Experimental Investigation of Hydrogen Spillover on Co-Clay Hydrotreating Catalysts by Nobel Metals

by

Mohammad Mozahar Hossain

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGINEERING

April, 2000
INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

Photographs included in the original manuscript have been reproduced xerographically in this copy. Higher quality 6" x 9" black and white photographic prints are available for any photographs or illustrations appearing in this copy for an additional charge. Contact UMI directly to order.

Bell & Howell Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0500

UMI
EXPERIMENTAL INVESTIGATION OF HYDROGEN SPILLOVER ON CO-CLAY HYDROTREATING CATALYSTS BY NOBLE METALS

BY

Mohammad Mozahar Hossain

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE
In
CHEMICAL ENGINEERING

April, 2000
KING FAHD UNIVERSITY OF PETROLEUM & MINERALS
DHAHRAN, SAUDI ARABIA
DEANSHIP OF GRADUATE STUDIES

This thesis, written by

MOHAMMAD MOZAHAR HOSSAIN

Under the direction of his thesis advisor and approved by his thesis committee, has been presented to and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

Thesis Committee

Dr. Muhammad A. Al-Saleh (Chairman)
Dr. Mazen A. Shalabi (Co-Chairman)
Dr. Habib H. Al-Ali (Member)
Dr. Takuma Kimura (Member)
Dr. Jorge N. Beltramini (Member)

(Department Chairman)
(Dean of Graduate Studies)
Dedicated to
My Three Generations
Maa, Mejda, Sejda and Upa
Acknowledgements

This work is an expression of my gratitude to Allah (swt). May Allah bestow peace on his Prophet, Muhammed (pbuh).

My special appreciation is extended to Professor Muhammed A. Al-Saleh, the thesis advisor, for his continuous guidance and encouragement during this investigation. His simple and straight attitude made this work easier and even better. Thanks a lot sir.

I am also expressing my appreciation to my learned thesis committee. Dr. Mazen A. Shalabi, Dr. Habib H. Al-Ali and Dr. Jorge N. Beltramini for their review and comments.

I owe thanks to Dr. Takuma Kimura, visiting research engineer at center for refining and petrochemicals (CRP) KFUPM-RI and a member of my thesis committee for introducing me to catalyst research. I was so fortunate to have worked with him.

A special thanks is extended to Professor T. Inui, visiting researcher at center for refining (CRP) and petrochemicals KFUPM-RI, for his important suggestion and comments.

I would also like to thank the laboratory staffs and technicians at CRP, KFUPM-RI, specially Mr. Elias Biswas, Mr. Khalid Al-Nawad, Mr. K. Alam, and Mr. Al-Yami for their help and service during the experimental works.

My deepest and sincere appreciation is extended to my mother and sejda, for their encouragement and support throughout my life. Thanks are also due to my other family members for their support in various ways. Lucky's silent sacrifice for me can go without mention.
I wish to acknowledge KFUPM for providing financial support in the form of assistantship. My appreciation also goes to CRP, KFUPM-RI for allowing me to work in their laboratory and to use their facilities.

Finally I would like to thank my friends, specially Hasib mia, Pulak bhai, Ifadat, Shahin bhai, Rakib(B) and Saif(Z), who have helped me in different times during my staying at north compound, KFUPM.
Contents

Acknowledgements i

List of Tables vi

List of Figures viii

Abstract (English) xii

Abstract (Arabic) xiii

INTRODUCTION 1

1.1 Chemistry of Hydrotreating Processes 3

1.1.1 Hydrodesulfurization (HDS) ........................................... 3
1.1.2 Hydrodenitrogenation (HDN) ........................................... 5
1.1.3 Hydrodemetalation (HDM) ............................................. 6
1.1.4 Hydrocracking (HDC) .................................................. 6

1.2 Hydrotreating Processes .................................................. 13

1.2.1 Fixed bed Processes .................................................... 14
1.2.2 Moving bed Processes ................................................... 15
1.2.3 Ebullated bed Processes .............................................. 16
1.2.4 Slurry Processes ........................................................ 17

1.3 Hydrotreating Catalysts Design .......................................... 18

1.4 Hydrogen Spillover ......................................................... 20

1.4.1 Hydrogen Spillover in Petroleum Processing ....................... 22
LITERATURE REVIEW

2.1 Alumina, and Silica-Alumina Supported Catalysts ..................................... 24
2.2 Zeolite Supported Catalysts ........................................................................ 28
2.3 Clay Supported Catalysts ........................................................................... 31
2.4 Hydrogen Spillover and Hydrotreating Catalysts ....................................... 34
2.5 Objectives ............................................................................................... 40

EXPERIMENTALS ............................................................................................ 43

3.1 Experimental Design .................................................................................. 43
3.2 Experimental Procedure ............................................................................ 45
  3.2.1 Catalyst Preparation ............................................................................. 45
  3.2.2 Temperature Programmed Reduction (TPR) ......................................... 48
  3.2.3 Pulse Microreactor ................................................................................ 50
  3.2.4 Batch Autoclave Reactor ...................................................................... 52

RESULTS AND DISCUSSIONS ........................................................................ 55

4.1 Elemental Analysis ...................................................................................... 56
4.2 Temperature Programmed Reduction (TPR) ................................................ 58
4.3 Pulse Microreactor Evaluation .................................................................... 68
  4.3.1 Hydrodesulfurization (HDS) of Thiophene ........................................... 69
  4.3.2 Cumene Cracking ................................................................................ 79
4.4 Batch Reactor Evaluation ........................................................................... 81
4.5 Spent Catalyst Analysis ............................................................................. 89

CONCLUSIONS AND RECOMMENDATIONS .................................................. 94

5.1 Conclusions ............................................................................................... 94
5.2 Recommendations ............................................................. 97

APPENDIX .............................................................................. 98

LITERATURE CITED ............................................................. 109
List of Tables

Table

1.1.1 Properties of residual oils ......................................................... 2

1.3.1 Composition and properties of hydrotreating catalysts .................... 19

1.3.2 Typical commercial hydrotreating catalysts ................................... 19

2.1.1 Summary of literature reviewed on alumina and silica-alumina supported catalysts ......................................................... 27

2.2.1 Summary of literature reviewed on zeolite based catalysts ............... 30

2.3.1 Summary of literature available on clay based catalysts .................. 33

2.4.1 Summary of literature available on hydrogen spillover .................... 39

3.1.1 Catalysts designed for the first stage ......................................... 44

3.1.2 Catalysts designed for second phase .......................................... 45

4.1.1 Elemental analysis of fresh catalysts for different metal loading .......... 57

4.1.2 Elemental analysis of fresh catalysts for two different batches of Pt-Rh promoted Co/HPS catalysts ......................................................... 58

4.3.1 HDS activity of single noble metal promoted Co/HPS catalysts

evaluated in pulse microreactor .......................................................... 70

4.3.2 HDS activity of bi-noble metal promoted Co/HPS catalysts

evaluated in pulse microreactor .......................................................... 75

4.3.3 Cumene cracking activity of bi-noble metal promoted Co/HPS catalysts evaluated in pulse microreactor ................................................. 80
4.4.1 Batch reactor evaluation results using VGO as a feed

at 400 °C temperature and 140 kg/cm² pressure ........................................ 83

4.5.1 Carbon on spent catalyst from batch reactor ........................................... 90
List of Figures

Figure

1.1.1 Generalized mechanism of hydrodesulfurization on molybdenum sulfide catalyst ................................................................. 5

1.1.2 Hydrocracking of hexamethylbenzene at 349 °C temperature and
14 atm pressure ................................................................. 8

1.1.3 Hydrocracking of C₁₂ cyclohexanes at 233 °C temperature and
82 atmospheric pressure .................................................... 8

1.1.4 Mechanism for the hydrocracking of tetramethylcyclohexane ................. 11

1.1.5 Iso-paraffin to n-paraffin ratios in the product from hydrocracking
of n-decane using strongly acidic catalysts .................................. 11

1.1.6 Products from hydrocracking of n-hexadecane with two different catalysts ... 12

1.2.1 Residue hydrotreating processes ........................................ 14

1.4.1 A possible mechanism of hydrogen spillover on a noble metal
promoted catalyst .................................................................... 21

3.2.1 Schematic diagram of catalyst preparation steps .................................. 47

3.2.2 The schematic flow diagram of temperature programmed
reduction (TPR) measurement apparatus system .............................. 49

3.2.3 Micro catalytic pulse method ................................................ 51

3.2.4 The schematic diagram of the batch autoclave reactor system ............... 53

4.2.1 TPR spectra of noble metal promoted Co/HPS catalysts and
unpromoted Co/HPS catalyst .................................................. 60

4.2.2 TPR peak temperature of different noble metal promoted

Co/HPS catalysts .................................................................... 62

4.2.3 TPR spectra of Pt-Rh promoted Co/HPS catalysts and unpromoted

Co/HPS catalysts .................................................................... 63

4.2.4 TPR spectra of Pd-Rh promoted Co/HPS catalysts and unpromoted

Co/HPS catalysts .................................................................... 64

4.2.5 Effect of Rh loading on TPR peak temperature on Co-Pt(1 wt%)-Rh/HPS

catalysts ................................................................................. 66

4.2.6 Effect of Rh loading on TPR peak temperature on Co-Pd(1 wt%)-Rh/HPS

catalysts ................................................................................. 66

4.2.7 Effect of catalyst preparation method on the reducibility of Co-Pt-Rh/HPS ... 67

4.3.1 Conversion of thiophene per atom-Co as a function of temperature on

2 wt% single noble metal promoted Co/HPS catalysts and unpromoted

Co/HPS catalyst .................................................................... 72

4.3.2 Conversion of thiophene per atom-Co as a function of temperature on

1 wt% single noble metal promoted Co/HPS catalysts and unpromoted

Co/HPS catalyst .................................................................... 72

4.3.3 Conversion of thiophene per atom-Co as a function of Pt loading on

Co/HPS catalysts .................................................................... 73

4.3.4 Conversion of thiophene per atom-Co as a function of Rh loading on

Co/HPS catalysts .................................................................... 73

4.3.5 Conversion of thiophene per atom-Co as a function of Pd loading on

ix
4.3.6 Conversion of thiophene per atom-Co as a function of temperature on
Pt-Rh (Pt: 1 wt%) promoted Co/HPS and unpromoted Co/HPS .................. 76

4.3.7 Conversion of thiophene per atom-Co as a function of temperature on
Pd-Rh (Pd: 1 wt%) promoted Co/HPS and unpromoted Co/HPS .................. 76

4.3.8 Effect of Rh loading on the catalytic activity of Co-Pt(1 wt%)-Rh/HPS
in HDS of thiophene ............................................................................. 78

4.3.9 Effect of Rh loading on the catalytic activity of Co-Pt(1 wt%)-Rh/HPS
in HDS of thiophene ............................................................................. 78

4.3.10 Cumene cracking activity per atom Co as a function of temperature
on Pt-Rh (Pt: 1 wt%) promoted Co/HPS catalysts and unpromoted
Co/HPS catalyst .................................................................................... 80

