. 4.11 and Fig. 4.12.

Results for the Pt(r)/SZ$_{550}$[r] fit a state of metal where Pt is mostly bound to S (Pt-S bond, CN = 3.9) as PtS (sulfide) [104]. The CN for Pt-S decreased only a small amount to a CN of 3.6 from a CN of 3.9 in an unreduced catalyst indicating that the bond between Pt and S is quite strong and not easily reducible. The XANES

![Figure 4.9. Magnitude of $k^2$ weighted FT of EXAFS data for a used Pt(o)/SZ$_{550}$ catalyst (solid line) compared with Pt(r)/SZ$_{550}$ (dashed line)](image-url)
Figure 4.10. Magnitude of $k^2$ weighted FT on EXAFS data. Comparison between Pt(r)/SZ$_{550}$ reduced ($\Delta k=3.01$-10.45 Å$^{-1}$) (solid line), Pt(r)/SZ$_{650}$ reduced ($\Delta k=2.75$-13.80 Å$^{-1}$) (dotted line) and Pt(r)/SZ$_{650}$ further oxidized (dashed line).

Figure 4.11. Fit of isolated shell and raw data for Pt(r)/SZ$_{550}$[r], ($\Delta k=3.01$-10.45 Å$^{-1}$, $\Delta r=1.51$-2.42 Å). (bold solid–real part of FT raw data, thin solid–imaginary part of FT raw data, bold dotted–real part of the fitted data, thin dotted–imaginary part of the fitted data)
<table>
<thead>
<tr>
<th>Sample</th>
<th>Treatment</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>$R$ (Å)</th>
<th>DWF $(\times 10^3) / (\text{Å}^2)$</th>
<th>$E_0$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(o)/SZ$_{550}[^u]$</td>
<td>used $[^b]$</td>
<td>Pt-O</td>
<td>6.0</td>
<td>2.04</td>
<td>3.3</td>
<td>0.4</td>
</tr>
<tr>
<td>- [u,r] reduced $[^c]$</td>
<td>Pt-Pt</td>
<td>2.4</td>
<td>2.76</td>
<td>1.0</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.7</td>
<td>2.32</td>
<td>3.3</td>
<td>5.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-O</td>
<td>1.1</td>
<td>2.05</td>
<td>3.33</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Pt(r)/SZ$_{550}$</td>
<td>Pt-S</td>
<td>3.9</td>
<td>2.32</td>
<td>2.1</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>- [r] reduced $[^c]$</td>
<td>Pt-S</td>
<td>3.6</td>
<td>2.32</td>
<td>2.3</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>Pt(r)/SZ$_{650}$</td>
<td>Pt-Pt</td>
<td>8.4</td>
<td>2.76</td>
<td>1.0</td>
<td>-1.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.4</td>
<td>2.32</td>
<td>2.1</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-O</td>
<td>1.0</td>
<td>2.05</td>
<td>1.0</td>
<td>-2.5</td>
<td></td>
</tr>
<tr>
<td>- [r] reduced $[^c]$</td>
<td>Pt-Pt</td>
<td>9.3</td>
<td>2.75</td>
<td>1.0</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.6</td>
<td>2.32</td>
<td>2.1</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>- [r,o] reduced,</td>
<td>Pt-Pt</td>
<td>7.8</td>
<td>2.76</td>
<td>1.0</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td>oxidized $[^d]$</td>
<td>Pt-S</td>
<td>0.2</td>
<td>2.32</td>
<td>2.1</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-O</td>
<td>1.2</td>
<td>2.05</td>
<td>1.0</td>
<td>-1.9</td>
<td></td>
</tr>
<tr>
<td>- [u] used $[^b]$</td>
<td>Pt-Pt</td>
<td>8.1</td>
<td>2.77</td>
<td>1.0</td>
<td>-0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pt-O</td>
<td>2.0</td>
<td>2.05</td>
<td>2.0</td>
<td>0.8</td>
<td></td>
</tr>
</tbody>
</table>

$[^a]$Co-ordination No.

$[^b]$3 cycles of reaction and regeneration

$[^c]$Reduction in flowing $\text{H}_2$ at 150°C for 1 hour

$[^d]$Oxidized in $\text{O}_2/\text{He}$ mix. at 150°C for 1 hour after reduction
confirm that state of Pt in Pt(r)/SZ\textsubscript{550}[r] is +2 oxidation state. The S species co-ordinated with Pt originates due to the loosely bound sulfur present on the SZ\textsubscript{550} which poisons the Pt by binding as PtS. Since Pt is not available in a metallic state to dissociate hydrogen, the Pt(r)/SZ\textsubscript{550} catalyst would not be expected to arrest deactivation which is consistent with the activity results on this catalyst (see Figure 3.18). The activity of the fresh Pt(r)/SZ\textsubscript{550} catalyst is comparable to that of the unmodified SZ\textsubscript{550} or SZ\textsubscript{650} catalysts. This also indicates that acid sites are active regardless of the state of Pt on the SZ surface.

In contrast to the SZ\textsubscript{550}-supported catalysts, a Pt(r)/SZ\textsubscript{650} catalyst shows high CN for Pt-Pt bond in all cases indicating the presence of moderate to large metallic Pt crystallites. A bulk metallic sample of Pt would show a co-ordination of 12 corresponding to an FCC lattice configuration. Even though the first shell of every Pt atom is not completely coordinated to Pt, the high CN values close to metal CN values indicate large particles with bond distance and characteristics similar to

![Figure 4.12. Fit of isolated shell and raw data for Pt(r)/SZ\textsubscript{650}[r] (Δk=2.75-13.80 Å\textsuperscript{-1}, Δr=1.84-2.92 Å). (bold solid–real part of FT raw data, thin solid–imaginary part of FT raw data, bold dotted–real part of the fitted data, thin dotted–imaginary part of the fitted data)](image-url)
metallic Pt. The agreement of the fitted data to raw data also indicates that there is a small amount of Pt-S bonds.

When Pt(r)/SZ$_{650}$[r] was subsequently oxidized (Pt(r)/SZ$_{650}$[r,o]), the Pt-O bond appears indicating formation of an oxide layer but not to a large extent since there is still a significant fraction of metallic crystallites present (CN = 7.8). Data presented in Table 4.4 also indicates that Pt-S bonds are getting reduced as the catalyst is treated with oxidation-reduction cycles as observed by a decreasing Pt-S CN from 0.4 in the fresh sample to 0.2 in the reacted-regenerated sample (Pt(r)/SZ$_{650}$[u]). This sample which has undergone 3 cycles of regeneration-reduction and a final regeneration in air, still has considerable metallic platinum present (Pt-Pt CN = 8.1), which suggests that the reduced Pt crystallites reach a stable structure after such pretreatments.

Hattori and co-workers have previously reported the presence of small Pt particles (Pt-Pt coordination of 4.9) [141] as well as larger Pt particles (CN = 7.8) [142] on Pt/SO$_4^{2-}$/ZrO$_2$ catalysts. B. Davis and coworkers have also used EXAFS to study Pt/SZ catalysts [140] and reported metallic Pt with almost same CN as that for a Pt foil. All these reported results, however, were obtained from catalysts in which Pt is added together with addition of sulfate group. Thus even though the catalysts mentioned in the above papers were reported to have Pt as metallic, they deactivated rapidly with TOS and showed low residual activity[123], as is the case with catalysts prepared as per the conventional 2-step method.

Figure 4.13 shows the normalized Pt-L$_3$-edge XANES for Pt(r)/SZ$_{550}$[r]. The XANES for Na$_2$PtCl$_4$ (Pt$^{+2}$ oxidation state) and H$_2$PtCl$_6$ (Pt$^{+4}$ oxidation state) are also included. The absorption edges shown have been normalized as per standard procedures. The shape and area of the adsorption edge of Pt(r)/SZ$_{550}$[r] are similar to that of Pt$^{+2}$ reference compound. In contrast, the XANES of the Pt(r)/SZ$_{650}$[r]
Figure 4.13. Normalized XANES spectra. solid–Pt(r)/SZ_{550}[r], dotted–Na_2PtCl_4 (reference), dashed–H_2PtCl_6 (reference)

TABLE 4.5

XANES FITS DATA (ERROR ESTIMATE: 5-10%)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fraction Pt^+2</th>
<th>Fraction Pt^0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(r)/SZ_{550}[r]</td>
<td>1.0</td>
<td>0.0</td>
</tr>
<tr>
<td>Pt(r)/SZ_{650}[r]</td>
<td>0.1</td>
<td>0.9</td>
</tr>
<tr>
<td>Pt(r)/SZ_{650}[r,o]</td>
<td>0.5</td>
<td>0.5</td>
</tr>
</tbody>
</table>

(Fig. 4.14) are close to, but not completely metallic Pt foil. Fractions of Pt^0 and Pt^+2 obtained by fitting the XANES data to fractions of the spectra of the reference compounds are shown in Table 4.5. The results indicate that Pt(r)/SZ_{550}[r] is only in Pt^+2 state where as over 90% of Pt in the Pt(r)/SZ_{650}[r] is metallic. Upon oxidation, as in Pt(r)/SZ_{650}[r,o], almost 40% of this metallic Pt is converted to a Pt with +2 oxidation state.
4.3.2 Effect of pretreatment on Pt in SZ$_{650}$-based catalyst

The previous section clearly shows that the temperature chosen for calcination of sulfated zirconium hydroxide has a dramatic effect on the state of Pt in the SZ-based catalysts. In order to evaluate the effect of pretreatment such as oxidation, reduction on the state of platinum on a SZ$_{650}$ catalyst, different series of samples were prepared. The catalysts were prepared from the same batch of SZ$_{650}$ since SZ$_{650}$ has been shown to result in presence of large metallic platinum crystallites on the SZ catalyst. It is also known from the activity studies that SZ$_{650}$-based catalysts have higher activity and stability than SZ$_{550}$-based ones.

PtSZ$_{650}$(o) and PtSZ$_{650}$(r) were prepared as per the 2-step procedure. After impregnating the Zr hydroxide with sulfuric acid, the dried sample was impregnated with Pt from t-AP Nitrate. A part of the sample was then either reduced (PtSZ$_{650}$(r)) or oxidized (PtSZ$_{650}$(o)).

Another set of catalysts was prepared with the 3-step procedure in which Pt was added to SZ$_{650}$. The pretreatment used in preparing this set of catalysts is explained.

![Normalized XANES spectra](image)

Figure 4.14. Normalized XANES spectra. dotted– Pt(r)/SZ$_{650}$(r), dashed–Pt(r)/SZ$_{650}$(r,o)
in Table 4.2. The samples were pressed in a thin wafer as described in Chapter 2 and were analyzed in the fluorescence mode. All the samples for which reduction was the last pretreatment used were reduced in flowing hydrogen at 150°C in the EXAFS reactor tube. This was done to ensure the measurements correspond to a catalyst surface in the state right after reduction pretreatment. The samples for which oxidation was the last pretreatment were analyzed without any reduction or oxidation prior to XAS measurement.

The EXAFS fitting procedure was performed after isolating $\chi(k)$ corresponding to a range of $\Delta(k) = 3.05 - 11.6 \, \text{Å}^{-1}$ from the whole data. A proper fit was a one in which there was a considerable match with the $\chi(k)$ in the k-space with different k weightings ($k$, $k^2$, $k^3$) and with the Fourier transform of $k^2 \chi(k)$ (both real and imaginary) in the R-space. The same procedure was adopted for the analysis of all the samples so as to maintain consistency in data reduction. Error estimates in the evaluation of coordination number was $\pm 0.1$ and in the bond distance (R) was $\pm 0.03 \, \text{Å}$. For the XANES analysis, the error range was approximately 10%.

The magnitude of Fourier transforms of PtSZ$_{650}$(o) and PtSZ$_{650}$(r) are shown in Figure 4.15. The large peak at 1.65 Å corresponding to oxidized Pt is stronger in PtSZ$_{650}$(o) as would be expected. In contrast, in the PtSZ$_{650}$(r) catalyst, reduction, after impregnation with S and Pt, has led to poisoning of the Pt in the catalyst as observed by the broad peak at 2.1 Å that corresponds to Pt-S scatter. It is clearly seen that the pretreatment had a detrimental effect in case of the reduced catalyst as compared to the oxidized one. Most likely, the loosely bound sulfur on the surface is getting reduced to H$_2$S in the presence of hydrogen which then poisons the Pt. It is important to recall that this catalyst also had 4 wt% of sulfur loaded in the beginning. As seen in results of the DTA-TGA studies of the catalyst samples in Chapter 3 almost 40% of the sulfur present on the surface is loose-bound and could
be removed from the catalyst.

The parameters derived from the best fit for the EXAFS of the above two catalyst samples are included in Table 4.6. The fits correspond to what could be interpreted from the FT magnitude. The Pt in PtSZ\(_{650}(o)\) is mostly coordinated with O where it is coordinated as Pt-S in PtSZ\(_{650}(r)\). The CN for Pt-O is 5.6 indicating that almost all the Pt is in an oxidized form and there is almost no presence of metallic Pt as opposed to a report by Dicko and Sayari [98] who prepared PtSZ by the two-step method as above and calcining at a temperature of over 600°C. These authors reported the platinum to be in a metallic state.

Figure 4.16 shows the Pt-L\(_{III}\) XANES edge for the above samples. The absorption energy shown has been normalized as per standard procedures. The shape and area of the absorption edge of PtSZ\(_{650}(o)\) indicate an oxidized form of Pt. In the case of PtSZ\(_{650}(r)\), the shape of the absorption edge is similar to that of a Pt that is less oxidized than that in PtSZ\(_{650}(o)\). The XANES data from the fits to the

![Graph](image-url)
Figure 4.16. Normalized XANES spectra: PtSZ\textsubscript{650}(o) and PtSZ\textsubscript{650}(r)

absorption edges is shown in Table 4.7. The fraction of Pt\textsuperscript{0} is mostly negligible and hard to determine with greater accuracy in both the samples. The XANES fit for the reduced catalyst sample shows all Pt present as Pt\textsuperscript{2+} that could be due to the formation of PtS. In the oxidized catalyst sample, the fraction of Pt in the Pt\textsuperscript{4+} state is 0.8. The remaining fraction (20\%) is in the Pt\textsuperscript{2+} state.

On comparing the magnitudes of Fourier transforms of Pt(o)/SZ\textsubscript{650} and Pt(\textsubscript{r}s)/SZ\textsubscript{650} or Pt(\textsubscript{r}l)/SZ\textsubscript{650}, there is a clearly marked visible difference in the intensity of the peak corresponding to Pt-Pt coordination at R = 2.45Å (Figure 4.17). The

\begin{table}[h]
\centering
\caption{Parameters Used in the EXAFS Fit of PtSZ\textsubscript{650}(o) and PtSZ\textsubscript{650}(r)}
\label{tab:exafsfits}
\begin{tabular}{llcccc}
\hline
Sample & Scatter & Coord. No. & R Å & \text{DWF (x10\textsuperscript{3})(Å\textsuperscript{2})} & E\textsubscript{0}, eV \\
\hline
PtSZ\textsubscript{650}(o) & Pt-O & 5.6 & 2.05 & 1.0 & 1.8 \\
PtSZ\textsubscript{650}(r) & Pt-S & 2.3 & 2.33 & 2.5 & 3.5 \\
\hline
\end{tabular}
\end{table}
EXAFS FT magnitude of the Pt(o)/SZ\textsubscript{650} is similar to that of the PtSZ\textsubscript{650}(o) catalyst sample. These FT plots of the catalyst samples reduced for shorter or longer duration show just a little difference indicating that reduction time may not be making too much difference in the chemical arrangement of Pt on the catalyst. The pattern of the plots of the reduced catalyst samples is representative of the larger crystallites of metallic Pt.