4.4.1 H/C ratio in the liquid product from batch autoclave reactor
as a function of reaction time ................................................................ 83

4.4.2 Hydrocracking (VGO) activity per atom-Co of Pt-Rh promoted
Co/HPS and unpromoted Co/HPS catalysts in batch reactor ................. 85

4.4.3 Hydrocracking (VGO) activity per atom-Co as a function of
reaction time in batch autoclave reactor for Pt-Rh promoted
Co/HPS and unpromoted Co/HPS ........................................................ 85

4.4.4 Hydrodesulfurization (HDS of VGO) activity per atom-Co of Pt-Rh
promoted Co/HPS and unpromoted Co/HPS catalysts in batch
autoclave reactor .................................................................................... 86

4.4.5 Hydrodesulfurization (HDS of VGO) activity per atom Co as a function
of reaction time in batch autoclave reactor for Pt-Rh promoted Co/HPS
and unpromoted Co/HPS ......................................................... 87
4.4.6 Hydrocracking of VGO over Co-Pt(1)-Rh(0.2)/HPS catalyst in batch
autoclave reactor for two different runs ........................................ 89
4.5.1 Weight percent of carbon deposited on different catalysts in batch reactor .... 91
4.5.2 Weight percent of carbon deposited on different catalysts for different
time reaction in batch reactor .................................................... 91
4.5.3 Carbon deposition on spent catalyst Co-Pt(1)-Rh(0.2)/HPS
for two different runs ............................................................ 93
Abstract

Name: Mohammad Mozahar Hossain
Thesis Title: Experimental Investigation of Hydrogen Spillover effect on Co-Clay Hydrotreating Catalysts by Noble Metals.
Major Field: Chemical Engineering
Date of Degree: April, 2000

Noble metal hydrogen spillover effect has been applied on the Co-Clay hydrotreating catalysts to increase their catalytic activity as well as to increase their lifetime. Direct impregnation technique was used for the loading of noble metals on the clay support while an ion-exchange method was followed for cobalt loading. Temperature programmed reduction (TPR) measurement technique has been applied to measure the hydrogen spillover effects of the supported catalysts. The reduction temperatures of the promoted catalysts have been found to decrease, indicating that the hydrogen spillover has taken place on the catalyst surface. Pulse microreactor activity results for hydrodesulfurization (HDS) of thiophene and cumene cracking are presented. Results show that a small amount of noble metal/metals can increase the catalytic activity of the catalysts. Two promising catalysts have been evaluated in a batch autoclave reactor for the performance test using vacuum gas oil (VGO) as a feed. These catalysts have been found to have a higher and sustained activity compared to the unpromoted Co-Clay catalyst. The elemental analysis of the spent catalysts shows that the amount of coke deposition on the noble metal promoted catalysts are significantly less than the unpromoted catalyst. Thus this research reveals the fact that hydrogen spillover can create, maintain and regenerate the catalytic activity of Co-Clay catalysts for an extended period of time.

Master of Science Degree

King Fahd University of Petroleum & Minerals

Dhahran, Saudi Arabia

April, 2000
العنوان الرسالة: الاستقصاء التجربي لتباين إفاضة الهيدروجين على الحفاز (Co-Clay) من قبل المعادن الخاملة.
التخصص: الهندسة الكيميائية.
تاريخ الرسالة: أبريل 2000م.

لقد تم تطبيق إفاضة الهيدروجين ودراسة تأثيرها على الحفاز (Co-Clay) وذلك لزيادة نشاطه وطول عمره أيضًا. ويتم استخدام الإيجار المباشر لحمل المعادن الخاملة على المصد الطيني وتُعَت أيضاً بتبادل الألوانات وتلك لحمل الكوبالتات. وقد تم تطبيق تقنية (TPR) لقياس مدى تأثير إفاضة الهيدروجين للحفاز، وبعد إجراء التجارب لوحظ انخفاض درجة حرارة الاختزال للحفاز مما دل على أن هناك إفاضة للهيدروجين تُعَت على سطحه.

النتائج من المفاعل البضعي (HDS) (batch autoclave reactor) للمذيبات والسيموين دلت على أن كمية قليلة من المعادن الخاملة (VGO) تستخدم لإنتاج إفاضة المحفزات في مفاعل. المحفزات غير المحترقة. كما وجد أيضًا أنه عند استخدام المحفزات المشحّعة أو المشحّعة تكون نسبة تراكم الكربون على المعادن الخاملة أقل مما هو عليه عند استخدام المحفزات غير المشحّعة أو المشحّعة.

هذا البحث يثبت أن إفاضة الهيدروجين باستطاعته أن يذيِّم نشاط الحفاز لفترة زمنية طويلة.

د. ك. خبراء في العلوم
جامعة الملك فهد للبترول والمعادن
الظهران - المملكة العربية السعودية
أبريل 2000م.
Hydrotreating is a catalytic process that simultaneously dehydrogenates cracks and hydrogenates the feedstocks, removing nitrogen, sulfur, oxygen, metal and aromatic constituents. In other words, hydrotreating is a part of complex refining processes to remove undesirable impurities and lower the molecular weight of heavy petroleum feedstocks in presence of hydrogen and a suitable catalyst. Basically, it is an efficient low temperature process of chemical addition of hydrogen to and rejection of carbon from hydrocarbon feedstocks.

Recent trends in heavy and residual oil processing are strongly influenced by the following major factors:

- Declining the availability of high quality lighter crude oils
- Supply of heavy oil is increasing
- The difference of prices between lighter and heavy crude oil is becoming more attractive for heavy oil processing
- Worldwide trend toward automobile engines with high compression ratios resulted in an increased demand for high quality gasoline
- Diminishing demand of fuel oils
- More stringent limits on sulfur, nitrogen and aromatics emission
Table 1.1.1 illustrates typical sulfur, nitrogen, hydrogen and aromatic contents along with physical properties of representative residual oils.

**Table 1.1.1 Properties of residual oils**

<table>
<thead>
<tr>
<th>Properties</th>
<th>VGO</th>
<th>Hydrotreated</th>
<th>VGO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (15°C) g/cm³</td>
<td>0.9342</td>
<td>0.8917</td>
<td></td>
</tr>
<tr>
<td>Estimated M.W</td>
<td>442.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nitrogen (wt.%)</td>
<td>0.205</td>
<td>0.057</td>
<td></td>
</tr>
<tr>
<td>Sulfur (wt%)</td>
<td>2.66</td>
<td>0.11</td>
<td></td>
</tr>
<tr>
<td>Hydrogen (wt.%)</td>
<td>11.95</td>
<td>13.43</td>
<td></td>
</tr>
<tr>
<td>H/C Atomic ratio</td>
<td>1.6848</td>
<td>1.8692</td>
<td></td>
</tr>
<tr>
<td>HPLC Analysis (wt.%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saturates</td>
<td>13.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aromatics</td>
<td>68.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polars</td>
<td>18.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Ref.: Center for R&P KFUPM-RI, VGO: Vacuum Gas Oil

The technique of sulfur removal known as hydrodesulfurization (HDS) is widespread and has been in use most of this century. The analogous procedure hydrodenitrogenation (HDN) and hydrodemetalation (HDM) are used to remove nitrogen and metals respectively from the petroleum feedstocks. Hydrocracking reactions applied to reject carbon from and add hydrogen to the heavy feed. The results of hydrotreating depend on the feedstock properties, catalysts properties and the operational conditions
such as temperature, total pressure and hydrogen pressure. During the main reaction nitrogen, and sulfur are converted to ammonia, and hydrosulfide respectively, while the metallic compounds are deposited on the catalyst as metal sulfides.

Hydrotreating catalysts of industrial importance are dual functional catalysts containing both a hydrogenating-dehydrogenating component (usually metals), and an acidic component. With this type of catalysts, cracking and isomerization reactions occur on the acidic component of the catalyst, while the other component dehydrogenates saturated hydrocarbons to produce reactive intermediates, hydrogenates the unsaturated products from cracking, and prevents catalyst deactivation by hydrogenating coke precursors.

1.1 Chemistry of Hydrotreating Processes

During hydrotreating processes removal of sulfur, nitrogen, metals occur. This is usually accompanied by hydrogenation of unsaturated hydrocarbons. Hydrocracking of long-chain aliphatics and naphthenes also occur. The basic hydroprocessing reactions with specific examples are as follows:

1.1.1 Hydrodesulfurization (HDS)

Petroleum containing sulfur compounds include thiols (mercaptans), sulfides, disulfides, thiophene and thiophene derivatives. The approximate order of reactivity is RSH > R-S-S-R’ > R-S- R’ > thiophenes, where R and R’ are various hydrocarbons groups. Reactivity decreases with increased molecular size and varies depending on whether R is an
aliphatic or aromatic group. The reactivity of thiophenes decreases in the order: thiophene > benzothiophene > dibenzothiophene > alkyl-benzothiophenes.

Thiols and sulfides react to form hydrogen sulfide and hydrocarbons

\[ \text{RSSR'} + \text{H}_2 \rightarrow \text{RH} + \text{R'H} + \text{H}_2\text{S} \]
\[ \text{RSH} + \text{H}_2 \rightarrow \text{RH} + \text{H}_2\text{S} \]
\[ \text{RSR'} + 2\text{H}_2 \rightarrow \text{RH} + \text{R'H} + \text{H}_2\text{S} \]

Thiophene reacts largely to mixed isomers of butene

\[
\begin{array}{c}
\text{S} \\
\end{array}
\]

\[\text{+ 3H}_2 \quad \rightarrow \quad \text{H}_2\text{S} + \text{C}_8\text{H}_8 \quad \text{(mixed isomers)}\]

Small amounts of butadines are formed, possibly as an intermediate, but this is rapidly hydrogenated to butene. The butenes in turn are more slowly hydrogenated to butane. The thiophene ring is not hydrogenated before sulfur is removed, although the first step may involve an essential simultaneous removal of sulfur atom and donation of two hydrogen atoms to the structure.

Benzothiophene and its derivatives are hydrogenated to thiophene derivatives before of sulfur atom is removed, in contrast to the behavior of thiophene.

\[
\begin{array}{c}
\text{S} \\
\text{H}_2 \\
\end{array}
\]

\[\text{+ H}_2 \rightarrow \quad \text{C}_8\text{H}_8 + \text{CH}_2\text{CH}_3 \quad \text{+ H}_2\text{S}\]

Dibenzothiophene (DBT) reacts primarily to form biphenyl, plus smaller atoms of phenycyclohexane.

\[
\begin{array}{c}
\text{S} \\
\text{H}_2 \\
\end{array}
\]

\[\text{+ H}_2 \rightarrow \quad \text{C}_8\text{H}_8 + \text{C}_8\text{H}_8 + \text{H}_2\text{S}\]

Biphenyl may be hydrogenated further to phenylcyclohexane, but there is a good evidence that some phenylcyclohexane is formed as an initial reaction product. HDS is catalyzed by promoted molybdenum sulfide, the defect structure of which is illustrated in
figure 1.1.1 A generalized mechanism for HDS on MoS₂ is also illustrated in the same figure [1].

Surface Structure of Molybdenum Sulfide

\[
\begin{array}{cccccccc}
\text{S} & \text{S} & \text{S} & \text{□} & \text{S} & \text{S} \\
\text{Mo}^{6+} & \text{Mo}^{6+} & \text{Mo}^{6+} & \text{Mo}^{3+} & \text{Mo}^{6+} & \text{Mo}^{6+}
\end{array}
\]

Reaction Mechanism in Hydrodesulfurization

Adsorption of H₂ near vacancy
\[\text{H}_2 + \text{MoS}_2 \rightarrow \text{MoS}_2\text{-H}_2\]

Adsorption of RS on vacancy
\[\text{RS} + \square \rightarrow \text{RS-□}\]

Hydrogenolysis of C-S bond
\[\text{RC-SH-□} + \text{H}_2 \rightarrow \text{RCH}_3 + \text{H}_2\text{S-□}\]

Desorption of HC
\[\text{RCH}_3 \rightarrow \text{RCH}_{\text{gas}}\]

Desorption of H₂S to create vacancy
\[\text{H}_2 + 2\text{Mo}^{6+} + \text{S}^{2-} \rightarrow \square + \text{H}_2\text{S} + 2\text{Mo}^{3+}\]
\[\text{H}_2\text{S-□} \rightarrow \square + \text{H}_2\text{S}\]

Figure 1.1.1: Generalized mechanism of hydrodesulfurization on molybdenum sulfide catalyst.

1.1.2 Hydrodenitrogenation (HDN)

Nitrogen compounds are generally less reactive than sulfur compounds of similar structure. Accordingly, the heterocyclic ring is generally saturated with hydrogen before the C-N bond can be broken. During HDN on a Ni-Mo catalyst, pyridine is first hydrogenated to piperidine which, after cleavage of the C-N bond, forms pentylamine which in turn reacts with hydrogen to pentane plus ammonia [3].
Most model compound HDN studies have been restricted to the six membered heterocyclic compounds, particularly pyridine, alkyl-pyridines, and quinoline. In literature quinoline HDN has been studied in some detail at pressures and temperatures of industrial relevance on a sulfided NiMo/Al₂O₃ industrial catalyst [1].

1.1.3 Hydrodemetallation (HDM)

Crude oil contains small quantities of nickel and vanadium in the form of high molecular weight organometallic compounds. A portion of the metals are present in the form of porphyrins, in which the metal atom surrounded by four pyrrole-type rings. The nonporphyrinic structures comprise a wide variety of organometallic complexes. To a large extent these organometallic compounds are associated with asphaltenes in the residua, and HDM as practiced commercially is not separate reaction but rather one of the group that includes HDS, HDN, and hydrogenation. Unlike others, in HDM metals are deposited on the catalysts, in the form of sulfides, causing irreversible fouling.

Only a small number of model compound studies of metal porphyrins have been reported [3]. The first step is a reversible hydrogenation followed by a series of hydrogenation-hydrogenolysis reaction culminating in metal deposition.

1.1.4 Hydrocracking (HDC)

In literature the chemistry of hydrocracking has been discussed with major categories of hydrocracking catalysts, which are i) dual-functional catalysts in which the acidic component is strong and the hydrogenation component is relatively weak, and ii) non
acidic catalysts with an active hydrogenation-dehydrogenation component. The catalysts used in most major commercial petroleum hydrocracking processes fall in the first category. Reactions of these dual-function catalysts are characterized by extensive isomerization and skeletal rearrangement typical of acid catalyzed reactions. With this type of catalyst, the isomerization and cracking reactions occur primarily on the acidic component of the catalyst. Very little cracking occurs on the hydrogenation sites. The hydrogenation component hydrogenates saturated reactants to produce reactive olefin intermediates, hydrogenates the unsaturated products from cracking, and prevents catalyst deactivation by hydrogenating coke precursors. The hydrocracking reactions for some representative compounds of residual oil are given below.

**Hydrocracking of Aromatics**

One of the earliest reactions to gain attention in screening tests was an unexpected type of hydrodealkylation observed when hydrocracking polysubstituted alkylbenzenes. This reaction produced lower boiling aromatics as desired. The concentration of aromatics in the product was, however, higher than would be explained by any known reaction mechanism, and the missing ethyl substituents appeared in the product mainly as isoparaffins rather than as methane. The importance of alkylbenzene disproportionation to the course of this reaction was readily apparent, but the fate of one important intermediate, hexamethylbenzene, was obscure. Sullivan, R.F [5] showed that hexamethylbenzene cracked over such simple catalysts as NiS-silica-alumina to give, mainly, lower boiling aromatics, isobutane, and isopentane. Figure 1.1.2 illustrates the unusual product distribution observed. This reaction, in its apparent effect, peels or pares methyl groups
Figure 1.1.2: Hydrocracking of hexamethylbenzene at 349 °C temperature and 14 atm pressure.

Figure 1.1.3: Hydrocracking of C_{12} cyclohexanes at 233 °C temperature and 82 atm pressure.
from the ring and, therefore, as een amed he aring eaction. eaction echanism was proposed which involves repeated contraction and expansion of aromatic rings adsorbed on acid sites on the catalytic surface. his robably roceeds by way of an isomerization between an aromatic C₆ ring and a relatively stable cyclopentadienyl cationic intermediate. Isomerization proceeds until a branched side chain is formed that can crack off to form an isoparaffin. The remainder of the molecule desorbs as a lower molecular weight aromatic. The plausibility of the cyclopentadienyl cations postulated as intermediates. It has been proposed that such intermediates have a nonclassical form. Further research showed that the paring reaction occurs on silica-alumina in the absence of hydrogen or the hydrogenation component. Cycloparaffins are not formed at the reaction conditions; therefore, they are not essential intermediates in the reaction. Under these conditions, the silica-alumina is deactivated rapidly, and the observed reaction rates are much lower.

**Hydrocracking of cycloparaffins**

A similar, even more rapid paring reaction occurs with cycloparaffins. For example, Figure 1.1.3 shows hexamethylcyclohexane reacts to form isobutane and a mixture of C₈ cycloparaffins (mainly cyclopentanes) as the most important products. Similarly diisopropylcyclohexane reacts to form isobutane and C₈ cycloparaffins instead of forming (as one might expect) large quantities of propane. As with aromatics, essentially all of the ring structures are preserved in the paring reaction of cycloparafins.

The cycloparaffins tend to form isobutane and a cycloparaffin of four carbon numbers lower than the reactant molecule. Therefore, the dominant products from C₁₀
cycloparaffins are isohutane and methylcyclopentane. A sequence of reactions to produce these compounds from tetramethylcyclohexane is given in Figure 1.1.4. The product distributions from different cycloparaffins of any given carbon number are very similar to each other—a strong indication that similar intermediates are involved in each case.

**Hydrocracking of Paraffins**

The reactions of paraffins, while somewhat less unexpected than the paring reaction of cyclic compounds, gave us an important key as to how to tailor catalysts to fit specific refining needs and to yield different product slates. It has been found a profound difference between the behavior of normal paraffins in hydrocracking with a catalyst containing a strong hydrogenation component such as nickel metal or a noble metal and a relatively weak hydrogenation component such as nickel sulfide. A carbonium ion mechanism is usually proposed similar to the mechanisms previously proposed for catalytic cracking except that hydrogenation and hydroisomerization are superimposed. Paraffins are first dehydrogenated to an olefin then are adsorbed as a cation on an acidic site, isomerized to the preferred tertiary configuration, and undergoes beta scission. Virtually no methane and ethane are formed. The reaction becomes more selective for isoparaffin production as the temperature is decreased. Figure 1.1.5 shows the iso-to-normal ratio of the combined pentanes and hexanes for the reaction of pure normal decane over catalysts with a strongly acidic component and illustrates the advantage of operating at low temperatures for maximum isoparaffin yields. The high iso-to-normal ratios in the product gave isocracking its name.
Figure 1.1.4: Mechanism for the hydrocracking of tetramethylicyclohexane.

Figure 1.1.5: Iso-paraffin to n-paraffin ratios in the product from hydrocracking of n-decane using strongly acidic catalysts.
Figure 1.1.6: Products from hydrocracking of n-hexadecane with two different catalysts.

By increasing the hydrogenation activity of the catalyst relative to its acidity, the product distribution from normal paraffin reactants can be dramatically changed. For example, for the hydrocracking of normal decane at comparable conditions, the following iso-to-normal ratios for the combined pentanes and hexanes were obtained with three different metal compositions on a single, acidic silica-alumina support:

<table>
<thead>
<tr>
<th></th>
<th>Iso/Normal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel metal</td>
<td>0.1</td>
</tr>
<tr>
<td>Platinum</td>
<td>1</td>
</tr>
<tr>
<td>Nickel sulfide</td>
<td>8</td>
</tr>
</tbody>
</table>

The catalysts with the high hydrogenation activity give product with low iso-to-normal ratios. Apparently, olefinic intermediates undergo a greater extent hydroisomerization occurs. With nickel metal, appreciable hydrogenolysis occurs without isomerization.

Figure 1.1.6 compares the reactions of n-hexadecane on a catalyst with strong hydrogenation activity (platinum on silica-alumina) and one with strong acidity and eaker
hydrogenation activity (nickel sulfide on the same silica-alumina support). Isoparaffins of carbon numbers of four, five, and six are the preferred products with the strongly acidic catalyst. The catalyst with the stronger hydrogenation activity makes much less isobutane, and the product distribution is spread more evenly over a wide molecular weight range. Therefore, the C5+ liquid yield is higher for the catalyst with strong hydrogenation activity, although iso-to-normal ratios are much lower.

1.2 Hydrotreating Processes

Atmospheric residue (AR) and vacuum residue (VR) are difficult feed to convert catalytically because they contain of the most of the impurities present in the crude oil in a concentrated form, among them are asphaltens and metals (essentially nickel and vanadium). Asphaltens are complex aggregates of large molecules containing heteroatoms (S, N, O and metals) which tend to inhibit all of the catalytic functions by coking and metal sulphides deposition during the reaction. In residue HDC one of the challenge is to convert as much asphaltens as possible into lighter compounds.

Both catalytic and thermal cracking occur in residue HDC processes and the proportion of each type of reactions depends mainly on the reaction temperature. Catalytic hydrocracking is favored by temperature and by hydrogen pressure. An increase of the hydrogen pressure also have a tremendous impact on the quality of the products by providing high level of desulphurisation and hydrogenation. Hence residue hydrocracking processes are high hydrogen pressure, high temperature and low contact time processes.

A large number of technology have been developed to overcome the troubles generated by the use of high reaction temperature in the processing of heavy feeds
containing metal contaminants like oil residua. Figure 1.2.1 indicates schematically the various combinations of fluid and catalyst flows that can be found in commercial reactors. Various types of reactors are employed such as fixed bed, co-current and counter-current moving bed and ebullated bed reactors.

![Diagram of reactor types](image)

Figure 1.2.1: Residue hydrotreating processes.

### 1.2.1 Fixed Bed Processes

The most standard residue hydroconversion processes use fixed bed catalytic reactors. Fixed bed hydroprocessing units can be operated in two modes, HDS and HDC by increasing the reaction temperature and using different catalysts.