EXAFS parameters obtained from the best fit for the above three samples are shown in Table 4.8. There is no metallic platinum in the Pt(o)/SZ\textsubscript{650} and all the Pt is coordinated as Pt-O with a CN of 6.0 (bond length = 2.02 Å). On the other hand, both the catalysts that are reduced after addition of platinum have a high CN of 8.1 and 9.2 for the Pt-Pt scatter (bond length of 2.75 Å) for Pt(r\textsubscript{s}) and Pt(r\textsubscript{l}) samples respectively. This result is similar to that presented in earlier section and shows that reduction at 300°C leads to a presence of large crystallites of metallic platinum in the catalyst. The reduction time does play some role in determining the size of the crystallites as the CN is higher in the case of the Pt(r\textsubscript{l}) catalyst sample. There is some amount of Pt-S also present in both cases (CN = 0.5 in Pt(r\textsubscript{s}), 0.4 in Pt(r\textsubscript{l})) and is most likely due to the effect of reduction of sulfates from the surface in the presence of hydrogen.

XANES analysis indeed shows that most of the platinum is in metallic form.

<table>
<thead>
<tr>
<th>TABLE 4.7</th>
<th>XANES ANALYSIS DATA (fractions)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Pt\textsuperscript{0}</td>
</tr>
<tr>
<td>PtSZ\textsubscript{650}(o)</td>
<td>–</td>
</tr>
<tr>
<td>PtSZ\textsubscript{650}(r)</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 4.17. Magnitude of FT of $k^2$-weighted EXAFS of Pt(o)/SZ$_{650}$, Pt(rs)/SZ$_{650}$ and Pt(r1)/SZ$_{650}$ (Pt$^0$) and the fraction of Pt in Pt$^{+2}$ (Table 4.9) is negligible within the error bounds of the analysis (5 - 10% error) in both catalyst samples. Apart from a somewhat larger size of Pt crystallite, it does not seem likely that reduction for a longer time had a significant effect on the state of Pt in the catalysts prepared by reduction after loading platinum. The XANES of these catalysts looks almost similar as seen in Figure 4.18.

In contrast to the reduced catalysts, the oxidized catalyst seems to have only oxidized Pt in it (Pt-O scatter with CN = 6.0). No other kind of Pt scatter could be used in order to obtain a good fit. XANES analysis confirms the oxidized nature of Pt and all of the platinum is in +4 oxidation state, bound to oxygen.

The oxidized catalyst samples i.e. Pt(o), Pt(rs,o), Pt(r1,o) display an interesting trend. The plots of magnitude of the Fourier transforms as shown in Figure 4.19 look similar to each other except for the differences in the peaks that correspond to Pt-O scatter from the sample. The amount of oxidized Pt decreases if the Pt-containing
<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R ˚Å</th>
<th>DWF (x10³)(Å²)</th>
<th>E₀, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(o)/SZ₆₅₀</td>
<td>Pt-O</td>
<td>6.0</td>
<td>2.02</td>
<td>1.0</td>
<td>-1.1</td>
</tr>
<tr>
<td>Pt(rs)/SZ₆₅₀</td>
<td>Pt-Pt</td>
<td>8.1</td>
<td>2.74</td>
<td>2.5</td>
<td>-5.0</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.5</td>
<td>2.30</td>
<td>2.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Pt(rl)/SZ₆₅₀</td>
<td>Pt-Pt</td>
<td>9.2</td>
<td>2.75</td>
<td>2.5</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.4</td>
<td>2.30</td>
<td>2.5</td>
<td>-2.5</td>
</tr>
</tbody>
</table>

Figure 4.18. Normalized XANES spectra: Pt(o)/SZ₆₅₀, Pt(rs)/SZ₆₅₀ and Pt(rl)/SZ₆₅₀.
sample has been prepared by reduction. It can also be interpreted from the plot that
the Pt in the catalyst sample prepared by longer reduction gets oxidized to a higher
extent than the one which has been prepared by shorter reduction duration. This
effect is probably due to the removal of sulfur from the sample during reduction. It
is well known that presence of sulfur in the sample along with platinum affects the
properties of the metal e.g. shift in the CO adsorption band in IR analysis [143].
It is possible that the presence of sulfur near the platinum crystallites is the cause
for hindrance in oxidation of Pt(r_s,o)/SZ_{650} as compared to the Pt(r_l,o)/SZ_{650}. The
evaluation of sulfur content in these samples did not show any appreciable difference
in sulfur content.

Parameters obtained from the EXAFS fit analysis show that although Pt(r_s)/
SZ_{650} has somewhat lower Pt-Pt coordination than Pt(r_l)/SZ_{650}, when oxidized at
500°C, both the samples experience considerable oxidation of platinum. The CN for
Pt-Pt decreases from 8.9 to 3.5 for Pt(r_s,o) and from 9.2 to 2.5 for Pt(r_l,o) samples
(Table 4.10). The content of oxidized platinum observed as the Pt-O scatter is not
considerably different from each other (CN of 3.4 in Pt(r_s,o) and 4.1 in Pt(r_l,o)).

XANES for the samples prepared with oxidation as the final pretreatment are
included in Figure 4.20. In the XANES plot, the fraction of platinum with lower

<table>
<thead>
<tr>
<th>TABLE 4.9</th>
</tr>
</thead>
<tbody>
<tr>
<td>XANES ANALYSIS DATA (fractions)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt^0</th>
<th>Pt^{+2}</th>
<th>Pt^{+4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(0)/SZ_{650}</td>
<td>–</td>
<td>–</td>
<td>1.0</td>
</tr>
<tr>
<td>Pt(r_s)/SZ_{650}</td>
<td>0.95</td>
<td>0.05</td>
<td>–</td>
</tr>
<tr>
<td>Pt(r_l)/SZ_{650}</td>
<td>1.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>
Figure 4.19. Magnitude of FT of $k^2$-weighted EXAFS of Pt(o)/SZ$_{650}$, Pt(r$_s$,o)/SZ$_{650}$ and Pt(r$_t$,o)/SZ$_{650}$

### TABLE 4.10

PARAMETERS USED IN THE EXAFS FIT OF Pt(r$_s$,o)SZ$_{650}$ AND Pt(r$_t$,o)SZ$_{650}$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R Å</th>
<th>DWF (x10$^2$)(Å$^2$)</th>
<th>$E_0$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(r$<em>s$,o)/SZ$</em>{650}$</td>
<td>Pt-Pt</td>
<td>3.5</td>
<td>2.74</td>
<td>2.5</td>
<td>-3.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3.4</td>
<td>2.02</td>
<td>1.0</td>
<td>-1.0</td>
</tr>
<tr>
<td>Pt(r$<em>t$,o)/SZ$</em>{650}$</td>
<td>Pt-Pt</td>
<td>2.5</td>
<td>2.74</td>
<td>2.5</td>
<td>-3.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4.1</td>
<td>2.04</td>
<td>1.0</td>
<td>0.8</td>
</tr>
</tbody>
</table>
oxidation number decreases as the height and area of the peak decreases. Pt(r,s,o) sample has the largest fraction of metallic platinum (0.45) and 55% platinum on +2 oxidation state (Table 4.11). Pt(r,l,o) sample has lesser percentage of metallic platinum (as also observed from EXAFS) and almost 70% is in the higher oxidation state of +4. As mentioned above, PtSZ_{650}(o) has all the platinum in +2 state (Table 4.7) and Pt(o)/SZ_{650} contains 100% the platinum in the +4 oxidation state (Table 4.9).

The above results also demonstrate that the amount of sulfur on the catalyst surface plays an important role in the oxidation state of the platinum in the sample. In PtSZ_{650}(o), there was 4 wt% sulfur in the sample when platinum was being added. Presence of this large amount of sulfur causes the final oxidation state of platinum as +2 which corresponds to most of the platinum bonded to the sulfur and not with oxygen. In the Pt(o)/SZ_{650}, where almost 50% of the sulfur has been removed due to calcination at 650°C, the platinum is in +4 state instead. The sulfur present in the sample does not affect the state of platinum at all. Similar effect is seen in the other oxidized samples – Pt(r,s,o)/SZ_{650} and Pt(r,l,o)/SZ_{650}, where there is no indication of the presence of Pt^{+2}.

The Fourier transform magnitude of the EXAFS spectra for the re-reduced samples – Pt(r,s,o,r,s)/SZ_{650} and Pt(r,s,o,r,l)/SZ_{650} are almost similar (Figure 4.21), and

| TABLE 4.11 |
|------------------|-----------------|-----------------|-----------------|
| Sample           | Pt^{0}          | Pt^{+2}         | Pt^{+4}         |
| Pt(r,s,o)/SZ_{650} | 0.45            | –               | 0.55            |
| Pt(r,l,o)/SZ_{650} | 0.3             | –               | 0.7             |

159
Figure 4.20. Normalized XANES spectra: Pt(o)/SZ$_{650}$, Pt(rs,o)/SZ$_{650}$ and Pt(rs,o)/SZ$_{650}$

the fitted parameters also indicate similarity in the size of the platinum crystallites (as indicated by the Pt-Pt coordination number in both that are close to each other). However, in both the samples, the platinum that was in the oxidized form (as in Pt(rs,o) and Pt(rs,o)) is turned into mostly metallic Pt again. There is no Pt-O in either sample and the amount of Pt-S does not change much upon reducing again and it seems that the sulfur on the surface reappears upon reducing. The change in the number of Pt-S coordination is not significant between the reduced only samples and the Pt(rs,o,rs) or the Pt(rs,o,rs) and remains almost constant at 0.4-0.5. The fact that Pt-S scatter is not observed in the EXAFS of the oxidized samples but reappears when those samples are reduced, confirms that there is a surface restructuring occurring during the reduction and oxidation processes carried out on Pt-containing SZ samples.

The XANES data (Figure 4.22) and the fits (Table 4.13) demonstrate that re-reduction brings back the metallic state of platinum in the catalyst samples as
Figure 4.21. Magnitude of FT of k²-weighted EXAFS of \( \text{Pt}(r_s,o,r_s)/SZ_{650} \) and \( \text{Pt}(r_s,o,r_l)/SZ_{650} \)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R Å</th>
<th>DWF ((x10^3))(Å²)</th>
<th>E₀, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Pt}(r_s,o,r_s)/SZ_{650} )</td>
<td>Pt-Pt</td>
<td>8.9</td>
<td>2.75</td>
<td>2.5</td>
<td>-2.8</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.4</td>
<td>2.30</td>
<td>2.5</td>
<td>-2.6</td>
</tr>
<tr>
<td>( \text{Pt}(r_s,o,r_l)/SZ_{650} )</td>
<td>Pt-Pt</td>
<td>9.4</td>
<td>2.76</td>
<td>2.5</td>
<td>-3.0</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.4</td>
<td>2.30</td>
<td>2.5</td>
<td>-2.7</td>
</tr>
</tbody>
</table>
Figure 4.22. Normalized XANES spectra: Pt\((r, o, r_s)/SZ_{650}\) and Pt\((r, o, r_l)/SZ_{650}\) compared to the 40-55% fraction of platinum in the +4 oxidation state observed in the Pt\((r, o)\) and the Pt\((r, l, o)\) samples. There is no discernible change in the state of the metal between samples which were reduced once (i.e. Pt\((r_s)\) or Pt\((r_l)\)) only and the samples which are re-reduced. EXAFS fit parameters show nearly the same CN for each of the Pt-Pt and Pt-S scatter present in each corresponding sample. XANES of both samples indicates platinum in the catalyst to be in a 95% metallic state (Pt\(^0\)).

From the above results, it is evident that the pretreatments used in the prepa-

**TABLE 4.13**

**XANES ANALYSIS DATA (fractions)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pt(^0)</th>
<th>Pt(^+2)</th>
<th>Pt(^+4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt((r, o, r_s)/SZ_{650})</td>
<td>0.95</td>
<td>0.05</td>
<td>–</td>
</tr>
<tr>
<td>Pt((r, o, r_l)/SZ_{650})</td>
<td>1.0</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

162
ration of an active catalyst have significant effect on the state of platinum in the catalyst. Depending on whether the last step in preparation is oxidation or reduction, one finds platinum to be in a metallic state or in an oxidized state. A study of repeated reduction pretreatment also reveals that there is almost no difference between the number of pretreatments and the oxidation state of Pt (thus, the size of Pt crystallites). It was also found out that reduction for a longer time in the 3-step preparation, leads to state wherein the platinum in the catalyst can be oxidized to a higher extent as compared to when the reduction is for a shorter period. This effect might be due to the removal of sulfur from the vicinity of the platinum crystallites, which results in lessening of the influence of sulfur that is present on the surface over the platinum present.

4.3.3 Influence of the Zr(OH)$_x$ support

Different kinds of supports were used to evaluate the influence of the support on the activity of the catalyst for n-pentane isomerization as well as the state of platinum. This also allowed assessment if preparation of zirconia influences the active SZ acid sites. The activity study on these catalyst is discussed earlier in Chapter 3. In this section, results of the EXAFS study on selected samples, which were prepared starting with Zr(OH)$_x$ that had either been modified by refluxing or obtained from a commercial supplier (Aldrich or MEI), are presented.

Table 4.14 lists the samples that were analyzed in this particular study.

Magnitudes of the Fourier transform of $k^2$-weighted $\chi(k)$ function for EXAFS of Pt(r)/SZ$_{650}$(Aldrich) and Pt(r)/SZ$_{650}$(MEI) are plotted in Figure 4.23. The Aldrich hydroxide precursor had a low surface area of 100 m$^2$/gm. The surface area of the MEI (FZO/922) hydroxide was very high – almost 350 m$^2$/gm. The MEI sample also had a higher pore size and pore volume.


**TABLE 4.14**

**LIST OF SAMPLES PREPARED FROM DIFFERENT Zr HYDROXIDE PRECURSORS**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Pt(r)/SZ\textsubscript{650} (Aldrich)</td>
<td>Aldrich Zr hydroxide</td>
</tr>
<tr>
<td>2 Pt(r)/SZ\textsubscript{650} (MEI)</td>
<td>MEI FZO/922 Zr hydroxide</td>
</tr>
<tr>
<td>3 Pt(r)/SZ\textsubscript{650} (Na)</td>
<td>used NaOH instead of NH\textsubscript{4}OH</td>
</tr>
<tr>
<td>4 Pt(r)/SZ\textsubscript{650} Na(l)</td>
<td>Aldrich Zr(OH)\textsubscript{x}, refluxed with NaOH, leached</td>
</tr>
<tr>
<td>5 Pt(r\textsubscript{s},o,r\textsubscript{s})/SZ\textsubscript{650} (MEI)</td>
<td>MEI FZO/935 Zr hydroxide</td>
</tr>
</tbody>
</table>

**Figure 4.23.** Magnitude of FT of \(k^2\)-weighted EXAFS of samples prepared from Zr hydroxide from Aldrich and MEI

---

164
TABLE 4.15
PARAMETERS USED IN THE EXAFS FIT OF Pt(r)/SZ_{650}(Aldrich) AND Pt(r)/SZ_{650}(MEI)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R Å</th>
<th>DWF (x10^3)(Å^2)</th>
<th>E₀, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(r)/SZ_{650}(Aldrich)</td>
<td>Pt-Pt</td>
<td>6.9</td>
<td>2.73</td>
<td>2.5</td>
<td>-5.4</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.6</td>
<td>2.30</td>
<td>2.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Pt(r)/SZ_{650}(MEI)</td>
<td>Pt-Pt</td>
<td>4.9</td>
<td>2.72</td>
<td>2.5</td>
<td>-5.0</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.7</td>
<td>2.30</td>
<td>2.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The shape of the Fourier transform curve for both the samples is similar although the intensity of the curve for MEI sample is slightly lower than that for the Aldrich sample. The EXAFS fit parameters (Table 4.15) show that the CN for Pt-S scatter does not differ to a large extent. The size of Pt crystallites in the MEI is relatively smaller (Pt-Pt CN = 4.9) than that of the Aldrich samples, which has medium size Pt particles (Pt-Pt CN = 6.9). The activity of the MEI sample analyzed by EXAFS was not very high (conversion of ca. 10%), however after regeneration the activity was similar on both samples, i.e., n-pentane conversion was exceeding 45%.