The HDS mode allows reaching a conversion of the 550°C residue of 35 wt%.
The converted product is mainly a desulphurised vacuum gas oil. For the HDC mode conversion of the 550°C residue reach 56 wt% and substantial amounts of gas oil and naphtha are obtained. In both modes of operation, the unconverted atmospheric residue is a desulphurised and stable high quality LSFO with 0.75 wt% or 0.8 wt% sulphur respectively.

The fixed bed process is well adapted for feedstock containing less than 100/120 wt ppm Ni+V for a one year cycle length. This cycle length is determined by the HDM activity and the saturation of the metal retention capacity of the HDM catalyst. The operability of the fixed bed process is good. For feedstock containing larger metal content (up to 250-300 wt ppm Ni+V), a new concept of fixed bed reactors including a swing guard reactors system has been developed by IFP. The process scheme includes swing guard fixed bed reactors which can be switched in operation and several downstream fixed bed reactors in series. When the HDM catalyst contained in one of the guard reactor in operation is deactivated, a suitable procedure and technology allow to bypass this reactor, replace the catalyst with a fresh one and put back the reactor on stream. All these operations are done without shutting down the unit, avoiding any production loss.

1.2.2 Moving Bed Processes

In moving bed reactors the catalyst circulates by gravity, in plug flow, inside the reactor and fresh catalyst is added periodically at the top of the reactor while spent catalyst is withdrawn at its bottom. The main advantage of the moving bed process is its capacity to process, with long cycle length, high metal content feedstock.

Out of two, the best configuration is the counter current mode because the spent
catalyst saturated by metals meet the fresh feed at the bottom of the reactor whereas the fresh catalyst reacts with an already demetallised feed at the top of the reactor. This configuration results in lower catalyst consumption than with other processes. When moving through the reactor, the catalyst is submitted to high mechanical forces that may lead to attrition of the catalyst and therefore to bed plugging problems on the top of the first downstream fixed bed reactor. The catalyst attrition in moving bed can be reduced through optimal hydrodynamic conditions and use of high attrition resistance catalysts.

Moving bed processes need however special equipment and procedures for a safe and effective catalyst transfer into and out of the high pressure and high temperature reactor.

The product yields and qualities are similar to fixed bed process for the same operating conditions. However, the operability is more difficult due to the operation of continuous catalyst renewal in high P-T conditions and to the entrainment of catalyst fines to the downstream fixed bed reactor.

With these processes the conversion can reach 70 wt % depending on the nature of the feed and the reactivity of the asphaltenes. To reach a higher conversion level is difficult because increasing the reaction temperature induce an extensive coking of the catalyst and catalyst bed plugging.

1.2.3 Ebullated Bed Process

In an ebullated reactor, the fluids circulate up flow in the reactor. A recirculating pump expands the catalytic bed and maintains the catalyst in suspension. The expanded bed volume is 30 to 50 % larger than the bed volume at rest. Due to the expansion of the
catalyst bed, the ebullated bed is perfectly mixed and isothermal and can work at a much higher temperature than fixed or moving bed reactors. Therefore a higher conversion of the feed can be reached. In addition, bed plugging due to coke build-up between the catalyst grains is prevented. However, the ebullated bed works at higher space velocity, i.e. smaller catalyst volume, than fixed or moving bed reactors with the same reactor volume.

The ebullated bed reactor uses also a continuous catalyst renewal system at the top of the reactor and a continuous withdrawal system at its bottom and this allows a continuous operation of the unit.

To reach a high level of conversion (>50-60%) the main problem is to limit the sedimentation of heavy compounds and asphaltenes, which lead to deposits on the reactor internal parts and downstream vessels as well as on the catalyst and cause operability problems and catalyst deactivation. This increases the catalyst consumption and decreases the stability of the residual fuel. The high temperature used in ebullated bed lead however to lower product qualities than with fixed and moving bed reactors.

1.2.4 Slurry Process

Several slurry reactor processes have been developed at the demonstration stage such as VEBA COMBI cracking, UCAN super oil cracking and HDH processes. Other slurry processes have been developed at the pilot stage such as MICROCAT RC and MRH processes. All these reactors use small amounts of additive, or catalyst precursors (from 0.1 to 3 wt%). The level of conversion can however reach 95%, but product quality is very poor.
1.3 Hydrotreating Catalysts Design

The high conversion hydrotreating catalysts combine an acidic component for cracking and a metal for catalyzing the hydrogenation reactions. The choice of catalyst depends on the nature of the feed and product distribution desired. Based metals such as Co, Mo, Ni, or W supported on either acid treated Al₂O₃, Al₂O₃-SiO₂ or zeolite are commonly used with the objective of producing lubricating oils and middle or heavy distillate fuels. Noble metals such Pt, and Pd supported on zeolites are used primarily with clean, pretreated feeds and highly selective towards producing gasoline, diesel or jet fuel. Composition and properties of typical hydrotreating catalysts are given in Table 1.3.1[1] and typical commercial hydrodesulfurization (HDS) and hydrocracking (HDC) catalysts with their life are listed in Table 1.3.2.

A key aspect of catalyst design in hydrotreating is the optimization of pore structures. Support mesoporosity (pore diameter of 3-50) is important for providing and maintaining a well-dispersed surface area sulfide layer; smaller pores provide a higher surface area for dispersing the active phase, and higher surface area results in higher catalytic activity. However, pores must be large enough to admit large hydrocarbon molecules and metal-containing cluster, but at the same time small enough to exclude asphaltenes and coke precursor. Pores must be large enough to allow for deposition of carbon and metals while minimizing pore diffusional resistance and or/pore plugging. These constraints require a careful optimization of the size distribution of mesopores in a resid hydrotreating catalyst with a compromise between high activity and a low deactivation rate.

Another aspect of catalyst design that influences catalyst activity and life is the
### Table 1.3.1 Composition and properties of hydrotreating catalysts

<table>
<thead>
<tr>
<th>Composition and properties</th>
<th>Range</th>
<th>Typical values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Active phases (wt%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoO₃</td>
<td>13-20</td>
<td>15</td>
</tr>
<tr>
<td>CoO</td>
<td>2.5-3.5</td>
<td>3.0</td>
</tr>
<tr>
<td>NiO</td>
<td>2.5-3.5</td>
<td>3.0</td>
</tr>
<tr>
<td><strong>Promoters (wt%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO</td>
<td>1-10</td>
<td>4</td>
</tr>
<tr>
<td>B₂P</td>
<td>1-10</td>
<td></td>
</tr>
<tr>
<td><strong>Physical properties</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Surface area (m²g⁻¹)</td>
<td>150-500</td>
<td>180-300</td>
</tr>
<tr>
<td>Pore volume (cm³g⁻¹)</td>
<td>0.25-0.8</td>
<td>0.5-0.6</td>
</tr>
<tr>
<td>Pore diameter (nm)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mesopores</td>
<td>3-50</td>
<td>7-20</td>
</tr>
<tr>
<td>Macropores</td>
<td>100-5000</td>
<td>600-1000</td>
</tr>
<tr>
<td>Extrudate diameter (nm)</td>
<td>0.8-4</td>
<td>3</td>
</tr>
<tr>
<td>Extrudate length/diameter</td>
<td>2-4</td>
<td>3</td>
</tr>
<tr>
<td>Bulk density (kgm⁻³)</td>
<td>500-1000</td>
<td>750</td>
</tr>
<tr>
<td>Average crush strength/length (kgmm⁻¹)</td>
<td>1.0-2.5</td>
<td>1.9</td>
</tr>
</tbody>
</table>

### Table 1.3.2 Typical commercial hydrotreating catalysts

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Purpose</th>
<th>Catalyst life (year)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co-Mo/Al₂O₃</td>
<td>Hydrodesulfurization (HDS)</td>
<td>2~3 (For lighter feed)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.5~1 (For heavy feed)</td>
</tr>
<tr>
<td>Ni-Mo/USY zeolites</td>
<td>Hydrocracking (HDC)</td>
<td>2~3 (For lighter feed)</td>
</tr>
<tr>
<td>Or Ni-W/USY zeolites</td>
<td></td>
<td>0.5~1 (For heavy feed)</td>
</tr>
</tbody>
</table>
profile of active material in the catalyst pellet, which can be varied by controlling preparation procedure. Since during HDM Ni and V deposits which deactivate the catalysts are concentrated in an outer shell of the pellet, there is a clear advantage to preparing hydrotreating catalysts for treatment of metal-containing feeds with active phase "center loaded", i.e. concentrated at an "inner shell" or yoke approximately halfway into the pellet.

1.4 Hydrogen Spillover

The phenomenon "Hydrogen Spillover" defined as the dissociative chemisorption or adsorption of hydrogen on the metal (mostly noble metals) and migration of active species to the surface of the support. Spillover involves the transport of active species sorbed or formed on a surface onto another surface that does not under the same condition of the previous surface. Thus, the adsorbed species gain to different surface phase (accepting surface) that is in contact with the original adsorbing and activating surface. Migration from the first surface may proceed spillover and several processes may take place on the accepting surface following spillover such as surface transport, reaction in the bulk, reactions on with the surface, and creation of sites capable of adsorption or catalysis.

For hydrogen spillover from a metal to an oxide, H\textsubscript{2} usually dissociates on the metal into atomic H, which then spills over onto the oxide support. Figure 1.4.2 shows a possible mechanism of hydrogen spillover on a noble metal promoted catalyst. H\textsubscript{2} spillover is envisioned to involve spillover of atoms formed by dissociation of the adsorbing molecules. However, adsorbing species can only partially dissociate or even
retain their molecular identity during spillover. Movement across the surface can take place by forming equivalent bonds with neighboring surface atoms. This effectively exchanges the bonds between the adsorbed species and the surface, and allows the adsorbed species to reach an interface between the activating and accepting surface. Conner and Falconer in their review paper “Spillover in Heterogeneous Catalysis”[7] described that spillover can take place from a metal to an oxide, from one metal to another, from an oxide to another, or from a metal oxide onto a metal.

\[ \text{H}_2 \]
\[ \text{H} \]
\[ \text{HH} \]
\[ \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \quad \text{H} \]
\[ \text{Noble metal/metals} \]
\[ \text{Acidic Support} \]

Figure 1.4.1: A possible mechanism of hydrogen spillover on a noble metal promoted catalyst.

Chemisorption on the original surface is exothermic, and the subsequent surface diffusion may have small activation energy. Spillover at the interface between the two surfaces requires that bonds with the adsorbing surface are broken and new bonds are formed with the accepting surface. This is represented as an endothermic process that must then be facilitated by an increase in entropy for the spillover species.
1.4.1 Hydrogen Spillover in Petroleum Processing

Petroleum processing involves several catalytic processes: cracking, hydrogenation-hydrocracking, skeletal isomerization, and aromatization. Prior to the manipulation of octane by these processes, the feed oil may need to be purged of nitrogen and sulfur containing molecules. Hydrotreating is increasingly employed to remove the heteroatoms (N and S) from the feed.

Reforming, a bifunctional catalysis where it is believed that acidity is responsible for the isomerization and a metal (often Pt) is responsible for reversible hydrogen transfer. In addition, these catalysts may be deactivated by the formation of coke.

Spillover could contribute to the storage of hydrogen removed from the hydrocarbon and recombination of hydrogen could occur on the metal back by spillover from the support. Spillover could also be involved in the creation of active sites during catalyst activation and/or maintenance of catalytic activity by removing coke or coke precursors.
Chapter 2

LITERATURE REVIEW

Modern catalytic hydroprocessing is probably the most versatile and certainly one of the most important conversion processes in contemporary refining technology. Research in 1950's led to the large commercial development of hydrotreating in 1960's, and modern commercial hydrotreating processes are continuing to evolve. However, hydrotreating is an earlier form of hydrocarbon conversion processes. It was the first catalytic cracking process to attain appreciable commercial importance.

Most modern hydrocracking processes are catalytic, and the catalyst employed is usually dual function with both a hydrogenation component and an acidic component (support).

Typical acidic components (support)

Amorphous silica, alumina, silica-alumina, clays, a large family of zeolites, carbon, titanium oxide, ceramics and some naturally occurring minerals.

Typical Hydrogenation components

Noble metals such as palladium, platinum, rhodium, and ruthenium and nonnoble metals such as nickel, cobalt, tungsten, aluminum, Iron, Zr etc. the nonnoble metals are
usually in sulfided form.

Most of the research has been done during the last few decades concentrated on the effect of various supports and metals on hydrotreating catalysts. The research into the catalysts on different support materials can be broadly subdivided by the following:

2.1 Alumina, and Silica-Alumina Supported Catalysts

Silica is a highly electronegative oxide with strong metal-oxygen bonds. Pyrogenic silica and silica gel without any foreign ions as impurities are inert surface. However, only a trace amount of acid producing impurities is sufficient to induce catalytic activity. Silica with small pore size but high surface area may favor segregation of Mo at the external surface of the particles and formation of \( \text{MoO}_3 \).

A large variety of aluminas exits, but \( \gamma-\text{Al}_2\text{O}_3 \) prepared either by thermal decomposition of crystallized hydroxides such as gibbsite or by precipitation of colloidal gels is probably the most versatile and most extensive used catalyst support. It has high surface areas, is adequately stable over the temperature range required for most catalytic reactions, easily formed in spheres or extrudates and is relatively inexpensive. In case of boehmite-driven \( \text{Al}_2\text{O}_3 \), control of microporosity, surface area, pore distribution and pore volume can be finely tuned aspect almost seperately, through the physical parameters of the oxyhydroxide crystallites. Furthermore, its acid-base character plays a central role during the impregnation with the precursor of the active phase, as well as the most of the commercial application of the \( \text{Al}_2\text{O}_3 \) supported catalysts.
Silica-alumina with alumina contents lower than 70% present both Lewis and Bronsted acid sites and the amount of basicity decreases when the alumina content decreases. Alumina rich catalysts contain mostly polymolybdate structures, while this polymolybdate formation is suppressed in silica-rich catalysts and alumina or silica containing heteropolyacids are formed. These effects are in line with the modification of the surface as a function of the silica content.

Effects of transition metal addition to CoMo/γ-Al₂O₃ catalyst on hydrotreating reactions of atmospheric residual oil shown by Lee et al. [8]. Ni, Ru, and W were used as additive to the catalyst. Among the additive modified CoMo/γ-Al₂O₃ catalysts, NiCoMo/γ-Al₂O₃ and WCoMo/γ-Al₂O₃ has been showed a more improve reaction performance than commercial CoMo/γ-Al₂O₃ whereas RuCoMo/γ-Al₂O₃ did not. Beer et al. [9] tested the thiophene hydrodesulfurization by Co-Mo, Fe and Mo catalysts supported on alumina and carbon. The hydrodesulfurization activity of Co-Mo and Fe catalysts increased in the order γ-Al₂O₃ <C-black composite<active carbon. Riley [10] reported the activity, selectivity and kinetics of the various reactions occurring during hydroprocessing of heavy feed with Co-Mo on alumina catalysts. Butz [11] conducted some experiments of hydrocracking of Arabian mixed asphaltenes without catalysts, with modified red mud and with an industrial Co-Mo/Al₂O₃ catalyst in a batch autoclave reactor at 435 and 460°C for 5-90 min. Due to the hydrogenation activity, both catalysts caused with similar efficiency, the decrease of coke formation and the increase of quality and quantity of oil.

Hydrodesulfurization of dibenzothiophene and 4,6-dimethylidibenzothio-phen and hydrocracking of polycyclic aromatic compounds with NiMo/γ-Al₂O₃ catalysts has
been conducted by Michaud et al. [12], Miki and Sugimoto [13]. Jones et al. [14] investigated the benefits of fluoride and phosphorus promoted NiMo/Al₂O₃ catalysts. Catalysts impregnated in the sequence phosphorus-metal (Ni and Mo)–fluoride were shown clearly superior to those prepared by adding first phosphorus, then fluoride and finally metals. The bi-promoted catalysts retained fluoride well and were quite effective in hydrogenation and hydrodesulphurization. They were even more effective than phosphorous-only promoted catalysts in hydrodenitrogenation.

Joo and Guin [15] examined the effects of Pt, Ru, and Ir promotion on Al₂O₃ supported NiMo, CoMo and NiW commercial catalysts using model compounds, pyridine and naphthalene, to investigate HDN and ring hydrogenation reactions, respectively. For sulfided forms of NiMo, all noble metals tested improved the HDN activity. Pt and Ir improved the activity of CoMo while NiW was not improved by any noble metal promotion. For ring hydrogenation of naphthalene, the Pt-promoted catalysts were more active than the original catalysts.

A study of co-precipitated Al₂O₃-AlPO₄ (APP) as supports of NiMo heavy oil upgrading catalysts has been completed by Smith et al. [16]. Results have been also compared with a commercial NiMo/Al₂O₃ catalyst. The HDM activity of NiMo/AlIP catalyst has been found approximately 10 percentage points greater than for commercial catalysts.

Rajagopal et al. [17] synthesized a series of silica-alumina with controlled composition and used as support for Mo oxide catalysts. TPR and XRD shown that reducibility of Mo increased with the increase of Mo loading, regardless the support composition. Ahmed et al. [18] studied the hydrocracking activity of Co-Mo/SiO₂-Al₂O₃
catalysts. They found highest cracking activity when molybdenum has been loaded first followed by cobalt impregnation. On the other hand, thiophene HDS activity has been highest in the case of simultaneous impregnation of cobalt and molybdenum on silica support. Catalytic effects of various hydrogenation-hydrocracking catalysts on coliquefaction of coal with high-density polyethylene (HDPE) has been investigated over Si₂-Al₂O₃ supported catalysts by Ding et al. [19]. Si₂-Al₂O₃ impregnated with Pt, Ni, Pd, or Fe has been shown higher catalytic activity than metal free catalysts. It has been concluded that the hydrogenation function was created on active metal sites while hydrocracking took place on active site of Si₂-Al₂O₃.

Table 2.1.1 Summary of literature reviewed on Alumina, and Silica-Alumina supported catalysts

<table>
<thead>
<tr>
<th>Support</th>
<th>Promoter /Metal loaded</th>
<th>Activity tested</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Ni, Ru, W/ Co- Mo</td>
<td>Hydrocracking of atmospheric resid-ual oil</td>
<td>Lee et al.[8] 1994</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Co-Mo</td>
<td>Hydroprocessing of heave feed</td>
<td>Riley[10] 1978</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>/Ni-Mo</td>
<td>HDS</td>
<td>Michaud et al.[12, 13,14], 1998</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pt, Ru, Ir/Ni-Mo, Co-Mo, Ni-W</td>
<td>HDN of pyridine and hydg. of naphthalene</td>
<td>Joo and Guin [15], 1996</td>
</tr>
<tr>
<td>Support</td>
<td>Promoter /Metal loaded</td>
<td>Activity tested</td>
<td>References</td>
</tr>
<tr>
<td>--------------</td>
<td>------------------------</td>
<td>--------------------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>Al₂O₃-AlPO₄</td>
<td>Ni-Mo</td>
<td>Bitumen hydrocracking</td>
<td>Smith et al.[16]</td>
</tr>
<tr>
<td>(AAP)</td>
<td></td>
<td></td>
<td>1994</td>
</tr>
<tr>
<td>Si₂-Al₂O₃</td>
<td>Mo</td>
<td>TPR and XRD characterization</td>
<td>Rajagopal et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[17], 1994</td>
</tr>
<tr>
<td>Si₂-Al₂O₃</td>
<td>Co-Mo</td>
<td>Hydrocracking and HDS of thiophene</td>
<td>Ahmed et al.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>[18], 1996</td>
</tr>
<tr>
<td>Si₂-Al₂O₃</td>
<td>Pt, Ni, Pd, or Fe</td>
<td>Hydrogenation and hydrocracking</td>
<td>Ding et al. [19]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1996</td>
</tr>
</tbody>
</table>

2.2 Zeolite Supported Catalysts

Zeolites are highly crystalline, hydrated aluminosilicates that upon hydration develop on ideal crystal of uniform pore structure having minimum channel diameter of about 0.3 to 1.0 nm. The size depends primarily on the type of zeolite and secondarily on the cations presents and the nature of treatments such as calcination, and various chemical treatments. The use of zeolites in hydrocarbon cracking now accounts for over 90 percent of the total consumption of zeolite catalysts. Zeolites in the acidic form are much more active than conventional silica-alumina. For catalytic cracking, the zeolites must have sufficiently large pore to accommodate most feed molecules, have good stability to high temperatures encountered in the reaction and regeneration; and have good stability to steam, which is formed in regeneration. Stability increases with Si/Al ratio. Type Y, which is more hydrothermally stable and has a higher SiO₂/Al₂O₃ ratio than X.

The hydrocracking reaction of several aromatic hydrocarbons over USY-zeolite has been investigated under rather severe conditions by Chareonpanich et al. [20].
higher temperatures such as 600°C, even three aromatic hydrocarbons were completely converted to BTX and light gases.

The hydrocracking properties of Ni, Mo and Ni-Mo sulphides supported on ultrastable HY zeolite by examined by Egia et. al. [21], Leglise et. al. [22] and Vazquez and Escardino [23]. The hydroconversion of n-decane, and n-heptane has been conducted at moderate pressure. The cracking conversion with those catalysts has been found significantly higher than that of blank HY zeolite. Hydrogenation and hydrocracking of a model light cycle oil feed, and properties of sulfided NiMo hydrocracking catalyst, reported by Bouchy et. al. [24]. They have shown that diaromatic undergoes a fast hydrogenation in quasi-equilibrium with the corresponding methyltetralins. The inhibition of the reactions by NH₃, H₂S, and the aromatics has also been investigated, and it has been found that the aromatics have the strongest effect.

Isoda et. al. [25] presented an experimental study on hydrocracking, hydrodenitrogenation and hydrodesulfurization of vacuum gas oil (VGO) using Ni-, Co-, and Fe-loaded and dealuminated Y-zeolites. The Ni-Hy-A zeolite of Si/2Al=16.0 exhibited an excellent hydrocracking of VGO and gave the highest yield of light fraction with lowest gas and coke yields among the catalysts has been studied.