The other three samples – Pt(r)/SZ_{650}(Na), Pt(r)/SZ_{650}-Na(l) and Pt(r_{s,o,r_{s}})/SZ_{650}(MEI) have the magnitude of Fourier transforms with similar shape (Figure 4.24) but the intensity of the (Na) sample indicates presence of more metallic Pt than on the others. The parameters obtained from the best fit of the EXAFS results are presented in Table 4.16. The (Na) sample has very large metallic particles with a Pt-Pt coordination of 9.8. The -Na(l) and the MEI (FZO/935) samples both have moderately large metallic particles with a Pt-Pt CN of 7.4 and 6.9, respectively. The Pt-S scatter is relatively similar but a bit small (0.3) in the MEI
Figure 4.24. Magnitude of FT of $k^2$-weighted EXAFS of (a) Pt(r)/SZ$_{650}$(Na), (b) Pt(r)/SZ$_{650}$-Na(l) and (c) Pt(r$_{o}$,r$_{s}$)/SZ$_{650}$(MEI) sample. The activity of the samples is quite different though. With the exception of the (Na) sample, the -Na(l) and the MEI samples have quite high activity with a n-pentane conversion over 50%. The (Na) sample is *inactive* in spite of the large metallic particles present in the catalyst. The presence of sodium in the sample, does not allow formation of acid sites by neutralizing the sulfates and hence the catalyst is not active for alkane activation.

Although difficult to quantify, the final color of the catalyst can be a helpful in estimating presence of metallic platinum on the catalyst. The samples prepared from Zr(OH)$_x$(MEI)MEI, did not have the usual dark gray color associated with catalysts that have moderately sized platinum crystallites. In fact, the color of these samples was close to that of the low activity samples made by the 2-step method. One reason for this anomaly could be the high porosity of the MEI samples as compared to that of the Zr hydroxide that was prepared by precipitation or from Aldrich.

On the basis of the above results, it is evident that the precursor hydroxide
seems to have an effect on the particle size of the platinum and thus the activity as well. The particle size of platinum on the catalyst determines the stability of the catalyst if the acidity is not affected by other factors such as with the presence of sodium. This effect is also observed in the previous results with samples that had large metallic platinum present in the catalyst.

4.3.4 State of platinum in the inactive catalysts

Inactive catalyst can give good information about the factors affecting of the activity or inactivity. Since the catalyst prepared for activity studies were mostly active or attained increasing activity upon regeneration, some of the samples were made inactive by exposing the prepared catalyst samples to heat treatment or varying the preparation such as increasing the amount of sulfur. A catalyst was said to be *inactive* if the usual pretreatment and/or regeneration did not lead to any increase of activity beyond that of 5% conversion. Table 4.17 lists the conditions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R Å</th>
<th>DWF (x10^3)(Å²)</th>
<th>E₀, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt(r)/SZ₆₅₀(Na)</td>
<td>Pt-Pt</td>
<td>9.8</td>
<td>2.76</td>
<td>2.5</td>
<td>-2.2</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.6</td>
<td>2.32</td>
<td>2.5</td>
<td>2.2</td>
</tr>
<tr>
<td>Pt(r)/SZ₆₅₀-Na(l)</td>
<td>Pt-Pt</td>
<td>7.4</td>
<td>2.75</td>
<td>2.5</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.6</td>
<td>2.31</td>
<td>2.5</td>
<td>2.1</td>
</tr>
<tr>
<td>Pt(ᵣᵣ,ᵣₛ)/SZ₆₅₀(MEI)</td>
<td>Pt-Pt</td>
<td>6.9</td>
<td>2.74</td>
<td>2.5</td>
<td>-2.9</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>0.3</td>
<td>2.30</td>
<td>2.5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

TABLE 4.16
PARAMETERS USED IN THE EXAFS FIT OF Pt(r)/SZ₆₅₀(Na), Pt(r)/SZ₆₅₀-Na(l) AND Pt(ᵣᵣ,ᵣₛ)/SZ₆₅₀(MEI)
TABLE 4.17
INACTIVE CATALYSTS

<table>
<thead>
<tr>
<th>Sample</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>heated in stagnant air at 500 °C</td>
</tr>
<tr>
<td>B</td>
<td>heated to 300 °C in absence of H₂ flow</td>
</tr>
<tr>
<td>C</td>
<td>10 wt% of S before calcination at 650°C</td>
</tr>
</tbody>
</table>

under which the catalyst was made inactive.

The magnitude of the FT for a catalyst with ca. 40% stable conversion and a sample after its heat treatment in stagnant air at 500 °C (sample A) makes it very obvious as to what is the state of platinum on the catalyst (Figure 4.25). The active catalyst had a curve characteristic of metallic platinum whereas the inactive sample showed no presence of a metallic platinum, and instead a peak that could correspond to only Pt-S is observed. The active catalyst did have a very large CN of 11.0 for Pt-Pt in the active catalyst. The presence of sulfur in the catalyst is too small to detect due to the presence of large crystallites of Pt.

Parameters used to fit the EXAFS function for sample A (Table 4.18) confirm that there is no metallic Pt in the inactive sample but only a Pt-S scatter with a CN of 4.7. Such a high CN value for Pt-S was also observed in the case of Pt(r)/SZ₅₅₀. The sulfided Pt in Pt(r)/SZ₅₅₀ did not get reduced indicating strong bonding of S with Pt.

Sample B was prepared by heating Pt-containing Sz₆₅₀ in hydrogen environment (no flow) at a temperature of 300 °C. The magnitude of its FT shows a profile that is similar to that of metallic platinum (Figure 4.26). The EXAFS parameters presented in Table 4.18 show that the sample B has a large fraction of metallic Pt with a Pt-Pt CN of 9.1. But it also have a very high Pt-S CN of 4.0. This can be
Figure 4.25. Magnitude of Fourier Transform of k²-weighted EXAFS of an active catalyst versus inactive catalyst

interpreted as a layer of sulfided Pt covering the metallic crystallites. If the metallic Pt is covered with a strong Pt-S layer, which does not get reduced by the usual pretreatments used during the activity studies, the Pt on the catalyst would not be able to provide rapid hydrogen to the acid sites and the activity of the catalysts would not be high.

Sample C also had a large CN of 4.0 for Pt-S and did not show any presence of metallic platinum. This sample was prepared by loading 10 wt% of sulfur on it prior to calcination. Although, there was removal of loose bound sulfur from the hydroxide during calcination at 650 °C (TGA studies in Chapter 3), there was much larger amount of sulfur present on the surface in this sample even after reduction that affected the platinum during its reduction. Formation of Pt-S in the sample indicates that the sulfur in the sample formed H₂S during the reduction procedure, which reacted with the platinum compound to give Pt-S on the surface. With accurate XPS measurements, this would be possible to notice, however, those measurements
Figure 4.26. Magnitude of FT of $k^2$-weighted EXAFS of inactive samples A, B and C would need to be done under controlled atmosphere using in-situ treatments for the catalyst prior to being moved into the analysis chamber.

The results presented in this section demonstrate that the presence of Pt-S in moderate to large coordination number, implying presence of platinum poisoned

<table>
<thead>
<tr>
<th>TABLE 4.18</th>
</tr>
</thead>
<tbody>
<tr>
<td>PARAMETERS USED IN THE EXAFS FIT OF THE INACTIVE Pt/SZ SAMPLES, A, B AND C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Scatter</th>
<th>Coord. No.</th>
<th>R Å</th>
<th>DWF $(x10^3)(Å^2)$</th>
<th>$E_0$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Pt-S</td>
<td>4.7</td>
<td>2.30</td>
<td>5.7</td>
<td>-0.4</td>
</tr>
<tr>
<td>B</td>
<td>Pt-Pt</td>
<td>9.1</td>
<td>2.77</td>
<td>2.5</td>
<td>-0.8</td>
</tr>
<tr>
<td></td>
<td>Pt-S</td>
<td>1.0</td>
<td>2.32</td>
<td>2.5</td>
<td>-4.3</td>
</tr>
<tr>
<td>C</td>
<td>Pt-S</td>
<td>4.0</td>
<td>2.30</td>
<td>6.0</td>
<td>-0.6</td>
</tr>
</tbody>
</table>
with sulfur, nullifies the positive synergistic effect of platinum in the presence of hydrogen to prevent the deactivation of the SZ-based catalysts. The conditions of preparation and pretreatment seem to be ideal for preparing such a catalyst and large modifications in the procedure lead to an inactive catalyst. It may be possible to reduce the Pt-S to metallic platinum but if that is carried out at a temperature higher than 350 °C, the acidity of the catalyst is likely to suffer, thus, yielding a catalyst with lower or no activity for alkane activation.

4.3.5 Summary of XAS results

The above analysis showed that in the SZ$_{550}$-based sample, most of the platinum was bound to either sulfur or oxygen and was not available as metallic platinum. In the case of Pt(r)/SZ$_{550}$, the Pt-S bonds were sufficiently strong and did not get reduced easily. All the SZ$_{650}$-based samples showed a strong presence of Pt-Pt bonds indicating metallic platinum present in the sample. The amount of Pt-S and Pt-O bonds was minimal. The XANES results confirmed that platinum was in the +2 state in the Pt(r)/SZ$_{550}$ whereas in the Pt(r)/SZ$_{650}$, it was present as Pt$^0$. Even in the catalysts prepared by the 2-step method and pretreated at 650 °C, the platinum was not present as Pt-Pt but as either Pt-O or Pt-S.

The study about the effect of pretreatments on the state of platinum showed without any doubt that longer reduction resulted in larger crystallites of metallic platinum on the SZ$_{650}$ sample. The large crystallites were also amenable to higher degree of oxidation when contacted with air and converted to Pt$+4$ oxidation state of PtO$_2$. The XAS studies also indicated an effect of the support precursor type on the platinum in the sample. On the low surface area Zr(OH)$_x$ (Aldrich) support, the size of the platinum crystallites was smaller (lesser Pt-Pt CN) than that on the MEI support which had larger surface area. Similarly, the Na-precipitated Zr(OH)$_x$
had a large Pt-Pt coordination. This was probably due to sodium that was trapped with the solid Zr(OH)$_x$ and reacted with the sulfates.

4.4 Platinum adsorption onto SZ$_{650}$

During the preparation of a heterogeneous catalyst, addition of the metal is commonly performed via the process of impregnation, whereby metal complexes dissolved in aqueous solutions are contacted with a porous oxide catalyst support such as alumina, silica and in this work, SZ. Typically, a contact time of an hour is allowed for the noble metal to adsorb from the aqueous solution onto the support surface. The support with adsorbed metal is then filtered, if excess solution has been employed, the catalyst dried and treated to transform the metal from its precursor state to its final state.

Adsorption of platinum onto the support dictates the dispersion of the active metal on the catalyst. By controlling the pH of the solution used in adsorption of platinum onto the catalyst support, the amount of the platinum adsorbed can, in principle, be regulated and hence, a catalyst with known dispersion can be prepared $^{[144, 145]}$.

Many models have been put forward describing the “adsorption-diffusion” process of metal on a support. A typical model is depicted in Figure 4.27. Three separate regimes have been identified – (a) the liquid phase in which the speciation of the coordination complexes of the noble metal is modeled as a function of pH, (b) the oxide surface and (c) the support-solution interface where the equilibration of between the metal complex and support surface take place.

A revised physical adsorption model (RPA) proposed by Regalbuto and coworkers $^{[109, 146]}$ is a recent attempt to “transform the art of catalyst preparation into a science”. The model predicts the experimental results obtained by various groups
for adsorption of platinum onto alumina support. According to the model, the adsorption of the hydrolyzable metal cations is largely a physical process, capable of being described by an a priori calculation of coulombic and solvation contributions to the adsorption free energy. Early qualitative studies suggest that the principal attraction is electrostatic [147]. PZC refers to the point of zero charge i.e. a pH where the net surface charge is zero. Positively charged oxide surfaces corresponding to pH < PZC, are capable of adsorbing anions, and negatively charged surfaces (pH > PZC) are capable of adsorbing cations [148].

With the aim of understanding the effect of the SZ support on the adsorption of platinum from chloroplatinic acid solution (CPA) and tetra ammonium platinum chloride (t-APCl) and possibly investigate preparation of catalysts with known dispersion, pH shift experiments were conducted in order to find the state of the surface of SZ_{550} and SZ_{650}. The results are presented in Figure 4.28 and 4.29, the plots corresponding to a basis surface loading (amount of support surface per solution volume)
The pH shift, that is the range of initial pH of the solution for which the final pH of solution and the support remains the same, is similar in both cases of surface loading. The final pH of this solution does not increase above 3 till the initial pH of the solution exceeded 11. Beyond the initial pH of 11, the final solution pH did not show any shift and remained almost the same as the initial pH. From a comparison of the data for plain zirconia support in the plots, it is evident that the SZ support surface (SZ$_{550}$ or SZ$_{650}$) are highly negatively charged. The data was fitted to a pH shift model [108] in order to estimate parameters for use in the revised RPA model. The PZC calculated from the model fit was at a low value of 2.5.

The results of the platinum adsorption experiments using a t-APCI solution are
Figure 4.29. pH shift measurement: experimental data and model fit [basis: 1000 m²/l]
presented in Figure 4.30 where uptake of platinum in $\mu$moles per area of the sample is plotted against the final pH of the solution. Tetra ammonium Platinum complex is a positively charged species and adsorbs onto the negatively charged SZ surface as seen in the plot. The platinum uptake ($\Gamma$) profile shows a hump-like curve for both SZ$_{550}$ and SZ$_{650}$ support samples. However, the revised RPA model predicts a higher adsorption plateau over the range of pH between 5 to 11. The range of pH where the pH shift was observed in Figure 4.29 is similar (4 to 10). For the case of plain zirconia, the revised RPA model predicts the trend in the uptake of platinum reasonably well.

Figure 4.31 shows the results of adsorption of platinum from CPA solution onto SZ$_{550}$ and SZ$_{650}$ support. The adsorption of platinum (quantified as uptake) was scattered and the pH range of 1 to 6. Since the SZ surface is negatively charged, most of the adsorption was measured for low to middle range of solution pH values. The expected profile for the RPA model fit predicts almost no uptake of platinum for all pH values. However, as seen in the plot, the uptake of platinum exceeds that with t-APCl in some cases. The amount platinum uptake over the plain ZrO$_2$, as calculated by the revised RPA model, follows the same trend as the experimental observation.

The results indicate significant differences between the experimental data and the prediction based on the revised RPA model. The obvious conclusion that can be drawn is that the model focuses mainly on the adsorption aspect of oxide supports. SZ is different than normal oxide surface since it has a tendency to adsorb water from the atmosphere. It is likely that the surface of SZ has more hydroxyl groups present on the surface than has been accounted for while performing the model calculations. While an accurate modeling effort would require extensive analysis based on the effects observed for SZ support, this preliminary study shows that
preparing an SZ catalyst with varying and controllable dispersion of platinum would entail implementation of procedures that have yet to be found either based on a proper understanding of the behavior of charged hydroxide support or by extensive experimental investigations.

4.5 Discussion

The results presented from this comprehensive study of Pt/SZ catalysts using XAS and XPS highlight the state of platinum metal necessary to obtain high activity for n-pentane isomerization over Pt-containing SZ catalysts. It is shown that presence of sulfided platinum (Pt-S, Pt$^{+2}$) on the catalyst results in low conversion activity where as if the state of platinum is resembling that of a metallic one (Pt$^{0}$),
Figure 4.31. Adsorption of platinum from CPA solution over SZ$_{550}$ and SZ$_{650}$ support (surface loading = 500 m$^2$/l)
the resultant catalyst shows exceptionally high activity as in the case of Pt(r_s)/SZ_{650} or Pt(r_s,o,r_s)/SZ_{650} samples.