Giannetto et al. [26] reported the transformation of n-heptane on a series of PtHY catalysts. The activities, stabilities, and selectivities of the catalysts are clearly governed by the number of their acid sites and hydrogenating sites. Isomerization and hydrocracking of heptane over bimetallic bifunctional PtPd/H-Beta and PtPd/USY zeolite catalysts conducted by Blomsma et al. [27]. In comparison to the Pt and Pd loaded acid
zeolite, bimetallic Pd-Pt zeolites found more active and selective in the isomerization of heptane.

**Table 2.2.1 Summary of literature reviewed on zeolite based catalysts**

<table>
<thead>
<tr>
<th>Support</th>
<th>Promoter/Metal loaded</th>
<th>Activity tested</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>USY-zeolite</td>
<td></td>
<td>Hydrocracking of aromatic hydrocarbons</td>
<td>Chareonpanich et al. [20], 1996</td>
</tr>
<tr>
<td>HY-zeolite-Alumina</td>
<td>Ni, Mo</td>
<td>Hydrogenation and hydrocracking</td>
<td>Bouchy et al. [24] 1993</td>
</tr>
<tr>
<td>HY-zeolite</td>
<td>Pt</td>
<td>Hydroisomerization and hydrocracking of n-alkanes</td>
<td>Giannetto et al. [26], 1996</td>
</tr>
<tr>
<td>H-Beta and USY zeolite</td>
<td>Pt, Pd</td>
<td>Isomerization and hydrocracking of heptane</td>
<td>Blomsma et al. [27], 1997</td>
</tr>
</tbody>
</table>
2.3 Clay Supported Catalysts

Naturally occurring clays, such as dioctahedral smectites, are composed of semicrystalline aluminosilicate layers held together by van der waals and electrostatic forces. Anionic charges on the siliceous layers (lamellae) are neutralized by cations in interlameller spaces. When these cations are metal hydroxy polymer cations, they act as pillars, propping the clay layers apart to afford a pillared interlayered clay. Upon heating, these polymers are converted to metal oxide, thus preventing the collapse of the clay layers and hence pillaring the clay. As a result, a two dimensional stable microporous solid is obtained with a pore size between 2 and 40 Å. Depending on the type of pillars used the pore size distribution and physicochemical properties can be altered.

Recently, metal oxide pillared clay has raised great interest as a porous solid acid catalytic material. Because of its acidic nature, metal oxide pillared clays may exhibit superior cracking functions and can be used as the cracking component in the hydrocracking catalysts. Other benefit of using the pillared clay is the higher dispersion of the metal oxide compared to conventional catalysts.

Swarnakar et al. [28] studied catalytic activity of Ti- and Al- pillared montmorillonite and beidellite for cumene cracking and hydrocracking. During studies of cumene conversion over these catalysts, the Ti₉ pillared were found to produce more α-methylstyrene than do the Al₁₃ pillars, which are very selective for benzene production.

Smith et al. [29] in their work, prepared pillared clay based on Al, Cr, Zr and Fe as a pillaring agents and characterized. Prepared clay used as supports of Ni-Mo upgrading catalysts. They showed that Ni-Mo supported on Al-pillared clay performed better as a bitumen upgrading catalyst than bentonite is used as the support.
Hydroconversion of heptane over pt-impregnated Zr- and Zr,Al-pillared smectite was conducted by Moreno et al.[30]. The conversion of heptane over the Zr-pillared montmorillonites was substantially enhanced with respect to the Al-pillared analogues, due to the enhanced hydrogenolysis on platinum. Hydroisomerization and hydrocracking of decane over Al-and Ga-pillared clays conducted by Monila et al. [31]. A comparative study between the catalytic properties of the pillared clays and ultrastable Y zeolites for decane isomerization showed that Al-pillared beidellites and ultrastable Y zeolites are similar catalysts. The activity of the pillared clays follows the sequence of lattice tetrahedral substitution. Sychev et al. [32] prepared chromia sulfided-pillared clay from naturally occurring montmorillonite. Sulfided-pillared material has an interlamellar distance of 1.01 nm, a BET surface area 256 m²g⁻¹, a micropore volume of 0.082 cm³g⁻¹, and a pore slitwidth of 1.24 nm. In the presence of this catalyst, thiophene hydrodesulfurization results exclusively in the formation of butane and butene.

Catalysts of cobalt oxide loaded on smectite clays having high surface areas were synthesized by Hayashi et al [33]. Smectite used were montmorillonite, saponite, porous saponite, hectorite and stevensite. Catalyst of cobalt oxide on high surface smectite was found to be one of the very promising HDS catalysts. Catalyst preparation method affects strongly the catalytic property of cobalt-smectatite catalyst as well as the surface area and pore volume of the support material.

Supported platinum catalysts were prepared using synthesized porous smectite-like clay minerals containing different cations of Ni²⁺, Co²⁺, Mg²⁺, and Zn²⁺ in trioctahedral sheets, Arai et al. [34]. The activities of the catalysts for n-butane
hydrogenolysis and ethylene hydrogenation showed to depend significantly on the support used, being in the order of Pt/SM(Ni)>Pt/SM(Co)>Pt/SM(Mg)>>Pt/SM(Zn), where SM denotes the smectite-like clay. The first three catalysts is much more active compared with a control Pt/SiO₂ catalyst.

Ali et al. [35] developed a series of novel hydrocracking catalysts supported on high-surface area saponite clay and pillared with either cobalt or nickel oxide. The catalyst evaluation for HDS, HDN and hydrocracking was conducted in a batch autoclave reactor using vacuum gas oil as feedstock. The results show that the HDS, HDM and cracking activities of the novel catalysts are comparable to that of a conventional NiW/SiO₂-Al₂O₃ catalyst. The Co catalyst shown better HDS activity while the Ni catalyst shown better HDN and cracking activity.

Table 2.3.1 Summary of literature available on clay based catalysts

<table>
<thead>
<tr>
<th>Types of clay</th>
<th>Metal loaded</th>
<th>Activity tested</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti- and Al-pillared Montmorillonite and Beidellite</td>
<td></td>
<td>Cumene cracking and hydrocracking</td>
<td>Swarnakar et al. [28], 1996</td>
</tr>
<tr>
<td>Al-, Cr-, and Fe-pillared clays</td>
<td>Ni-Mo</td>
<td>Heavy oil upgrading</td>
<td>Smith et al.[29]</td>
</tr>
<tr>
<td>Al-, Al,Zr- and Zr-pillared montmorillonite</td>
<td></td>
<td>Heptane hydroconversion</td>
<td>Moreno et al.[30] 1999</td>
</tr>
<tr>
<td>Al-, Ga-pillared beidellite and natural montmorillonite</td>
<td></td>
<td>Hydrocracking of decane</td>
<td>Molina et al.[31] 1994</td>
</tr>
<tr>
<td>Types of clay</td>
<td>Metal loaded</td>
<td>Activity tested</td>
<td>References</td>
</tr>
<tr>
<td>-------------------------------------------</td>
<td>--------------</td>
<td>----------------------------------</td>
<td>--------------------------</td>
</tr>
<tr>
<td>Montmorillonite, saponite, porous saponite, hectorite, stevensite</td>
<td>Pt</td>
<td>Butane hydrogenolysis, ethylene hydrogenation</td>
<td>Arai et al.[34] 1996</td>
</tr>
<tr>
<td>High surface saponite</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.4 Hydrogen Spillover and Hydotreating Catalysts

Parera et al. [36] were one of the first groups to recognize one of the major contribution of spillover to reforming. They showed that spillover hydrogen and spillover oxygen were effective in removing coke from Pt/Al₂O₃ naphtha reforming catalysts. When Pt/Al₂O₃ reforming catalysts were mixed with a sample of coked alumina, the coke was removed by hydrogen or oxygen at substantially lower temperatures than without contact with the reforming catalysts. The authors concluded that spillover is involved in the removal of coke and that “During naphtha reforming on Pt/Al₂O₃, coke formation is decreased by hydrogen spillover from Pt during the regeneration of this coke is eliminated by oxygen spillover”. Inui [37] studied Rh modified Ni-Ce₂O₃-Pt catalysts for ultra-rapid reforming of methane to syngas in which he described that Rh had been
played the role of porthole for hydrogen spillover and prevents coke deposition on the catalyst surface.

More recent studies have implicated hydrogen spillover more directly in the creation of active sites and as a reagent in the catalysis. The creation of Brønsted acidic sites from spillover hydrogen has been proposed [38,39]. The sites are proposed to create on transition metal oxides as well as on zeolites.

Inui [40] described spillover effect as the key concept for realizing rapid catalytic reactions. He studied the redox property as well as catalytic properties of supported copper catalysts modified with precious metals (Rh and Pt). He also shown the application of spillover effect to enhance catalytic reaction rate in methanation of CO₂, elimination of O₂ in hydrogen gas and rapid reforming reactions. Inui et. al. [41] concluded that the catalyst deactivation and coke deposition in n-octane conversion can be reduced markedly by neutralizing the external acid sites with CeO₂ by means of the mechanochemical method and combination with Pt.

Steinberg et al [42] showed that mechanical mixtures of Pt/Al₂O₃ and H-ZSM-5 catalyzed hydrocracking of n-heptane, whereas, separately, hydroisomerization and oligomerization of olefene intermediates are favored.

Chen et al. [43] found two types of spillover hydrogen that they suggested, are involved in catalytic reforming of n-hexane by Pt/Al₂O₃, i.e., one is irreversible while the other is reversible. They concluded that the reversible hydrogen is involved in hydrocracking and isomerization, and it also involved in maintenance of catalytic activity (preventing coke formation). The irreversible hydrogen is associated with aromatization
activity. They point out that the amount and type of spillover hydrogen is sensitive to catalyst preparation.

Becker et al. [44] used pilot plant studies of the hydroconversion of o-xylene, ethylbenzene, and other C₄ aromatics, and the hydrocracking of middle distillate to conclude that hydrogen spillover from a metal to the zeolite contributed to the catalysis. Extruded physical mixtures of supported metal with hydrotreated catalysts were also shown to retain their activity for middle distillate feeds. They suggested that spillover hydrogen controls the reactions at the acidic sites on the zeolites. Further, it can generates or consume intermediates and keep the acidic sites clear of poisons.

Nakamura et. al. [39] showed that H spillover can promote acid-catalyzed reactions on zeolite. Conversions for toluene disproportionation are much higher for hybrid catalysts than for the individual catalysts. Both disproportionation activity and hydrogenation activity showed similar dependence on the USY content in hybrid catalysts but these activities did not correlate with the coke content. Thus, disproportionation on hydrocracking catalysts in the presence of H₂ was promoted by spillover H to acid sites in the zeolite, and not by coke removal from acid sites. That is, Co-Mo/Al₂O₃ adsorbs H₂, which spills over onto the USY zeolite, where it promotes acid-catalyzed reactions.

Hydrotreating involves the reaction of hydrogen with hydrocarbons to remove sulfur (HDS) or nitrogen (HDN) often present in petroleum. The most active catalysts are supported mixed-metal oxides (e.g., Co-Mo/Al₂O₃ or Co-Ni/Al₂O₃) that are sulfided with H₂S prior to reaction. The cobalt and molybdenum form alternate layers and are exposed on different surfaces [45]. Delmon et al. [46, 47, 48] have shown that physical mixture of
Co/Al₂O₃ and Mo/Al₂O₃ shown an enhancement of HDS activity compared to the sum of the activities of the individual surfaces; although, the activity is not as high as that found for the Co-Mo/Al₂O₃ where the Co-Mo-S state is formed. Delmon et. al.[46, 47, 48] concluded that Co spilled hydrogen over to the Mo⁶⁺, which was reduced to an active form. Interestingly, spillover was not deduced following hydrogen reduction of the precursor mixed oxides but only on the H₂S sulfided catalyst. Physical mixtures of Mo/Al₂O₃ with platinum and rhodium sulfides on alumina were also able to effect an enhancement of HDS activity [47].

An excellent recent example is the study by Ioannides and Verykios [49] of hydrogenation of aromatics. By comparison of supported Rh catalysts and the individual supports (SiO₂, Al₂O₃, TiO₂), they showed that benzene and toluene adsorbed on the supports in weekly held molecular forms. During TPD these aromatic hydrocarbons desorb from the Rh catalyst in the same manner as from the support alone. Peak temperatures are below 403 K. the benzene or toluene that adsorbed on the Rh surface was a fraction of the total amount adsorbed and these species were more strongly held on Rh so that they did not desorb molecularly. Temperature-programmed desorption was used to determine how much molecularly adsorbed aromatics remained and the supports after exposure to H₂ at 298, 338, and 388 K. For SiO₂, Al₂O₃, and TiO₂, all without Rh metal, no reaction took place upon H₂ exposure, and instead benzene and toluene desorbed unchanged from the supports during subsequent TPD. On the supported Rh catalysts, however, the results were quite different [49]. For all Rh catalysts, exposure to H₂, even at 298 K, resulted in hydrogenation of weakly adsorbed benzene to form cyclohexane. That is, H₂ dissociated on Rh, spilled over onto the support, and
hydrogenated the benzene on the support. This experiment is a clear demonstration of spillover because no hydrogenation took place in absence of Rh metal. Since the adsorption sites of the benzene (on the support) and hydrogen (on the metal) were known at the start of the reaction, reaction of these two species must involve spillover.

Ioannides and Vrykios [49] carried out temperature-programmed reaction and observed toluene and methylcyclohexane as spillover H hydrogenated toluene that was adsorbed on the support. Similar results have been obtained for Pd/Al₂O₃ catalyst [50]. The weakly adsorbed benzene and toluene readily react to form cyclohexane and methylcyclohexane, respectively, during temperature-programmed hydrogenation, with reaction starting below room temperature. When CO was adsorbed on the Pd, not much hydrogenation took place, showing that H spillover was inhibited because the strongly adsorbed CO blocked most of the H₂ adsorption. The weakly adsorbed benzene and toluene desorbed prior to their hydrogenation. This experiment also shows that hydrogenation was not due to the creation of active sites on the Al₂O₃ during the high temperature catalyst pretreatment.

Miller et al. [51] shown that H₂-TPD of Pt/Al₂O₃ catalysts display multiple hydrogen desorption. In the presence of Pt, the chemisorbed ammonia undergoes isotopic exchange with deuterium by a spillover hydrogen process, even in mixtures where chemisorbed ammonia and Pt are located on separate support particles. Although spillover hydrogen species affect D₂ exchange of ammonium ions, they do not contribute to the catalytic activity of platinum for neopentane hydrogenolysis or isomerization.

Zhang et al. [52] found that pyridine strongly adsorbed on acid sites of ZSM-5 was hydrogenated over Pt/H-ZSM-5 and a Pt hybrid catalyst (a physically mixed catalyst
with a weight ratio of Pt/SiO2(2.5wt%)/H-ZSM-5=1.4) to adsorbed piperidine in the presence of gaseous hydrogen at around 473 K, whereas no such phenomena were observed on either H-ZSM-5 or Pt/SiO2.

Table 2.4.1 Summary of literature available on hydrogen spillover

<table>
<thead>
<tr>
<th>Support</th>
<th>Promoter /Metal loaded</th>
<th>Activity tested</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>Pt</td>
<td>Hydrogen Spillover to Reforming</td>
<td>Parera et al. [36]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1983</td>
</tr>
<tr>
<td>Ce₂O₃</td>
<td>Pt</td>
<td>Reforming of methane</td>
<td>Inui [37]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1999</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pt</td>
<td>Reforming of methane</td>
<td>Inui [40]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1993</td>
</tr>
<tr>
<td>Ga-Silicate</td>
<td>Pt</td>
<td>Paraffin aromatization</td>
<td>Inui et. al. [41],</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1997</td>
</tr>
<tr>
<td>Al₂O₃, H-ZSM-5</td>
<td>Pt</td>
<td>Catalytic Hydrocracking of n-hexane</td>
<td>Steinberg et al. [42], 1989</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pt</td>
<td>Catalytic Reforming of n-hexane</td>
<td>Chen et al.[43]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1993</td>
</tr>
<tr>
<td>Zeolite</td>
<td></td>
<td>Hydroconversion of o-xylene, ethybenzene and Hydrocracking of Middle Distillate</td>
<td>Becker et al.[44]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1989</td>
</tr>
<tr>
<td>USY Zeolite</td>
<td>Co-Mo</td>
<td>Disproportionation on Hydrocracking</td>
<td>Nakamura et al. [39], 1993</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Co, Mo</td>
<td>HDS, HDN</td>
<td>Delmon et al. [46], 1990,  [47]</td>
</tr>
</tbody>
</table>

20
<table>
<thead>
<tr>
<th>Support</th>
<th>Promoter /Metal loaded</th>
<th>Activity tested</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂, Al₂O₃, TiO₂</td>
<td>Rh</td>
<td>Hydrogenation of Aromatics, TPR</td>
<td>Ioannides and Verykios [49], 1993</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pd</td>
<td>Hydrogenation of Toluene</td>
<td>Holman et al.[50] 1995</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Pt</td>
<td>H₂-TPD</td>
<td>Millar et al.[51] 1996</td>
</tr>
<tr>
<td>H-ZSM-5</td>
<td>Pt</td>
<td>Pyridine Hydrogenation</td>
<td>Zhang et al.[52] 1997</td>
</tr>
</tbody>
</table>

### 2.5 Objectives

A survey of the literature showed that conventionally SiO₂-Al₂O₃ and/or zeolites have been used as a support for the commercial purpose of heavy oil upgrading catalysts. Due to limited pore size of these support materials to access the large molecules of residual and heavy oils research is underway to investigate the possibility of utilizing the clays as an alternative. Usually clays are amorphous materials having a large pore size compared to the conventional supports, which makes interest to the current researches. It has been already investigated that clay supported cobalt catalysts are showing both high HDS and cracking activities compared to a commercial catalyst but the deactivation rate of such catalysts are also high. On the other hand in literature it has also been reported that hydrogen spillover is an effective phenomenon to extend the catalyst life by removing the
coke formed by cracking of hydrocarbons. Usually noble metals such as Pt, Rh, Pd and Ru are employed as a promoter for hydrogen spillover. Based on this ongoing research and above information from literature the following line of research has been adopted for this work.

1) Co-Clay might be a promising catalyst if it would be possible to minimize the deactivation rate. An attempt was taken to introduce hydrogen spillover on Co-Clay catalysts to increase the activity as well as to minimize the rate of deactivation. In this work the Pt, Pd and Rh was used as an active promoter to hydrogen spillover on Co-Clay catalysts.

2) Among the three noble metals mentioned above, Rh is highly active compared to the others as found in literature but the very high price of Rh makes the restriction of its maximum use. In this work an attempt was taken to minimize its use at the same time getting maximum activity by employing a combination of Rh with on of between Pt and Pd.

3) Measurement of noble metal hydrogen spillover effects on the reducibility of Co-Clay catalysts by Temperature Programmed Reduction (TPR).

4) An important part of this work was to screen out the promising catalysts with respect to their cracking activity. For this purpose pulse evaluation was conducted using the model compounds thiophene and cumene as a reactant.
5) Finally the promising catalysts found from pulse reactor evaluation results and TPR measurement were evaluated in a batch autoclave reactor by using VGO as a real feed and the results were compared with the unpromoted Co-Clay catalyst.
Chapter 3

EXPERIMENTALS

3.1 Experimental Design

For successful completion of a project whether it is might be a research oriented or else there should have a plan and strategy before starting the actual work. In this project the plan was to find out promising catalysts and the strategy was to minimize the use of expensive chemicals and number of long run experiments. Having this strategy the experiments were designed into to stages.

The first stage was for screening of promising catalysts. In this stage a small amount of proposed catalysts were prepared and tested its reducibility, ie hydrogen spillover capability by TPR measurement and activity by phase microreactor. At first a single noble metal (from Pt, Rh, and Pd) was loaded on Co-Clay catalyst, then the effect of two different combination of bi-noble metal (Pt-Rh and Pd-Rh) were also investigated by loading on Co-Clay catalysts. For bi-noble metal promoted catalysts the loading of comparatively less expensive noble metals Pt and Pd were kept constant (1 wt%) for the respective catalysts while the loading of more expensive noble metal Rh was varied (0.1~0.8 wt%).

In this stage total 13 catalysts were designed and tested its reducibility by TPR measurement and HDS activity in pulse reactor. The first series (H) was single noble
metal promoted Co-Clay, the second series (A) was Pt-Rh promoted Co-Clay and the third series (B) was Pd-Rh promoted Co-Clay catalysts. Table 3.1.1 represents all catalysts designed and amounts of different noble metals loading on each.

PtCl₂ and RhCl₃ was used for Pt and Rh respectively whereas Pd(NO₃)₂ for Pd. Co(NO₃)₂.6H₂O was used for Co loading. PtCl₂ is not easily soluble in water that's why a small amounts (0.2 ml/gm of catalyst) of concentrate hydrochloric was added to dissolve it into the water.