The SZ_{550}-based catalysts had a higher sulfur content and hence addition of platinum on the sample led to the poisoning which was evident in the fast decay in the activity observed in these catalysts. Similarly, adding Pt to S-Zr(OH)_x as in the conventional 2-step preparation along with high temperature reduction or oxidation also results in platinum being present as either Pt-S or Pt-O depending on the pretreatment. The large amount of sulfur present on S-Zr(OH)_x, again poisons the platinum by forming PtS_2 whereas in the case of oxidation the platinum is oxidized instead of forming larger crystallites of metallic platinum, which would result in higher activity. These catalyst samples did not show any improvement in the isomerization activity.

It was possible to reduce the oxidized platinum to some extent but sulfur forms a strong bond with platinum that was not possible to break easily by hydrogen reduction. This does not allow reduction of platinum to metallic state, thus rendering it ineffective for its role in the isomerization reaction.

SZ_{650} has a lower sulfur content and is more crystalline. After adding platinum to SZ_{650}, further pretreatments dictate the state of the metal. The oxidation of the platinum-loaded sample leaves all the platinum as PtO_2 with +4 oxidation state. Reduction instead caused the platinum to form relatively large crystallites of metallic platinum. This amounts to very low values of dispersion of metal on the support.

Hattori and coworkers also reported a similar result from their studies on state of palladium on supports of varying acidity [149]. They observed the acidic support affects the dispersion of the metal i.e lower dispersion with increasing acidity of the support, and further prevents it from being oxidized. Much earlier, Adamiec et al. reported on the influence of acid-base properties of the oxide supports on the
dispersion of the metal during oxygen treatments.

By performing various treatments on a catalyst prepared by the 3-step method, the Pt in the catalyst was found to exist as large crystallites of metallic platinum but even these large metallic particles of Pt are susceptible to oxidation and a thin layer of oxide forms when exposed to oxidizing conditions. This oxidation was found to be easily reversed. This is concurrent with the results of Adamiec et al. who found that oxygen treatment at 550 °C did not lead to re-dispersion of the metal if the support did not have appreciable basicity, instead it caused a decrease in Pt dispersion. Thus during the oxidation pretreatment for Pt(r_s,o)/SZ_{650} or for Pt(r_s,o,r_s)/SZ_{650}, only a small layer of oxide formed which was reducible back to metallic platinum. The Pt(r_s,o,r_s)/SZ_{650} and Pt(r_s,o,r_l)/SZ_{650} samples also showed a higher CN for Pt-Pt scatter than that of Pt(r_s)/SZ_{650}, indicating a slight increase in the crystallite size and, hence, a lower dispersion.

It is clear from the XPS results that surface of the catalyst undergoes some sort of arrangement during the various treatments. This result is in spite of the major drawback of XPS that it is an ex-situ technique and the catalyst sample was exposed to air while it was being prepared for analysis. The surface that is probed in vacuum is much different that what would be if not exposed to air prior to measurement. Hence, it was not possible to ascertain if the metallic platinum is covered with a thin layer of oxidized or sulfided platinum.

Adsorption studies of platinum complexes revealed that SZ can not be treated as a typical oxide support and does not allow adsorption of platinum such that catalysts with known dispersion can be prepared. The RPA model failed considerably in predicting the uptake of platinum onto the support in solutions of different pH. Since SZ is a highly acidic support, there appears to be an enhanced interaction and solvation effect which is not accounted for in the formulation of this model.
In general, wet impregnation does not adsorb as much platinum as when forced incipient wetness is used as was done throughout this work.

A most recent paper by Furuta [151] dealt with the effect of the electric type of platinum complex ion on the isomerization activity of the Pt/SZA samples. The author used spray impregnation (similar to incipient wetness) and reported that a catalyst with anionic chloroplatinic acid precursor (CPA) showed lower dispersion than one prepared from a cationic precursor.
CHAPTER 5

OPERANDO INFRARED SPECTROSCOPY STUDIES

5.1 Introduction

Infrared spectroscopy can be considered as the first and the most important of the modern spectroscopic techniques that has found general acceptance in characterization of the surface chemistry of heterogeneous catalysts. The most common application of infrared spectroscopy in catalysis is to identify species adsorbed or chemisorbed on the catalyst surface, since it permits to monitor directly the way in which these species are chemisorbed. In addition, the technique is useful in identifying phases that are present in precursor stages of the catalyst during its preparation [120].

In this chapter, the in-situ studies carried out with a few selected samples of SZ-based catalyst is presented. The study was carried out to evaluate the changes in the surface of the SZ-based catalyst during the various pretreatments and during the reaction with the aim of elucidating the possible causes of enhanced activity of Pt(r_s,o,r_s)/SZ_{650} catalyst. The experiments were carried out as described in Chapter 2. For the experiments involving in-situ reduction of the samples, the steps in the flow and temperature program were the same as that for the actual reduction in the quartz tubular reactor. For the experiments involving in-situ n-pentane isomerization, the reaction was carried out at 250 °C in flow of hydrogen that was bubbled through n-pentane maintained at 0 °C.
Various authors have adopted different approaches in experimentation and interpretation of their results with infrared spectroscopy on SZ and modified SZ catalysts, which are presented briefly below.

5.2 Literature Review

Most of the reported literature includes the use of infrared spectroscopy to probe the acid sites on the surface of the catalyst. Despite the numerous reports of use of infrared spectroscopy to characterize SZ-based catalyst, there are very few reports of its use in *operando* i.e. during the reaction and treatments itself. The study presented in this chapter is an attempt to investigate the effects of the preparation and pretreatment on the catalyst as well as during a reaction. Hence, the rest of the section presents a brief review of the published works that have included similar studies.

The acidity measurements and characterization of the SZ catalysts has been extensively reviewed by Song and Sayari [8]. The presence of both Brønsted and Lewis acid sites is considered necessary for a SZ-based catalyst to have good isomerization activity. The acidity is usually studied with a probe molecule such as pyridine, CO, ammonia etc. For e.g., pyridine adsorbs on both Lewis and Brønsted acid sites with distinct characteristic bands [75, 152].

Characteristic band positions from various studies reported in literature are tabulated in Table 5.1. The most important one among these are the bands in the region corresponding to the -OH stretching (3800-3600 cm$^{-1}$, ZrOH groups) and the sulfate stretching regions (1500-800 cm$^{-1}$).

Jin et al. assigned a band at 1390 cm$^{-1}$ to the asymmetric O=S=O stretching vibration of bidentate surface sulfate species with high covalent character [64]. Infrared bands at $\sim$ 1355 and 1370 have been assigned to stretching vibrations of
<table>
<thead>
<tr>
<th>Band position (cm$^{-1}$)</th>
<th>Mode of oscillator</th>
</tr>
</thead>
<tbody>
<tr>
<td>3770</td>
<td>terminal -OH (with Zr)</td>
</tr>
<tr>
<td>3670</td>
<td>bridging -OH (with others)</td>
</tr>
<tr>
<td>1600</td>
<td>$\delta$(HOH), physisorbed or coordinated</td>
</tr>
<tr>
<td>1450-1300</td>
<td>$\nu$(S=O)</td>
</tr>
<tr>
<td>1370-1395</td>
<td>asmm. O=S=O stretching in $(\text{ZrO})_2\text{SO}_2$</td>
</tr>
<tr>
<td>1200-950</td>
<td>$\nu$(S-O)</td>
</tr>
<tr>
<td>1300-1195</td>
<td>sym. O=S=O stretching in $\text{Zr}_2\text{SO}_2$</td>
</tr>
<tr>
<td>800-650</td>
<td>$\delta$(O-S-O)</td>
</tr>
</tbody>
</table>

single S=O groups in two different tridentate complexes ($\text{(ZrO)}_3\text{S}=\text{O}$) [9]. This assignment was supported by *ab initio* calculations performed by Haase and Sa¨ ur [153]. Polynuclear species (e.g. $\text{S}_2\text{O}_7$), characterized by S=O stretching frequencies above 1400 cm$^{-1}$ has also been suggested. Babou et al., on the basis of the sharp band 1391 cm$^{-1}$, suggested the formation of SO$_3$ molecules grafted on zirconia under high dehydration conditions [69]. In general, the structure of surface sulfates strongly depends on the degree of hydration. With increasing degree of hydration highly covalent sulfates are converted into less covalent forms and finally into ionic sulfates [16].

By using different activation temperatures for the pretreatment of SZ$_{620}$, Song and Kydd [154] studied the effect of water content on the acidity and activity. These authors found an increase in Lewis acid sites as well as a decrease in Brønsted sites with decreasing water content (i.e. increase in drying temperature). However,
introducing water vapor in the catalyst restored the Brønsted sites.

Davis et al. [155] used pyridine adsorption to probe SZ acid sites upon various drying conditions. Their study showed that the ratio of Lewis to Brønsted acid sites changed from 0.45 to 0.3 with increase in drying temperature. Thus they suggested a pretreatment temperature lower than 315°C. In their other work [156] about a study of interaction of isobutene with SZ and mesostructured SZ, they found that olefin adsorption did not cause sulfur reduction in meso-SZ and claimed a different sulfur binding mechanism for meso SZ sample.

Reaction-initiated surface modification during benzoylation of anisole observed by Trunschke et al. [157] indicate that sulfur is not evenly distributed on the surface (evidenced by presence of S-free domains and non-acidic ZrOH species), and that the presence of carbonaceous deposits caused deactivation of SZ.

By using DRIFTS during n-butane isomerization on conventional SZ and sulfated mesoporous zirconia with MCM-41 structure, Jentoft et al. [158] concluded that the nature of the surface is influenced by the support and that there are two groups of active sites responsible for short-term and long-term activity of the catalyst.

Li and Gonzalez [152] studied regeneration of SZ catalysts with DRIFTS and found that regeneration in N₂ resulted in elimination of surface sulfate species making the catalyst inactive even though the acid strength decreased only to a small extent. Regeneration in O₂ restored the initial activity of the deactivated catalyst.

Lavalley and coworkers [159] studied the sulfation of ZrO₂ and found that the total band area between 1200-800 cm⁻¹ was nearly proportional to the amount of sulfur on the catalyst. The same is observed in the case of SZ₅₅₀ and SZ₆₅₀ as well.

These authors also found that the spectra of the samples dosed with different amounts of SO₂ became identical upon oxidation of the samples for longer time. In an earlier article, they performed reduction of SZ sample in hydrogen at elevated
temperatures of 450, 500 and 550 °C and found a uniform decrease in the all band intensities indicating loss of sulfur from the surface and hence a decrease in the acidity of the sample [9]. A similar result was also reported by Morterra et al. for reduction of Pt-containing SZ sample at 500 °C [127].

In their recent study of adsorption/desorption dynamics on SZ and Pt/SZ samples, Stevens Jr. et al. also exposed their catalysts to hydrogen at 150 °C [160]. Their conclusion was that increased exposure to hydrogen results in growth in adsorbed H$_2$O and loss of S=O, however lack of formation of the terminal ZrOH (∼3770 cm$^{-1}$) or the S-OH near 3639 cm$^{-1}$ suggests a significantly different interpretation.

In another very recent study, Hattori et al. used CO and H$_2$ adsorption on platinum-modified SZ catalysts [130]. These authors performed their IR measurements on samples maintained at a high temperature of 250 °C and exposed to either CO or H$_2$. They reported that formation of H$_2$O (with band assignments at 3450, 3050 and 1610 cm$^{-1}$) was crucial to obtain an active catalyst. These authors however also found that unmodified SZ$_{650}$ was not affected by H$_2$ adsorption.

5.3 *Operando* DRIFTS results

Transmission IR was attempted initially and Figure 5.1 shows the transmission spectra obtained for KBr-supported wafers of the SZ$_{650}$ and Pt-modified SZ samples. The wafers were heated in the IR reactor chamber in the flow of He till 150 °C to dry the sample prior to measurements. The spectra for SZ samples are, in general, quite complex in the SO stretching regions. From this figure, it is clear that there are definite variations observed between spectra of the unmodified versus the Pt-modified sample. At the same time, it is also clear that it would be difficult to reproduce the results due to non-uniformities in mixing and pelletizing the sample.
Figure 5.1. Transmission spectra of SZ samples with KBr powder. Moreover, the differences between different samples are not pronounced enough to allow a good analysis. The DRIFTS was then carried out in order to get more detailed information about the catalyst than transmission IR.

Figure 5.2 shows the DRIFTS spectra obtained for SZ samples prepared from the Zr hydroxide obtained from MEI in the mid-IR range. The samples were dried at 125 °C by flowing helium through the catalyst sampling bed. The spectra was collected after cooling the sample to a temperature of 30 °C while maintaining the flow of helium.

The spectra are different from those that have been reported in the literature. This is mainly due to differences in the sample preparation, preparation of the SZ and different techniques, such as transmission or reflection IR, used to report the results [161].
Figure 5.2. DRIFTS spectra for SZ (MEI) samples

In the Figure 5.2, two separate spectral regions belonging to characteristic groups present in SZ-based material can be identified: (a) the region between wavenumbers of 3600-2800 cm\(^{-1}\), attributed to the presence of hydrogen bonded OH groups and strongly bound water molecules, and (b) the sulfate stretching region in the 1400-900 cm\(^{-1}\) range. The interaction between the sulfate and surface hydroxyl groups has a strong bearing on the sulfate groups that are generated on the surface.

The spectra for the calcined SZ samples show two main bands in the OH stretching region: a narrow weak one at 3640 cm\(^{-1}\), and a broad one centered at ca. 3400 cm\(^{-1}\). The broad band centered at 3400 cm\(^{-1}\) is asymmetric and consists of several unresolved bands such as the ones arising due to multi-center bonded protons in the surface HSO\(_4^-\) structures at ca. 3390 and 3230 cm\(^{-1}\) [65]. In general, all
these bands could be assigned to hydrogen bonded hydroxyl groups associated with surface sulfates. The weak band appearing at 3640 is due to the isolated bridging OH groups on ZrO$_2$ [162]. The corresponding hydroxyl species have been considered responsible for the strong Bronsted acidity of SZ [69].

The appearance of the bending mode of H$_2$O centered at ca. 1620 cm$^{-1}$ in the calcined samples as compared to the uncalcined one, also gives evidence of the presence of the strongly bound OH groups similar to the ones observed in sample with strongly adsorbed water molecules. This band also seems to be consisting of bands from different kinds of OH groups because of its asymmetric and broad shape. Again, this band does not appear in the uncalcined S-Zr(OH)$_x$ and is generated only after calcination of the sulfated hydroxide.

In the region corresponding to the S=O stretching vibrations (1450-1300 cm$^{-1}$), a strong narrow band appears at 1375 cm$^{-1}$, which is assigned to tridentate sulfates with a single S=O oscillator. Jin et al. referred to this species as covalent, organic-like sulfate [64]. In contrast, a sulfate species with ionic character corresponding to bidentate sulfates is expected to give rise to a band in the S=O stretching region of 1280-1230 cm$^{-1}$ [127]. Such a band is also observed in the spectra shown in Figure 5.2. The intensity of the band at ca. 1245 cm$^{-1}$ is very strong in the case of the uncalcined S-Zr(OH)$_x$ and SZ$_{550}$, but has diminished in the SZ$_{650}$ and the SZ$_{650}$-Na samples.

The area of the band in S=O stretching region with broad peaks in the uncalcined S-Zr(OH)$_x$ and SZ$_{550}$ is much greater than that in the SZ$_{650}$ and SZ$_{650}$-Na samples, which corresponds to higher wt% of sulfur present in the former samples. This is consistent with the result reported by Lavalley and coworkers [159].

The spectrum for the uncalcined sample contains another distinct broad envelope centered at 1125 cm$^{-1}$, which is not as prominent as in the other samples. This band
is tentatively assigned to S-OH bending vibration in SZ [130]. Beside these bands, 
there is a weak band present near 875 cm$^{-1}$ in the SZ$_{550}$ sample that undergoes a 
red shift of about 5 cm$^{-1}$ in the case of the SZ$_{650}$ sample. This band can also be 
attributed to be due to the bending mode of the O-S-O bond in SO$_3$.

The DRIFTS spectra of SZ$_{650}$ and its platinum-modified counterparts are shown 
in Figure 5.3. In all the samples shown, the spectrum of plain Zr(OH)$_x$ has been 
chosen as the reference spectrum. Note that the spectrum for the SZ$_{650}$ sample is 
very different than that obtained with the SZ$_{650}$(MEI) sample in Figure 5.2. It has 
been shown earlier in chapters 3 and 4 that the support used makes a considerable 
difference in the properties of the final catalyst. It is evident from the spectra that 
there are differences between the surface S=O, -OH and S-O structures between the 
SZ samples. These differences are important because such species are involved in 
the acid site formation.

The effect of adding platinum and various pretreatments is clearly observed 
in the spectra in Figure 5.3. The differences between the unmodified versus Pt- 
modified samples can be mainly seen as (a) an overall increase of the bands in 
the OH stretching region, (b) a large decrease in the intensity of the set of bands 
at 1240, 1150 and 1060 cm$^{-1}$, and (c) the appearance of a new band in the SO 
bending region of wavenumbers below 900 cm$^{-1}$. The intensity of the band near 
3690 cm$^{-1}$ with a shoulder at 3770 cm$^{-1}$ has also increased. Presence of platinum 
with large metallic crystallites (Pt/SZ$_{650}$) in the presence of hydrogen results in the 
appearance of bands corresponding to the formation of large amount of hydroxides 
on the surface of the catalyst.

Oxidation of the reduced sample (Pt(r$_s$,o)/SZ$_{650}$) causes a decrease in the intensity 
of the broad envelope belonging to the OH stretching region and an increase in 
the bands in the SO stretching region near 1150 cm$^{-1}$. A decrease in the intensity
Figure 5.3. DRIFTS spectra for Pt-modified $SZ_{650}$ samples
of the band corresponding to the terminal OH in ZrO$_2$ (bands in 3600-3750 cm$^{-1}$) is also observed. A small decrease in the band intensity of the O-S-O bending at 770 cm$^{-1}$ indicates that some of it has been converted into S=O upon oxidation. The Pt(r$_s$,o,r$_s$)/SZ$_{650}$ sample shows that the changes reversed and its spectrum looks similar to that of the Pt(r$_s$)/SZ$_{650}$. The Pt(r$_s$,o,r$_s$)/SZ$_{650}$ sample is very active giving the highest conversion of n-pentane. From the spectrum, it can be concluded that, increasing presence of the OH groups, S-O and S=O groups is important for obtaining a good activity.

Among the samples, it is also observed that some of the bands appear to have either red-shifted (to lower wavenumbers) or blue-shifted. This is most notable observed in the S=O stretching region (1550-1300 cm$^{-1}$) and the O-S-O bending region (900-760 cm$^{-1}$). As mentioned earlier, these broad bands are made of several different kinds of sulfate-like species present on the surface that appear or disappear depending on the pretreatment used.

A better comparison of the bands and their impact on the activity of the sample can be seen in the spectra obtained for two of the inactive samples from Table 4.17 as shown in Figure 5.4. For the sample A, which was heated to 500 °C without air flow, the spectrum is not significantly different than that for a Pt-modified SZ$_{650}$ (Figure 5.3). The noticeable difference, though, lies in the regions which maybe responsible for the active acid sites. The bands in the S-O stretching region (1200-1050 cm$^{-1}$) are quite diminished and the OH stretching region shows a broad and intense hump-like band. In contrast, the sample B, which was heated to 300 °C without hydrogen flow (i.e. no flow of hydrogen during the reduction), has a very different spectrum. The OH stretching region contains a broad band corresponding to the presence of hydroxides on the surface. The bands corresponding to OH terminally and bridge bonded to ZrO$_2$ near 3760 and 3660 are not seen, instead the
Figure 5.4. DRIFTS spectra of the inactive samples A and B (Table 4.17)

spectrum beyond wavenumber of 3770 cm\(^{-1}\) corresponds hydroxides different than those which were present in the active samples. The band at ca. 1570 is very strong in the case of sample B, which implies that a particular kind of sulfate species is particularly concentrated in this sample. Similarly the band at low wavenumbers corresponding to OSO bending vibration is also very pronounced. There are a few small bands between the range of 1300-1100 cm\(^{-1}\) which all can be assigned to different kind of sulfate-like species on the ZrO\(_2\) surface. The intensity of these bands is lower indicating that these species might have contributed to the activity of the catalyst. It is noteworthy that both these samples showed Pt-S with a high coordination number (EXAFS).
Thus, the DRIFTS results show that the sulfur species on the catalyst not only undergo significant changes upon addition of platinum, but also upon being exposed to various pretreatments as well. To further monitor the appearance of different kinds of species, further experiments were conducted to monitor the surface during the reduction. The current reactor setup did not allow experiments with temperatures exceeding 350 °C to be carried out, hence *in-situ* oxidation of the catalysts could not be attempted. Regardless, the data gathered from these experiments enables a quantitative understanding of the changes occurring during the pretreatments used.

5.3.1 Effect of pretreatments on SZ

To verify these changes and to elucidate the dynamic behavior of the acidic as well as the basic groups on the surface during the reduction pretreatment, the following samples were reduced *in-situ* while being monitored with DRIFTS:

1. Unmodified SZ\textsubscript{650}

2. Pt-loaded SZ\textsubscript{650}, and

3. Pt(r\textsubscript{s},o)/SZ\textsubscript{650}

The background-corrected spectra obtained for the reduction of these samples are shown as Figure 5.5, 5.7, and 5.9. The variations in the band intensity as a function of time (as well as the temperature) are also plotted. The numbers along the right side of the plots indicate the temperature of the sample (in °C) when the spectra was recorded. The temperature program was the same as the one used for the actual reduction process in the flow reactor. The hydrogen flow through the catalyst bed was maintained at 100 cc/min during this set of experiments, and the temperature was increased linearly for 2 hours until the steady value of 300 °C.
The background-corrected spectra were obtained by selecting the spectrum of the sample at room temperature as the background for further measurements and hence only the changes that occurred during the pretreatments performed on a particular sample were visible. In this way, the spectra obtained were similar to difference spectra with respect to a common reference and not to each other.

The spectra shown in Figure 5.5 obtained during the reduction of unmodified SZ$_{650}$ highlight the evolution of the various bands corresponding to the species present on the surface. It can be seen that more terminal-type OH (3650-3770 cm$^{-1}$) species formed during the heating process. However, upon keeping the temperature at 300 °C, a broad band appearing in the -OH stretching region envelopes this small band. During the same period, two separate valleys near the wavenumbers of 3050 and 2900 cm$^{-1}$ start developing, which indicates the depletion of particular species of -OH from the surface. In general, these changes on the surface occur during the period when the temperature was kept constant at 300 °C. The frequency of the species responsible for the valley near 3050 also shows a slight blue shift during this period, but reverts back to its earlier position as the temperature was kept constant.

Figure 5.6 shows the variations in the band intensity at maximum value for a selected bands from the spectra in Figure 5.5. Most of the bands show an increase in the intensity with increasing temperature until 300 °C, thereafter the intensities of these bands remained constant. The weak bands at 1364 and 1470 cm$^{-1}$ show a slight increase with the increasing temperature but then the band intensity starts diminishing by the time a temperature of 300 °C is reached. Two of the bands (at 1234 and 2910 cm$^{-1}$), however, show a decline in their intensity after the steady temperature is maintained. The band at 1234 cm$^{-1}$ arises due to the S=O stretching vibration. The band centered at 2910 cm$^{-1}$, is unusual in the sense that it has been observed for SZ-based catalysts [130] but has not been assigned to any particular...
group. It is speculated to be due to the symmetric stretch vibration mode of chelated
-OH species (as in SH₂O, or -COOH), that has bands near 2800-3200 cm⁻¹ [163, 164].

The same reduction procedure was performed over an unreduced Pt-containing
SZ₆₅₀ sample. This step was similar to actual reduction of platinum loaded SZ to
prepare Pt(r)/SZ₆₅₀ catalyst samples. The background-corrected spectra collected
during the reduction of this sample are shown in Figure 5.7 From the spectra, two
clear regions can be identified – above the wavenumber of 2750 cm⁻¹ and below the
wavenumber of 1750 cm⁻¹. Between these wavenumber limits, there was no change
observed in the spectra during the increase in temperature and thereafter at the
steady temperature. The background-corrected spectra obtained in this case are
significantly different than those obtained for unmodified SZ₆₅₀ sample where there
was somewhat uniform increase in the band intensity in this region with the tem-
perature. Another significant difference observed is in the region with wavenumbers
>3600 cm⁻¹. As the temperature increased above 140 °C, and as the intensity of the
weak band at 3701 cm⁻¹ disappeared, another broad and relatively stronger band
started appearing. There are no known reports in the literature where such a band
(>3750 cm⁻¹) has been observed. It is likely that this would correspond to many
other kinds of hydroxyl species on the surface that are coordinated with Zr as the
terminal -OH appearing at 3770 cm⁻¹.

The two regions show appearance of many bands whose variations at maximum
intensities are plotted in Figure 5.8. As the temperature of the sample increased,
The bands showed a maxima in their intensity at about temperature of 115 °C
corresponding to loss of water from the surface. The bands also show a red-shift
from their corresponding position in the unmodified SZ₆₅₀ sample (e.g. 1340 from
1371 cm⁻¹, 1697 from 1743 cm⁻¹, 1221 from 1234 cm⁻¹). Most of the new bands
Figure 5.5. Background-corrected DRIFTS spectra obtained during reduction of unmodified SZ$_{650}$
Figure 5.6. Intensity of bands at selected wavenumbers during reduction of $SZ_{650}$
that appear (1419, 1340, 1221 and 1136 cm\(^{-1}\)) are in the SO stretching region. and show nearly constant intensity once the temperature is maintained constant. The band at 1628 cm\(^{-1}\) which could be assigned to the vibration mode - \(\delta\)(HOH), show a decrease once the temperature reached 300 °C.

A similar experiment of reducing the sample while monitoring the DRIFTS spectrum was also performed on Pt(\(r_s\),o)/SZ\(_{650}\) and the resulting background-corrected spectra are plotted in Figure 5.9. The evolution of various bands in this sample was similar to that of the unmodified SZ\(_{650}\) itself. The band at \(\sim\) 1638 corresponding to \(\delta\)(HOH) vibrational mode appears to be comprised of two separate sharp bands. The bands at \(\sim\) 3050, 2950 and 2850 appeared once the temperature was kept steady at 300 °C. The variations in the maximum intensity of the selected bands are plotted in Figure 5.10. In this sample, the band near 2900 cm\(^{-1}\) shows a decrease in intensity after reaching a maximum at the end of the period of increasing temperature. Another band at 1640 cm\(^{-1}\) also shows similar profile. Both these bands could be due to the gradual removal of surface H\(_2\)O that was formed during the increase in temperature. The bands at 1415 cm\(^{-1}\) and 1515 cm\(^{-1}\) show a slight increase in their intensity beyond the temperature of 250 °C. These bands are tentatively assigned to polynuclear SO species which give rise to bands at wavenumbers >1400 cm\(^{-1}\).

By performing in-situ reduction on unmodified SZ\(_{650}\), platinum-loaded SZ\(_{650}\) and Pt(\(r_s\),o)/SZ\(_{650}\), it has been shown that different kinds of species form in each sample. On the platinum-loaded SZ\(_{650}\) sample, the formation of larger crystallites of platinum (Chapter 4) occurs during this reduction stage. It seems that platinum does not spillover hydrogen during this stage, since there was no presence of broad band in the entire range of 3800-2500 cm\(^{-1}\) as was seen for the DRIFTS background-corrected spectra of other samples. Instead, the stronger band centered at \(\sim\) 3400 cm\(^{-1}\) seems to be favored selectively.
Figure 5.7. Background-corrected DRIFTS spectra obtained during reduction of Pt-loaded Sz650
Figure 5.8. Intensity of bands at selected wavenumbers during reduction of Pt-loaded Sz$_{650}$
Figure 5.9. Background-corrected DRIFTS spectra obtained during reduction of Pt(r,0)/SZ_{650}
Figure 5.10. Intensity of bands at selected wavenumbers during reduction of $\text{Pt}(r_{s,0})/\text{SZ}_{650}$.
On the unmodified SZ$_{650}$, the reduction at 300 °C did not lead to loss of sulfate species as reported by many authors [9, 127, 160]. The most plausible reason for the different between the findings in this work and their results is the temperature at which the process was carried out. At the relatively low temperature of 300 °C, the sulfates on the surface are not affected by hydrogen whereas all these studies in literature used temperatures above 450 °C for carrying out reduction.

The difference spectrum of once-reduced sample Pt(r$_s$)/SZ$_{650}$ is similar to that of the SZ$_{650}$. The noteworthy difference between the two is the bands in the region 1500-1400 cm$^{-1}$. In the former, the intensity of these bands increases after reaction at a temperature of 300 °C whereas for the latter, the changes occur prior to reaching the reaction temperature.

The bands in the region 3050-2800 cm$^{-1}$ seem to hold a clue to the activity of the catalyst. The following study with in-situ isomerization clearly shows the change in the surface during the reaction carried out over different catalysts.

### 5.3.2 n-Pentane isomerization

The n-pentane isomerization with *operando* DRIFTS was carried out with four representative catalysts – SZ$_{650}$, Pt(r$_s$)/SZ$_{650}$, Pt(r$_s$ o,r$_s$)/SZ$_{650}$ and sample A (Table 4.17, inactive) while being monitored by IR to observe the surface during the reaction. After increasing the catalyst temperature to 250 °C (reaction temperature) in flowing hydrogen (10 cc/min NTP), the flow was diverted to a bubbler containing n-pentane and measurement of the spectra was started 2 minutes later. The reaction was stopped after sometime by resuming the hydrogen flow without n-pentane (i.e. bypassing the bubbler) and a few more spectra were obtained while the catalyst was still at the reaction temperature.

For the SZ$_{650}$ catalyst, the difference DRIFTS spectra are shown in Figure 5.11.
The spectra till the reaction temperature were similar to that in Figure 5.5 however, once the reaction had begun, there were remarkable differences in the wavenumber range of 3050-2800 cm\(^{-1}\) and in the \(\delta(\text{HOH})\) region. The multiple broad bands in the region with wavenumbers between 3050-2800 cm\(^{-1}\) were diminished considerably. These bands seemed to be composed of a combination of the stretching mode of the OH groups in H\(_2\)O\(^+\). A similar decrease in intensity was also noticed for the band at 1680 cm\(^{-1}\). This band would correspond to blue-shifted bending mode of H\(_2\)O removed from the surface. Both of these bands reappeared once the flow of n-pentane was stopped.

The intensity of selected bands from the spectra is plotted in Figure 5.12. The band at 1632 cm\(^{-1}\) did not get affected by the reaction or the presence of n-pentane but instead the band at 1678 cm\(^{-1}\) got reduced to almost 50% intensity of what it would have had without reaction. These bands were not present in the corresponding spectra obtained during the reduction of the same sample. It is quite likely that onset of the reaction caused these bands to become stronger than they were in Figure 5.5. The bands corresponding to the presence of hydrocarbon on the surface were not observed as well. The medium bands of CH stretching would normally occur in the same region of 3000-2800 cm\(^{-1}\).

The reaction over Pt\((r_s)/\text{SZ}_{650}\) was carried out and the difference DRIFTS spectra are plotted in Figure 5.13. The three bands in the SO stretch region showed a small variation in their intensity. The weak band at near 1460 cm\(^{-1}\) started appearing and shifted towards lower wavenumber of 1440 cm\(^{-1}\). The strong band due to the bending mode of H\(_2\)O appeared at 1660 and showed a slight red shift from 1680 cm\(^{-1}\) observed in the spectrum of unmodified SZ\(_{650}\) (Figure 5.11). The band corresponding to terminal OH groups at 3750 cm\(^{-1}\) also did not show much variation in the periods before, during and after the reaction. The strong asymmetric
Figure 5.11. Background-corrected DRIFTS spectra obtained during n-pentane isomerization on unmodified $SZ_{650}$
Figure 5.12. Intensity of bands at selected wavenumbers during n-pentane isomerization on unmodified SZ$_{050}$
envelope due to various hydroxyl oscillators was centered at $\sim 3440 \text{ cm}^{-1}$. The weak bands centered at 2900 cm$^{-1}$ started to appear before the reaction, but became more intense during reaction. As pointed out earlier, this band was comprised of several small bands – due to chelated -OH stretching and possible due to the presence of -CH stretching vibrations as well. After the flow of n-pentane was stopped, these bands were still quite distinct. The variation of one of the bands in this region is plotted in Figure 5.14. The band at 2926 cm$^{-1}$ indicated complete absence of this particular species of OH groups once the reaction has begun, whereas the intensity of the bending stretch band at 1660 cm$^{-1}$ remained fairly constant during the reaction and started declining after the reaction was stopped. A band with similar behavior appeared at 1632 cm$^{-1}$ in Figure 5.12. This blue shift of the band seems to be due to relaxation caused by a decline in the hydrogen bonding between the water-like molecules. After stopping the reaction, the band at 2926 cm$^{-1}$ showed increased band intensity again as that for isomerization over unmodified SZ$_{650}$.

Figure 5.15 presents the background-corrected spectra during reaction on Pt(r$_s$,o,r$_s$)/SZ$_{650}$ sample. To recall, Pt(r$_s$,o,r$_s$)/SZ$_{650}$ is the most active catalyst for the n-pentane isomerization (Chapter 3) and has considerably larger crystallites of metallic platinum present in the catalyst (Chapter 4). The main regions of interest in this set of spectra is also the same as in the two earlier sets and there is little variation in the bands in the SO stretching region. The bending mode band appeared at a wavenumber of 1630 cm$^{-1}$, which is about 30 cm$^{-1}$ less than that for the Pt(r$_s$)/SZ$_{650}$ sample, but is almost the same as that for the unmodified SZ$_{650}$ sample. The terminal -OH did not undergo any changes in the whole experiment as indicated by the absence of the band at $\sim 3750 \text{ cm}^{-1}$.

The chelated -OH band region in the wavenumber range of 3050-2800 cm$^{-1}$, was considerably different than in the earlier two cases. Prior to the reaction, there was
Figure 5.13. Background-corrected DRIFTS spectra obtained during n-pentane isomerization on Pt(rs)/SZ_{650} sample
Figure 5.14. Intensity of bands at selected wavenumbers during n-pentane isomerization on Pt(rs)/SZ_{650}
no indication of any separate band(s) in this region except the overall broad band due to the hydroxyl species. As the reaction began, there was a decrease in the intensity of all the bands in this region, however, the asymmetric band at 2964 cm\(^{-1}\) showed an increase following the initial decrease, and attained a high value (Figure 5.16). The intensity of the band decreased once the reaction was stopped. If this band was due to \(-CH\) stretching, it would mean presence of some of hydrocarbon fragments on the surface of the catalyst. Keeping in mind the earlier background-corrected spectra during the reaction as well as from separate experiments, it became certain that this band corresponded to the presence of hydrocarbons adsorbed on the surface.

Since this catalyst was found to be very active and converted over 70% of n-pentane with many by-products, the presence of a \(-CH\) band confirms the assertion that this active catalyst cracks the alkane into many smaller fragments that remain on the surface and can thus be observed by IR measurements.

A similar experiment was also repeated with one of the inactive catalyst (cf. Table 4.17, page 168) that had largest coordination of Pt-S bonds present in any catalyst. The background-corrected spectra obtained for this sample are presented in Figure 5.17. In the SO stretching region of 1450-1000 cm\(^{-1}\), the bands started appearing as the temperature was increased. No sudden changes were observed as the reaction began, however, the intensity of the bands decreased as the reaction progressed and became much lesser towards the end of the experiment. The band at 1636 cm\(^{-1}\) also followed the same trend and became lesser in the intensity with time after the temperature remained constant at 250 °C. As in Figs. 5.11, 5.13 and 5.15, the bands near 2950 cm\(^{-1}\) did not show during the heating up period, but decreased in intensity with the onset of reaction. After the reaction was stopped, these bands were still observed in the spectrum. The band at 3760 cm\(^{-1}\) due to the terminal \(-OH\) coordinated with Zr appeared and remained at same level as that at
Figure 5.15. Background-corrected DRIFTS spectra obtained during n-pentane isomerization on Pt(r_{s},o,r_{s})/SZ_{650}
Figure 5.16. Intensity of bands at selected wavenumbers during n-pentane isomerization on Pt(r_s, o, r_s)/SZ_{650}
250 °C throughout the experiment. These trends are clearer in Figure 5.18. The band at 2964 cm$^{-1}$ decreased with the start of the reaction but increased during the reaction. The band at 1636 cm$^{-1}$ indeed displayed considerable decrease in its intensity with time. This is remarkably different than all other earlier cases where the intensity of this band remained fairly constant after the heating period.

The more significant difference, however, lies in the relative intensity of the band at 1636 cm$^{-1}$ and the broad asymmetric band that is centered at 3400 cm$^{-1}$. The band at 1636 cm$^{-1}$ had much lower intensity compared to that in the 3 previous cases with active samples. This band arises due to the bending mode of the HOH present on the surface and implied a decrease in the formation of this kind of species.

Clearly, this DRIFTS study shows that the bands associated with the sulfate or sulfate-like species appearing in the S=O and S-O stretching region did not change considerably during the reaction. Instead, the most distinct changes were observed in the bands that are associated with the surface hydroxyl species, specifically a particular kind of hydroxyl species characterized by a broad band $\sim$ 2950-2900 cm$^{-1}$ that disappeared once the reaction was started.

It seems that upon heating the samples even in presence of hydrogen causes this particular kind of hydroxyl species to start disappearing from the surface selectively as was seen the case of the samples, which were reduced in-situ. When in contact with n-pentane, the samples show vibration bands in this region (3100-2800 cm$^{-1}$), which could be due to accumulation of hydrocarbons on the surface or due to the presence of a higher concentration of hydrocarbon fragments. The presence of the bending mode vibration at ca. 1620 cm$^{-1}$ was also an indicator of the activity of the catalysts, as this band was diminished in the case of the inactive sample.
Figure 5.17. Background-corrected DRIFTS spectra obtained during n-pentane isomerization on inactive sample A (cf. Table 4.17)
Figure 5.18. Intensity of bands at selected wavenumbers during n-pentane isomerization on inactive sample A (cf. Table 4.17)
5.4 Discussion

The results show presence of many different features on the SZ surface and how their concentration is affected by the pretreatments and by the reaction environment. These *operando* results showing the novel features detected have not been presented before. Most of the changes observed occurred in the OH-stretching region instead of the regions related to sulfur groups.

From the transmission IR of the samples – SZ\(_{650}\), Pt(r)/SZ\(_{550}\) and Pt(r)/SZ\(_{650}\), it is clear that the differences observed in the spectra were very marginal. Difficulties in preparing a uniformly distributed SZ+Kbr wafer and low transmission intensity made qualitative interpretation with transmission IR difficult. However, in each of the samples, a few bands are common. These include two bands that are characteristic of the S=O and the S-O stretching modes observed in sulfates and SO\(_2\), and the band at \(\sim 1620 \text{ cm}^{-1}\) corresponding to the bending mode vibration of the water or water-like hydroxyl species on the surface. If the -OH bonds form hydrogen bonds with either S or O on the surface, this band would appear as observed in all the samples analyzed.

The above mentioned bands are quite distinctly visible in the DRIFTS spectra of the SZ samples. All the samples that have been calcined show a broad asymmetric band on the OH stretching region between 3700-2700 cm\(^{-1}\) implying the presence of hydroxyl species on the surface. The band is composed of several hydroxyl species with varying strength of hydrogen bonds which causes the envelope of such bands to be broad and spread out over the whole range. These groups were not observed in the spectrum of the uncalcined sulfated-Zr(OH)\(_x\), and hence were formed during the calcination step that also caused formation of another band appearing at 1625 cm\(^{-1}\). This band appears due to the bending mode vibration of water or HOH groups on the surface. Since this band is not entirely symmetric, the presence of two similar
species with varying bond order is likely. Another interesting band that appears at \( \sim 1380 \text{ cm}^{-1} \) belongs to the stretching mode oscillations of S=O belonging to the sulfate group. This band has been attributed to be the one responsible for the acid function of SZ catalysts.

A different set of bands in the S-O stretch region at lower wavenumbers of 1200-950 cm\(^{-1}\) is also seen in the uncalcined and SZ\(_{550}\) samples. This set of bands decreased to a lower intensity once the calcination was carried out the higher temperature of SZ\(_{650}\). Thus, these bands would correspond to the loosely bound sulfur species which has been removed by calcination from the SZ\(_{650}\) sample.

In addition, it is noticed that the DRIFTS spectra are not similar for the two different samples of SZ\(_{650}\) – normally prepared SZ\(_{650}\) and MEI SZ\(_{650}\). The commercial Zr(OH)\(_x\) (MEI) sample is known to contain only 55-65\% ZrO\(_2\) and the preparation process is not known, hence the differences are expected. The main spectral features are nonetheless similar in the two with the exception of a sharp band at 3740 cm\(^{-1}\). This band, along with a small band at 3770-3760 cm\(^{-1}\), is due to the bridging -OH and terminal -OH species respectively, and is characteristic of the SZ and ZrO\(_2\)-based materials. In the case of SZ\(_{650}\) prepared by the precipitation of Zr(OH)\(_x\), the band corresponding to bridging -OH groups is very strong, indicating a different sort of short-order structure from that observed in SZ\(_{650}\) (MEI). It is important to recall that these bridging -OH groups are said to be responsible for generation of Brønsted acid sites.

Calcination results in loss of sulfur and water from the surface and results in crystallization of zirconia into the meta-stable tetragonal form. During the crystallization, the acid sites are also formed corresponding to the crystal phase formation. While there is not concrete evidence of the structure of a SZ surface, many different models have been put forward in the literature, in which the sulfate groups are
assumed to be tethered to the zirconia surface forming the acid sites.

Addition of platinum followed by reduction results in decrease in the S-O species characterized by the set of bands in the range of 1300-1000 cm\(^{-1}\). Instead, another band corresponding to the bending mode vibrations of OSO appears centered at 825 cm\(^{-1}\) for all the Pt-modified samples. This change in the surface species is due to the reduction step in which some of the surface sulfur would be reduced but not lost from the surface. The inactive samples A and B also had a strong presence of these vibrational modes at the expense of the species that give rise to bands in the S=O and S-O stretching region.

The inactive sample B has a very different profile compared to the any other Pt-modified SZ\(_{650}\) samples, including sample A. To recall, sample A was made inactive by heating without flowing air till 500 °C and sample B became inactive due to heating it at 300 °C in the absence of hydrogen flow. From the EXAFS results (Table 4.18), the sample A has significant amount of sulfur bonded to the platinum exhibiting a large coordination number of 4.7, whereas, the sample B had large crystallites of metallic platinum as evident by the large coordination of the Pt-Pt species. Although the DRIFTS spectrum of sample A, looks similar to that of Pt(r\(_s\))/SZ\(_{650}\), it was inactive because the platinum was completely covered with S and could not provide dissociated hydrogen onto the support and the acid sites. In contrast, the sample B has a much stronger band in the OSO bending region as well as no bridging -OH groups present on the surface. The pretreatment process (heating till 300 °C in the absence of hydrogen) resulted in a catalyst which had a significantly different structure on the surface, as a result of which very few acid sites would have been generated. Lack of sufficient active acid sites would cause the catalyst to be inactive.

During the in-situ reduction of the SZ\(_{650}\), several bands appeared as the temper-
ature increased. The regions of particular interest were located in the -OH stretching region and the region above the wavenumber of 1600 cm\(^{-1}\). The bands near wavenumber of 3000 cm\(^{-1}\) started decreasing as the sample was maintained at 300 °C in flowing hydrogen. This OH stretch caused by the chelated -OH groups decreased, suggesting that these groups were either being lost from the surface by formation of water, or being restructured into other types of hydroxyl species, which is evident by the increase in the intensity of the overall envelope of bands between 2750 and 1750 cm\(^{-1}\). A gradual increase in the S-O band instead of S=O hints towards the decline in the activity of SZ\(_{650}\) when reduced prior to reaction.

After addition of platinum to SZ\(_{650}\), this trend changed. The profile of the curves indicated that while the platinum on the surface is being formed into the large crystallites (from EXAFS studies, Chapter 4), hydrogen availability on the surface by dissociation causes selective increase of hydroxyl groups in the OH stretching region alone. There was no change in the 2750-1750 cm\(^{-1}\) region as for SZ\(_{650}\). The dissociated hydrogen also seems to cause an increase in the amount of OH groups with vibrational frequency above that of 3750 cm\(^{-1}\).

The effect of the oxidation step between Pt\((r_s)/SZ_{650}\) and Pt\((r_s,o,r_s)/SZ_{650}\) is not so obvious by simple observation of the difference DRIFTS spectra during reduction. However, it is certainly obvious that the bands in the region of 3050-2800 cm\(^{-1}\) start appearing much earlier than for unmodified SZ\(_{650}\) or Pt-loaded SZ\(_{650}\).

While performing \textit{in-situ} reaction over SZ\(_{650}\), the presence of the bands in 3050-2800 cm\(^{-1}\) did not appear until the reaction began and after the reaction, the profile of the curve is same as that with reduction alone. The decrease in these bands during reaction with all the catalyst samples studied indicate that these kind of species are involved either in adsorption of n-pentane or in generation of active acid sites in the reaction pathway. For these reactions, it also seems important that the water-like
species which give a bending mode at $\sim$ 1620-1640 cm$^{-1}$, are present on the surface. These bands were very much diminished in the case of reaction with an inactive sample.

The features observed cannot be correlated directly with the specific reaction sites and intermediates formed without carrying out detailed isotopic experiments. Nonetheless the results show why these catalysts are so variable and they the resultant activity is dependent on so many parameters in preparation and pretreatment. The results also point out that the role of hydroxyl species in arresting the deactivation is more complex than that reported in literature.

5.5 Summary

Use of DRIFTS in characterization of the SZ-based catalysts gives better insight on the presence of the species on the surface. Some of these species are responsible for the enhanced activity of the catalysts. The DRIFTS spectra of the Pt(r$_s$)/SZ$_{650}$, Pt(r$_s$,o)/SZ$_{650}$ and Pt(r$_s$,o,r$_s$)/SZ$_{650}$ indicates that an active catalyst should have lesser S-O presence than S=O on the surface. All the platinum-modified samples, had clear defined presence of hydrogen-bonded hydroxyl groups on the surface besides indication of varying amounts of sulfate species on the surface.

By carrying out reduction over SZ$_{650}$-based samples, the effect of reduction step between Pt-loaded SZ$_{650}$ and Pt(r$_s$,o)/SZ$_{650}$ was elucidated. The results of the in-situ DRIFTS during reaction clearly reflect on the importance of the hydroxyl species absent or present on the surface. While the presence of the sulfate-like species is considered important for acidity, the presence of certain hydroxyl species seems to be the one affecting the activity the most.
CHAPTER 6

SITE-JUXTAPOSITION HYPOTHESIS AND MODELING RESULTS

6.1 Introduction

From the activity results presented in Chapter 3, the positive effect of Pt (and H2) is obvious i.e. both a metallic component and hydrogen are necessary for arresting deactivation and for sustained activity. Spectroscopic analysis showed that there is little difference if any in the state and dispersion of the metallic component of the catalyst which had been pretreated with an oxidation-reduction step as compared to one that was not pretreated. Results from the infrared study indicate that even though there are different sulfur-oxygen species present in the catalyst samples pretreated with or without oxidation-reduction step, their concentration is very small compared to other common species of bidentate S=O and -OH. The question that arises then is what is the change that occurs on the catalyst during the oxidation-reduction stage which causes the activity to increase further than when no oxidation-reduction is carried out. To gain proper understanding of this, one needs to consider the process of hydrogen spillover and its role in bifunctional catalysis.

In heterogeneous catalysis, the term spillover is applied to the transport of active species sorbed or formed on one phase to another phase which does not sorb or generate these species by itself under the given conditions [165]. The phase generating the active species is called the initiator (or activator), while the phase providing sites for the adsorption of the active species is known as the acceptor. If these phases are
in direct contact, the spillover is said to be primary, but when they are separated by an additional inert carrier, it is said to be secondary. In case of hydrogen spillover on supported catalysts, the active species is hydrogen – it undergoes dissociation on platinum or other metal species and migrate onto the support.

It is generally believed that the first stage of the process is the homolytic dissociation of the H-H bond on the metal [166]. Further on, the H-spillover species may coexist under the form of a radical-like mono hydrogen H along with a charged species, namely H\(^+\) that is formed after electron transfer to the surface region, as claimed by Roland et al. [167] (Figure 6.1).

6.1.1 Bifunctional versus spillover-reaction mechanism

The classical concept of bifunctional catalysis during naphtha reforming to yield aromatics, as put forward by Mills [168], and Weisz and Swegler [169] involves two kind of sites and a four-step pathway: (i) hydrogenation/dehydrogenation of the paraffin at the metal site, (ii) subsequent gas-phase diffusion of the olefin to the acid site followed by (iii) its isomerization at the acid site to form isoalkene and (iv) gas-phase migration of the isoalkene back to the metal site for further hydrogenation. On the basis of results of hydrocarbon conversion reactions in layered catalysts, Roessner
and co-workers [170, 171] questioned the validity of this classical understanding and incorporated the concept of hydrogen spillover for hydroconversion reactions. In this model, (a) the hydrocarbon conversion proceeds entirely at one surface center and (b) spilled-over hydrogen is involved in the hydrocarbon reaction as well when present in the active form(s). Briefly speaking, the role of the H-spilling species (the two possible forms), once created in the platinum sites, is to migrate on the surface of the Pt-free part of the 'bifunctional catalyst' and react with the hydrocarbon at one surface site only.

It is generally accepted that Pt-modified sulfated zirconia acts as a bifunctional catalyst in the n-butane isomerization, however, the mechanism in the case of C\textsubscript{5} and higher paraffins is still debated as either due to classical bifunctional properties of Pt/SZ or spillover-reaction in the presence of hydrogen [86].

6.1.2 Hydrogen spillover in Pt/SZ catalysts

Ebitani and Hattori were among the first to report occurrence of hydrogen spillover in Pt/SZ catalyst samples. Based on infrared experiments, these authors showed that a treatment under hydrogen caused the development of Brønsted sites at the expense of Lewis ones [104] thus recognizing that the H-spillover moieties also interact with Brønsted and/or Lewis sites, besides reinforcing the acidic active sites by the electron-transfer to the support. Since then, Hattori and coworkers, exclusively, have published a series of papers dealing with spillover of hydrogen on platinum-modified SZ catalysts, in particular the effect of hydrogen on generation of acid sites [172, 173] and the TPD results of sequential adsorption of H\textsubscript{2} and D\textsubscript{2} indicating clear spillover and migration of hydrogen atoms away from the active centers into the surrounding regions of the support [174, 175]. The authors even proposed Pt/SZ as a possible hydrogen storage material [176]. More recently, they
studied adsorption of hydrogen over elongated periods and time and found that at temperatures up to 250°C, the catalyst sample adsorbed hydrogen for over 24 hours [128]. The authors also concluded that the adsorption of hydrogen in Pt/SZ is surface diffusion controlled. Another study by Xu and Sachtler [177].

Most recently, using FTIR spectroscopy, Wang et al. [130] presented direct evidence of hydrogen spillover in catalytically active versus an inactive catalyst by observing the transformation of Lewis acid sites to Brønsted acid sites, along with formation of H₂O and zirconium -OH species on a catalyst prepared by a method similar to the 3-step method used in this work. The authors postulated a mechanism of H₂O and -OH formation involving active oxygen species from the immediate sulfate groups in n-butane isomerization.

The results obtained by Hattori’s group and a few others provide evidence that the spillover phenomenon occurs on the Pt-modified SZ catalysts in presence of hydrogen. In Chapter 3 of this work, the results of chemisorption performed at temperatures of 150, 200 and 250 °C, also point to hydrogen adsorption being a function of temperature and thus occurrence of spillover. It is then feasible that this spilled-over H species takes part in the reaction as well as scavenging the oligomeric coke precursors by hydrogenating them and hence, preventing deactivation. Such a model is consistent with the results obtained previously and provides the basis of the hypothesis presented below, to explain the effect of pretreatment on deactivation.

6.2 Site-Juxtaposition Hypothesis

Based on the data presented in previous chapters, a hypothesis that attempts to interpret the significance of the synthesis method and pretreatments used is presented.

The basis of the Site-Juxtaposition hypothesis lies in the following observations:
• There are two kinds of functions present in Pt/SZ catalyst – metal and acid.

• Alkane activation and the isomerization takes place only at the active acid sites.

• A spillover-reaction model similar to that discussed above is applicable i.e. the role of platinum is to provide spilled-over hydrogen alone, not to hydro- genate/dehydrogenate as in typical bifunctional catalysis.

The surface of the sulfated zirconia can be considered as a matrix of zirconia with dispersed acid sites as proposed by Signoretto et al. [35].

6.2.1 Subsurface and poisoned platinum

According to this hypothesis, if the catalyst is prepared from SZ550, then the labile sulfur present on SZ attacks the Pt species added to the sample and forms a stable Pt-S layer covering the platinum surface. The platinum is not present in metallic state and is not able to participate in the hydrogen-spillover phenomenon (Figure 6.2) and the catalyst deactivates.

A similar situation occurs when the catalyst is prepared as per the conventional 2-step method of adding Pt and S species prior to any calcination. During the calcination step that make SZ active, some of the poisoned Pt is trapped within subsurface of the zirconia matrix [178].

In each case, the lack of spilled-over hydrogen, causes rapid cracking of the alkane in the initial period of contact with the catalyst. The coking and disproportionation reactions then cover up of the acid sites leading to fast deactivation. The regeneration step is not able to eliminate most of the strongly bound Pt-S and transform the subsurface platinum to metallic platinum. This is evident in small increase in the stability of the catalyst with TOS.
6.2.2 Distant sites

When the catalyst is prepared as per the three-step method from SZ$_{450}$, the platinum not only remains free of sulfur but also forms larger crystallites as seen from the EXAFS results in Chapter 4. The larger metallic platinum crystallites facilitate H-spillover to the support. However, the separation between the acid and the metallic site centers dictates the stability of the catalyst (Figure 6.3), since the surface diffusion of H is a slow process. The rate of supply of spillover species is small, which causes cracking accompanied with coking to occur but the extent of such deactivation is decreased due to partial availability of the H-spillover species.
6.2.3 Sites juxtaposed by pretreatment

The oxidation-reduction pretreatment results in surface restructuring such that the separation of the sites is reduced (Figure 6.4). The juxtaposition of the two kinds of active sites results in rapid transfer of H-spillover species from one to the other resulting in a significant decrease in the poisoning of the active acid sites and hence the catalyst attains a stable activity.

6.3 Reaction path model

Based on the hypothesis described above, a lumped reaction pathway, can be proposed as follows:

- The rate determining step for n-pentane isomerization is the conversion of adsorbed n-pentane to isopentane on the acid sites on the SZ surface.
- The adsorbed n-pentane can also convert to a species which poisons the acid sites.
- The poisoned sites can be recovered by reaction with the hydrogen that is adsorbed on sites different than the acid sites.
### TABLE 6.1
SIMPLIFIED REACTION PATHWAY FOR n-PENTANE ISOMERIZATION

<table>
<thead>
<tr>
<th>Step</th>
<th>Schematic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface conversion</td>
<td>( A \cdot S_1 \xrightarrow{k_A} B \cdot S_1 )</td>
</tr>
<tr>
<td>Surface poisoning</td>
<td>( A \cdot S_1 \xrightarrow{k_P} P \cdot S_1 )</td>
</tr>
<tr>
<td>Site recovery 1</td>
<td>( P \cdot S_1 + H \cdot S_2 \xrightleftharpoons{k_{-P}} A \cdot S_1 )</td>
</tr>
<tr>
<td>Site recovery 2</td>
<td>( P \cdot S_1 + H \cdot S_2 \xrightleftharpoons{} B \cdot S_1 + S_2 )</td>
</tr>
<tr>
<td>Adsorption/desorption</td>
<td>( A + S_1 \xrightleftharpoons{} A \cdot S_1 )</td>
</tr>
<tr>
<td></td>
<td>( B + S_1 \xrightleftharpoons{} B \cdot S_1 )</td>
</tr>
<tr>
<td></td>
<td>( H_2 + 2 \cdot S_2 \xrightleftharpoons{} 2 \cdot H \cdot S_2 )</td>
</tr>
</tbody>
</table>

- The effect of the separation of metal site and the acid sites, as well as the surface diffusional resistance due to spillover is implicit in the concentration of the adsorbed hydrogen.

- The adsorption and desorption of n-pentane, isopentane, and hydrogen species is rapid and in a quasi-steady state.

The reaction pathway can then be depicted as in Table 6.1, where \( S_1 \) is an unoccupied active acid site (SZ), \( S_2 \) is an unoccupied hydrogen site (Pt). \( A \) and \( B \) denote n-pentane and isopentane respectively, and \( P \) is the poison or coking species. Mathematically this model can be expressed as follows:

1. The rate of consumption of \( A \) is expressed as:

\[-r_A = k_A[A \cdot S_1]\]
2. The rate of deactivation of the acid sites is expressed as

\[ r_P = \frac{d[P \cdot S1]}{dt} = k_P[A \cdot S1] - k_{-P}[P \cdot S1]^n[H \cdot S2] \]

3. The rapid-equilibrium of the recovery step yields

\[ [B \cdot S1][S2] = K_R[P \cdot S1][H \cdot S2] \]

4. The total number of each of the sites (i.e. \( S1^0, S2^0 \)) remains constant.

\[ [S1^0] = [S1] + [A \cdot S1] + [B \cdot S1] + [P \cdot S1] \]
\[ [S2^0] = [S2] + [H \cdot S2] \]

5. The equilibrium relationships of \( S1 \) and \( S2 \) with \( A, B \) and \( H_2 \) is expressed as:

\[ [A \cdot S1] = K_{AP}[S1] \]
\[ [B \cdot S1] = K_{BP}[S1] \]
\[ [H \cdot S2] = K_{H\sqrt{pH_2}}[S2] \]

where \( k_A \) is the rate constant for the forward conversion of adsorbed isopentane, \( k_P \) and \( k_{-P} \) are the rate constants for the poisoning step. Quantities in [ ] correspond to the surface concentration of the particular species. \( K_R \) is the equilibrium constant for the recovery step and \( K_A, K_B, K_H \) are the adsorption constants for \( A, B \) and \( H_2 \), respectively. \( n \) is the order of the reverse reaction to form \( [A \cdot S1] \).

By defining the fraction of unpoisoned sites, \( \theta \), as \( 1 - [P \cdot S1]/[S1^0] \), and with appropriate substitutions, we arrive at the following set of equations:

\[
-r_A = k_A'_{P_A}\theta \\
\frac{d\theta}{dt} = \frac{-d[P \cdot S1]}{dt} = -k_P'_{P_A}\theta + k_{-P}'_{P_B}\theta^n
\]
where

\[ k_{A'} = k_A \frac{K_A[S1^0]}{(1 + k_{AP_A} + k_{BP_B})} \]
\[ k_{P'} = k_P \frac{K_A[S1^0]}{(1 + k_{AP_A} + k_{BP_B})} \]

and

\[ k'_P = k_pK_H \left[ \frac{K_B[S1^0]S2}{(1 + k_{AP_A} + k_{BP_B})K_RK_H} \right]^n \sqrt{P_{H_2}^{(1-n)}} \]

Since the conversion is high, the kinetics have to be evaluated considering the reactor as an integral or a plug-flow reactor, hence

\[ \frac{\partial p_A}{\partial t} = -vz \frac{\partial p_A}{\partial z} + r_A \tag{6.3} \]

where \( v \) is space velocity of n-pentane through the catalyst bed.

6.3.1 Method of solution

If the kinetics of the poisoning of the active acid sites and their recovery is a slow process, one can assume that \( p_A \) attains a quasi-steady state within the reactor instantaneously and \( \partial p_A/\partial t \ll \partial \theta/\partial t \). In such a case, one obtains 2 ODEs, one for change in concentration of \( p_A \) along the length of the catalyst bed, and other for change in fraction of unoccupied sites \( \theta \) with respect to time. The conversion recorded (\( X(t) \)) is then defined as

\[ X(t) = 1 - \frac{p_A(z = L, t)}{p_A(z = 0, t)} \tag{6.4} \]

where \( L \) is the length of the catalyst bed along the flow direction.

After writing them in dimensionless form, the two equations are solved sequentially with \( \theta \) evaluated at each intermediate point along the length of the catalyst bed. A simple fourth-fifth order Runge-Kutta’s numerical method was used for solving the ODEs.
6.4 Results and Discussion

It was found that the order of the 'Site recovery 1' step needed to be zero in order to compare with the experimental data. At higher values of n, the numerical conversion decreased with time and a steady value was not obtained. This implies that the recovery of the unoccupied sites $\theta$ did not depend on surface concentration of isopentane, instead on the concentration of the adsorbed hydrogen alone.

Conversion versus TOS obtained by solving the model equations numerically is shown in Figure 6.5. By increasing the value of $k'_{-P}$ which is dependent on the surface concentration of adsorbed hydrogen through the $p_{H_2}$ term, the steady state value of the conversion of n-pentane increases. The numerical results shown here match the experimentally obtained conversion values for two sets of catalysts – Pt(r)/SZ$_{650}$ reg. 1 (Figure 3.22) and Pt($r_s$,$o$,$r_s$)/SZ$_{650}$ (Figure 3.27).

The concentration of adsorbed hydrogen is in turn dependent on the migration and diffusion of spilled-over hydrogen away from the platinum crystallites. Large separation between the platinum site and acid site would result in decreased concentration profile radially away from center of the metal site, and hence would result in a lower $k'_{-P}$, and lower stable conversion. The Pt(r)/SZ$_{650}$ catalyst had been regenerated once and it would be expected that the inter-site separation would be lesser than an unregenerated one. On the other hand, Pt($r_s$,$o$,$r_s$)/SZ$_{650}$ catalyst probably has the optimum inter-site separation which allows fairly rapid transfer of hydrogen and hence, the conversion stabilizes at a higher value.

These results obtained by the simple model proposed in this chapter clearly show that the increased presence of atomic hydrogen near the acid sites plays an important role in arresting the deactivation and attaining a stable value of conversion. The actual process might be more complex. Indeed, with the current modeling effort, it was not possible to reproduce the decay and rise in conversion observed in some of
Figure 6.5. Conversion vs. TOS obtained by solving the model described above with $k'_A = 0.86 \text{ s}^{-1}$, $k'_P = 8.8 \text{ s}^{-1} \text{ atm.}^{-1}$. The steady state conversion value rises with increasing value of $k'_P$. The plots shown correspond to $k'_P = 1.0, 1.5, 2.0, 3.0$ and $3.8 \text{ s}^{-1} \text{ atm.}^{-1}$. 
the catalysts described in Chapter 3 and a more complex model based on detailed study of the mechanism would certainly be needed.

An alternate explanation of the increase in the stable conversion values could also be put forward. The metallic platinum crystallites present on the zirconia surface could be covered with a layer of sulfided platinum even in the \( \text{SZ}_{650} \)-based catalysts. Inaccessible metallic platinum would prevent dissociative adsorption of hydrogen and hence the surface concentration of adsorbed hydrogen would be lower, resulting in either complete deactivation or lower stable conversion. If such a catalyst was treated with oxidative-regeneration step, the sulfided platinum could be converted to oxidized platinum layer, which then gets reduced to metallic platinum during the reduction pretreatment prior to reaction. Availability of larger metallic area on the platinum crystallites would then enhance the hydrogen dissociation and spillover onto the zirconia surface, leading to higher availability of adsorbed hydrogen near the acid sites. The site-deactivation would then be suppressed and the stable conversion would be at a higher value.

However, the above explanation is very unlikely since the XPS, EXAFS and XANES results presented in Chapter 4 make it clear that the platinum present on \( \text{Pt}(t_s)/\text{SZ}_{650} \) samples is not coordinated to sulfur to the extent that it gets when it is oxidized. The Pt-S coordination numbers are very minimal to make a difference to this extent even before oxidative regeneration.

6.5 Summary

A Site-Juxtaposition hypothesis that attempts to explain quantitatively the observations for the activity of various Pt/SZ catalysts in n-pentane isomerization is presented. The dynamic intervention of H-spillover species coupled with a one-site type of catalysis is proposed as the one responsible for arresting the deactivation
commonly observed in the isomerization reactions in presence of Pt/SZ catalysts. A simple model based on the Site-Juxtaposition hypothesis was used to show that indeed that stable n-pentane conversion can be increased by increasing the availability of atomic hydrogen for site-recovery by coke hydrogenation.
Sulfated Zirconia constitutes an important class of promising catalyst material for replacing the liquid-acid catalysts for use in hydroconversion processes. Rapid deactivation seen in the isomerization and other hydroconversion reactions, if carried out the atmospheric conditions, puts a limit on its use in industrial practice.

In this work, a new 3-step method of synthesizing platinum-modified SZ catalyst was studied. SZ-based catalysts prepared by this 3-step method yield high conversion of n-pentane to isopentane and do not undergo the usual deactivation. The novelty of the method lies in the sequential activation of the active function i.e. activating the acid function by calcining prior to activation of metal function by reduction.

7.1 Results

First noteworthy features of the 3-step preparation are seen in the physical characterization of these catalysts. The results of the surface area measurement of the SZ catalysts show that the calcination causes reduction in the surface area of the catalyst. The surface area of the catalyst is inversely proportional to increases in the temperature. The catalysts prepared by the 3-step method have an average surface area of 125 m$^2$/g. The calcination at a higher temperature of 650 °C also results in a rapid loss in weight at a temperature of 600 °C that is due to the loss of labile
sulfur species present on the sulfated Zr(OH)$_x$. At the end of the calcination, the SZ contains about 2% by wt of sulfur and is mainly in tetragonal phase. During the period of calcination, the usual exothermicity associated with the crystallization or phase change was absent. The presence of labile sulfur affected the exothermicity and, hence, the crystallization as well as the phase change.

The Pt-containing SZ catalysts did not show appreciable chemisorption of H$_2$ or CO at room temperature. However, when the hydrogen adsorption was carried out at higher temperature, the catalyst adsorbed increasing quantities of hydrogen with the increase in temperature. This result indicated spillover of hydrogen to be occurring at higher temperatures. The significance of this hydrogen spillover phenomenon in Pt/SZ catalysts became clearer with the results obtained with X-ray absorption and infrared spectroscopy.

The activity studies carried out with n-pentane isomerization as the test reaction showed interesting results. It was observed that a catalyst prepared by the 3-step method with SZ$_{650}$, with calcination or reduction as the final pretreatment, allowed increased conversion after carrying out oxidative-regeneration followed by a reduction. The increase in n-pentane conversion obtained after carrying the oxidation-reduction cycle was observed in all the active samples. The effect of the pretreatment was even more clearer with the catalyst prepared as Pt(r$_{s,o,r_s}$)/SZ$_{650}$. The n-pentane conversion obtained with this catalyst exceeded 70% in value, the highest conversion known yet for reaction at atmospheric pressure. Activity studies with catalyst prepared from different sources of Zr(OH)$_x$ also showed such high and stable conversion. The isomerization of another light alkane, n-butane, was also studied. However, the activity of these catalysts for n-butane isomerization was minimal and did not increase upon oxidation-reduction pretreatments as it did for n-pentane isomerization. It is speculated that this was due to the different reaction mechanism.
involved in the n-butane isomerization.

Using X-ray spectroscopic methods, it was possible to conclusively determine the state of the platinum metal present in the SZ$_{650}$-based catalysts. In the catalysts that showed exceptionally high stable activity, the platinum was present as relatively large metallic crystallites with little or no oxide and sulfide present. The metallic nature of the platinum was also obvious from the XANES results. In the inactive or deactivated samples, the state of platinum was either that of +2 or +4. It was found that the presence of sulfided platinum was the cause of the inactivity or rapid deactivation. The Pt-sulfide bonds were sufficiently strong that did not get reduced to metallic platinum during the reduction conditions used in this work and it was not possible to recover the activity of these catalysts. This comprehensive analysis of the various samples, thus, correlated the activity to the state of platinum present on the SZ$_{650}$-based catalysts. A related study of platinum adsorption onto the SZ$_{650}$ showed that SZ surface was highly acidic such that the uptake of platinum dependent on the precursor ion as well as the pH of the platinum salt solution, if wet impregnation is used to impregnate Pt onto the SZ support.

The activity study highlighted the importance of proper pretreatments for obtaining a high activity alkane isomerization catalyst. The novel use of operando diffuse reflectance infrared spectroscopy for studying these catalysts revealed further clues into the effect of the pretreatments and state of the catalyst surface during the reaction itself. The catalysts showed that the nature of sulfate groups present on the SZ-catalyst was much more complex than had been reported in the literature. Addition of platinum followed by reduction pretreatment leads to a re-structuring of sulfates and lesser bending vibrations are observed. Moreover, during the reduction pretreatment, the Pt-containing samples showed appearance of even more complex nature of sulfate/sulfite species with heating and time as compared
to unmodified SZ catalysts.

Operando IR results demonstrated the usefulness of observing the catalyst during the reactions itself (i.e. under “operando” conditions). The results of the isomerization over Pt/SZ catalysts are remarkably unique in the sense that these results demonstrate that isomerization reaction affects a particular kind of hydroxide species which disappears as soon as the reaction is begun. The change in the sulfate species was negligible in comparison. This result emphasizes the importance of presence of surface hydrides and hydroxides for the activity and stability of the catalyst.

Based on the results obtained, a hypothesis accounting the synergistic effect of (a) calcination at higher temperature, (b) reduction of platinum leading to large metallic crystallites on the catalyst, (c) necessity of hydrogen during the reaction and (d) the increase in activity upon oxidation-reduction pretreatments, was put forward. According to this Site-Juxtaposition hypothesis, the oxidation-reduction pretreatments allowed for restructuring and/or rearrangement of the sulfates on the surface, which lead to appearance of the acid sites in proximity of the metallic crystallites. The decreased separation then results in rapid transfer of spilled-over atomic hydrogen to the acid sites for coke hydrogenation as well as maintaining the acidity of these sites. A simple model demonstrated the applicability of such a pathway towards more detailed understanding of the sequence of reaction.

7.2 Recommendations

The 3-step method for synthesis of SZ-based catalysts used in this work made it possible to achieve the level of stable activity not achieved earlier at atmospheric conditions. The results prompt further investigation in many related subjects, some of which are listed below:

1. The first question that arises is what caused low activity in n-butane isomer-
ization with the catalysts that were highly active for n-pentane isomerization. There could be two reasons for this. First, the large crystallites of Pt adsorb and dissociate higher amounts of H₂, which, in turn, would hinder dehydrogenation to n-butene intermediate, which forms according to the bimolecular mechanism applicable in n-butane isomerization. Second, the dehydrogenation properties of platinum are affected by the size the platinum crystallite. With the low dispersion of the metal, the rate of dehydrogenation falls, leading to reduced n-butene formation and hence low conversion to isobutane. To investigate which of these could be the leading cause of low activity, one needs catalysts with high dispersion of platinum on SZ₆₅₀. To achieve this, a proper understanding and detailed study of the effect of the preparatory variables on the platinum crystallite size is needed.

2. The effect of the concentration of hydrogen and further control of isopentane yield needs to be studied further. Such a study was not undertaken during the course of this work. Investigating this would again involve detailed understanding of the reaction mechanism and preparation of a catalyst with higher dispersion of platinum or other metal modifier. Carrying out operando experiments to monitor the crystallite formation during the reduction of Pt-loaded SZ₆₅₀ would aid in that understanding.

3. Since Fe,Mn-promoted SZ catalysts have been reported to exhibit higher activity at low temperatures, one could use a similar 3-step method for their preparation to investigate the effect of pretreatments on their activity. It would be interesting to find out if the reduction pretreatment as used for platinum, would also lead to low dispersion for iron and manganese, and if they are still active for n-butane isomerization.
4. The hydroxide species present on the surface seem to be important in achieving higher and stable conversion. By proper control of the extent of hydration of the catalyst prior and during the reaction, it could be possible to generate similar species. By using an appropriate ratio of the hydration effect and the hydrogen spillover from platinum, it should be possible to achieve high yield of the desired product.

5. The support, in this case SZ, could be replaced with other supports with slightly lower acidity in order to evaluate the metal support interaction. Of these, the more promising support are sulfated alumina-zirconia (SZ-Al), tungstated zirconia (W-Zr) and the heteropoly acid (HPAs) class of compounds. In various studies, they have been shown to catalytically active for hydroconversion reactions. It would be worthwhile to investigate the 3-step preparation for their synthesis as well.

6. Lastly, it cannot be overemphasized that a detailed mechanistic understanding of the whole reaction is the key to obtaining high yield catalyst. Such an exercise would require collaborative and collective effort from various groups.

As a final note, it is important to point that the preparation of catalyst depends on many factors - big and small, all of which are equally important in obtaining an active as well as stable catalyst. The synthesis method used in this work highlights how some of the variables can “make or break” a catalyst. With the proper understanding of the support and the mechanistic pathway of the reaction, this approach can be turned into a science rather than a purely empirical exercise.
EXAFS is best understood in terms of the wave behavior of the photo-electron created in the absorption process.

Because of this, the x-ray energy is converted to \( k \), the wave number of the photoelectron as
\[
k = \sqrt{\frac{2m_e(E - E_0)}{\hbar^2}}
\]
(A.1)
or \( k \approx \sqrt{0.263(E - E_0)} \) (in eV Å units) and the primary quantity \( \chi(k) \) is often referred simply as “the EXAFS”.

This EXAFS function \( \chi(E) \) representing the oscillations as a function of the photo-electron wavenumber, is defined as
\[
\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta \mu_0(E)}
\]
(A.2)
where \( \mu(E) \) is the measured absorption coefficient, \( \mu_0(E) \) is a smooth background function representing the absorption of an isolated atom, and \( \Delta \mu_0 \) is the measured jump in the absorption \( \mu(E) \) at the threshold energy \( E_0 \). The different frequencies apparent in the oscillations of \( \chi(k) \) correspond to different near-neighbor coordination shells.

Using Fermi’s golden rule, many simplifying approximations for the static disorder in the bond distances, inelastic scattering of the outgoing photo-electron along with averaging over multiple atomic pairs, Stern, Sayers and Lytle arrived at
the classical EXAFS equation as:

\[ \chi(k) = \sum_j N_j \frac{k r_j}{\lambda(k)} f_j(k) \sin(2kr_j + \delta_j(k)) e^{-2k^2 \sigma_j^2} e^{-2r_j/\lambda(k)} \]  

(A.3)

In the above equation, \( j \) represents the individual coordination shell of identical atoms at approximately the same distance from the central atom. \( f_j(k) \) and \( \delta_j \) are scattering properties of the atoms neighboring the excited atom, \( N_j \) is the number of neighboring atoms, \( r_j \) is the distance to the neighboring atom, and \( \sigma_j^2 \) is the disorder in the neighbor distance. \( \lambda(k) \) is the mean-free-path of the photo-electron (typically 5-30 Å) and \( \sigma_j^2 \) is the mean-square-displacement in the bond distance \( r_j \).

From the equation (A.3), once can draw a few physical conclusions about EXAFS. Due to the \( \lambda(k) \) term and the \( 1/r_j^2 \) term, EXAFS is seen to be an inherently local probe, i.e. not able to see much further than 5 or so angstroms from the absorbing/excited atom. Since the EXAFS oscillations consist of different frequencies, each corresponding to the different distance for each coordination shell, use of Fourier transforms becomes important.

Knowing accurate values of the scattering amplitude \( f_j(k) \) and the phase-shift \( \delta_j(k) \), the EXAFS equation allows us to determine \( N_j \), \( r_j \) and \( \sigma_j^2 \). The scattering amplitude and the phase shift can be calculated or determined from the experimental spectra in which the near-neighbor distances and species are known.
BIBLIOGRAPHY


20. J. R. Sohn and H. W. Kim. Catalytic and surface-properties of zro2 modified with sulfur-compounds. *Journal of Molecular Catalysis*, 52(3):361–374, 1989. 1.3.2.1 1.4.1 1.4.4


30. D. Farcasiu and Jing Qi Li. Preparation of sulfated zirconia catalysts with improved control of sulfur-content III. effect of conditions of catalyst synthesis on physical properties and catalytic activity. *Appl. Cat. A-Gen.*, 175:1–9, 1998. 1.3.2.1


32. D. A. Ward and E. I. Ko. One-step synthesis and characterization of zirconia-sulfate aerogels as solid superacids. *J. Cat.*, 150:18–33, 1994. 1.3.2.2, 1.4.2


247


75. K. T. Wan, C. B. Khouw, and M. E. Davis. Studies on the catalytic activity of zirconia promoted with sulfate, iron, and manganese. J. Cat., 158(1):311–326, 1996. 1.5.1, 1.9, 1.5.3, 5.2


80. H. Liu, G. D. Lei, and W. M. H. Sachtler. Pentane and butane isomerization over platinum promoted sulfated zirconia catalysts. Appl. Cat. A-Gen., 146 (1):165–180, 1996. 1.5.1, 1.5.1, 1.11, 3.3.2


106. M. A. Risch. *Synthesis, characterization and light n-alkane isomerization activity of mesoporous sulfated zirconia catalysts*. PhD thesis, University of Notre Dame, Notre Dame IN, USA, 1999. 2.1, 3.3, 3.3.1, 3.3.1, 3.3.5, 4.3.1


111. N. Fairley. CasaXPS VAMAS processing software. Website. [http://www.casaxps.com](http://www.casaxps.com) 2.5.1


123. K. Ebitani, J. Konishi, and H. Hattori. Skeletal isomerization of hydrocarbons over zirconium-oxide promoted by platinum and sulfate ion. *J. Cat.*, 130(1):257–267, 1991. 3.2.5, 4.3.1


256


163. Alexis T. Bell, Michael L. Hair, American Chemical Society. Division of Colloid, and Surface Chemistry. *Vibrational spectroscopies for adsorbed species : based on a symposium sponsored by the Division of Colloid and Surface Chemistry*