<table>
<thead>
<tr>
<th>No</th>
<th>Group</th>
<th>Catalysts</th>
<th>Noble metal loaded (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>01</td>
<td>R</td>
<td>Co/HPS (Reference)</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td></td>
<td>Co-Pt/HPS (H1)</td>
<td>2.0</td>
</tr>
<tr>
<td>03</td>
<td></td>
<td>Co-Pt/HPS (H5)</td>
<td>1.0</td>
</tr>
<tr>
<td>04</td>
<td>H</td>
<td>Co-Rh/HPS (H2)</td>
<td>-</td>
</tr>
<tr>
<td>05</td>
<td></td>
<td>Co-Rh/HPS (H4)</td>
<td>-</td>
</tr>
<tr>
<td>06</td>
<td></td>
<td>Co-Pd/HPS (H3)</td>
<td>-</td>
</tr>
<tr>
<td>07</td>
<td></td>
<td>Co-Pd/HPS (H6)</td>
<td>-</td>
</tr>
<tr>
<td>08</td>
<td>A</td>
<td>Co-Pt-Rh/HPS (A4)</td>
<td>1.0</td>
</tr>
<tr>
<td>09</td>
<td></td>
<td>Co-Pt-Rh/HPS (A1)</td>
<td>1.0</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Co-Pt-Rh/HPS (A2)</td>
<td>1.0</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Co-Pt-Rh/HPS (A3)</td>
<td>1.0</td>
</tr>
<tr>
<td>12</td>
<td>B</td>
<td>Co-Pd-Rh/HPS (B1)</td>
<td>-</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>Co-Pd-Rh/HPS (B2)</td>
<td>-</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>Co-Pd-Rh/HPS (B3)</td>
<td>-</td>
</tr>
</tbody>
</table>

In the second stage, promising catalysts found form first stage were further tested in pulse reactor for cumene cracking to find its cracking ability and acidic functionality as
well. Finally these catalysts were evaluated in a batch autoclave reactor where VGO was used as a real feed. Two bi-noble metals promoted catalysts were selected from the first stage for this evaluation. Details of these are presented in Table 3.1.2.

<table>
<thead>
<tr>
<th>No</th>
<th>Group</th>
<th>Name of the catalyst</th>
<th>Noble metal loading (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Pt</td>
</tr>
<tr>
<td>01</td>
<td>A</td>
<td>Co-Pt-Rh/HPS (A4)</td>
<td>1.0</td>
</tr>
<tr>
<td>02</td>
<td></td>
<td>Co-Pt-Rh/HPS (A1)</td>
<td>1.0</td>
</tr>
</tbody>
</table>

3.2 Experimental Procedure

This section will cover the following three subsections.

3.2.1 Catalyst preparation
3.2.2 TPR measurement
3.2.3 Pulse evaluation
3.2.4 Batch evaluation

3.2.1 Catalyst Preparation

Direct impregnation followed by ion exchange technique was adapted to prepare the noble metal promoted Co-Clay catalysts. In impregnation method the carrier (clay) was
added to the aqueous noble metal solution. For ion exchange calcinated sample from impregnation step was added to Co(NO₃)₂.6H₂O solution and kept on stirring for 1.5 hour at >80°C. The detailed steps are as follows

i) **Preparation of noble metal solution:** Aqueous solution of noble metal salts (Pt, Pd, Ru and Rh) was prepared by adding distilled water, and a small amount of concentrate hydrochloric acid. The solution have to be put on stirring at >80°C temperature up to complete dissolving the metal salts.

ii) **Impregnation of HPS:** Required amount of high porous saponite (H.P.S) calcinated at 600°C was impregnated into the noble metal solution.

iii) **Drying and Calcination:** Impregnated sample was dried at 120°C and then it was put into the furnace to calcine at 600°C for 4 hours.

iv) **Preparation of cobalt nitrate solution:** Aqueous solution of Co(NO₃)₂.6H₂O (5.82 gm/gm H.P.S) was prepared by adding distilled water into required amount of Co(NO₃)₂.6H₂O and proper stirring and heating at >80°C.

v) **Co-ion exchange:** Calcinated noble metal-Clay powder was added into the Co(NO₃)₂.6H₂O solution and to keep stirring for 1.5 hrs at >80°C for ion exchange.

vi) **Filtration and Washing:** The ion-exchanged clay was filtered then it was washed by distilled water followed by ethanol.

vii) **Drying and Calcination:** Filtrated noble metal-Cobalt/HPS catalyst was dried at 120°C then it was calcinated at 400°C for 4 hours.

viii) **Pelletization:** This is the final step of catalyst preparation. Here the prepared catalyst was pelletized to desired mesh size.
was pelletized to desired mesh size.

The following flow diagram shows the preparation steps:

**Step 1**
Noble metal salts (PtCl₂, RhCl₃), Pd(NO₃)₂
+ Dist. Water + Conc. HCl.
Stirring at >80°C until the salts dissolve

**Step 2**
Impregnation of H.P.S calcinated at 600°C in noble metal salt solution

**Step 3**
Drying and calcination at 600°C for 4 hr

**Step 4**
Cobalt salt (Co(NO₃)₂·6H₂O) +
Distilled water
Stirring for up to dissolve the metal salt at >80°C

**Step 5**
Co ion-exchange

**Step 6**
Filtration, washing by distilled water followed by ethanol.

**Step 7**
Drying & calcination at 400°C for 4 hr.

**Step 8**
Making pellets

*Figure 3.2.1: Schematic diagram of catalyst preparation steps*
3.2.2 Temperature Programmed Reduction (TPR)

The success or otherwise of catalyst preparation or modification depends on the availability of characterization techniques to determine the condition of the catalyst. There are many techniques available for this purpose including X-ray power diffraction (XRD), electron microscopy (EMR), photoelectron spectroscopy, infrared spectroscopy, temperature programmed reduction (TPR), temperature programmed desorption (TPD), temperature programmed sulfiding (TPD). TPR, TPS and TPD are usually applied to characterize the hydrotreating catalysts in terms of hydrogenation functionality and acidity function. In this study TPR was used for catalyst characterization.

Temperature programmed reduction (TPR) methods are used to monitor metal support interactions. It also provides a useful information about the temperatures needed for the complete reduction of a catalyst. For bimetallic catalysts, TPR patterns often indicate whether two components are mixed or not.

Setup

Temperature programmed reduction (TPR) experiments were carried out in system supplied by Ohkura Riken Co. Ltd., (model TP-200). A schematic flow diagram of apparatus is given in figure 3.2.2. This equipment has been developed to enable the user to obtain data related to reduction and sulfiding characteristics of metal oxides or catalysts containing metals.

Operational Procedure

The procedure for various samples pretreatment and subsequent TPR experiments are as
Figure 3.2.2: Temperature programmed reduction (TPR) apparatus
follows:

At first, 150 mg of catalyst sample (particle size 600-212 μm) was weighed and then placed in quartz tube (8.0 mm OD) reactor and it was held in the middle by quartz wool plugs. In order to remove the water from the catalyst, the sample was pretreated in flowing dry air (30 cm³/min). The temperature was raised to 400°C at a rate of 10°C for 2 hrs, then cooled to ambient temperature. Air was purged by flowing dry air (30 cm³/min) for 30 minutes at ambient temperature.

The gas mixture used for reduction was 5% H₂ in Ar at a flow rate of 20 cm³/min. The temperature of the reactor was programmed to increase linearly from room temperature to 1030°C by a heating rate of 10°C and then retained isothermally for 15 minutes. A 5A molecular sieve trapped the water formed either by reduction or from dehydration process. The hydrogen concentration was determined with a thermal conductivity detector (TCD). The TCD and molecular sieve trap were thermostated at 50±0.1°C. The temperature of the catalyst and the TCD current response were monitored and recorded continuously on a dedicated personal computer (NEC Model PC9821-Xe10).

3.2.3 Pulse Microreactor

Pulse micro reactor is an easy tool for evaluating catalysts. This method has found wide applications in qualitative and quantitative investigations of heterogeneous catalytic reactions.
Setup

The pulse micro reactor was designed by PEC and fabricated by Ohkura Riken Co. Ltd., Japan. It consists of two identical, parallel units, A and B. Each unit comprises a gas inlet, injection port, microreactor and a gas chromatograph (GC). A well-designed control panel is also attached with the system to control and monitor the reactor temperature, pressure, and flow rates. Figure 3.2.3 shows the schematic flow diagram of pulse microreactor system.

![Diagram of pulse microreactor system]

Figure: 3.2.3 Micro catalytic pulse method

Operational procedure

The micro-reactors were filled with 0.05 gm of catalyst. Quartz wool was inserted at both the ends of the reactor tube to make sure that catalyst bed was located at the middle of the tube.

Before starting the actual run, the catalyst was be pre-treated for six hours. The pre-treatment was done either by hydrogen/hydrogen sulfide gas mixture (pre-sulfided). The reactor temperature was programmed to increase from room temperature to 400°C at the end of the pretreatment. The inert gas was introduced to purge the system.

To start the actual experiment run the carrier gas flow rate and pressure was adjusted. The
GC was to be started and the temperature of the column oven, the detector oven, and injector were also adjusted. The 4 way valves (4 RC1 and 4RC3) were adjusted to set the required direction of flow.

The reactant was injected into the port by using a syringe, at the same time the GC was started to record the composition of the reactor outlet. The reactant came into contact with the catalyst and reacted. The analysis by the GC indicated the conversion.

3.2.4 Batch Autoclave Reactor

Batch autoclave reactor is suitable for studying high exothermic hydrocracking reactions. The advantages of this reactor are excellent fluid solid contacts, isothermicity within the reactor, and simple to operate. It provides information about cracking activity, selectivity, and stability of catalyst. It also provides kinetic data that can be used to determine the intrinsic reaction order and activation energy.

Setup

The size of the autoclave reactor unit was 300 ml. The reactor was housed in a furnace. The system consists of programmed control system to control temperature, speed of the stirrer. Pressure and flows was controlled manually. A schematic flow diagram of this system is shown in figure 3.2.4.

Operational procedure

Pre-sulfided catalyst from pulse micro reactor was used in batch autoclave reactor to test its hydrocracking and hydrodesulfurization activity, and its coking tendency in short run.
Figure 3.2.4: Experimental setup of batch autoclave reactor
reactions. 100 gm. of feed (VGO) and 3.0 gm. of sulfided catalyst was to be loaded inside the reactor. Before the reaction the reactant and catalyst was purged by \( N_2 \) and \( H_2 \) and at the same time any leakage checked by a \( H_2 \) detector.

The experiment was started with a pressure of 80 kg/cm\(^2\) and the temperature increasing rate 5°C/min. from room temperature. The stirrer was started at 50°C temperature with a speed of 800-900 rpm. The system pressure and temperature was maintained at 140/cm\(^2\) kg (\( H_2 \)) and 400°C respectively for the specific time allowed for reaction.

The system was allowed to cool down to the room temperature. Then the reactor was purged by \( N_2 \), after taking the product gas sample. Finally spent catalyst sample and liquid sample was taken for analysis.

The gas sample was analyzed by thermal conductivity detector and flame ionization detector, while the liquid product was analyzed by simulated distillation gas chromatograph and CHNS analyzer. CHNS analyzer for percentage of coke deposition also analyzed the spent catalyst.
Chapter 4

RESULTS AND DISCUSSION

In this chapter, experimental results are presented and discussed. The experiments were designed into two stages. The first stage was to screen the promising catalysts while the second stage was for the performance test of the potential catalysts.

Temperature Programmed Reduction (TPR), and Pulse micro reactor were employed in the first stage to find the promising catalysts while the promising catalysts were employed for performance test into a batch autoclave reactor. In three series total 13 catalysts were designed, which are the followings

1. H-series, single noble metal (Pt, Rh and Pd) promoted Co/HPS

2. A-series, Pt-Rh promoted Co/HPS and

3. B-series, Pd-Rh promoted Co/HPS catalysts

Synthetic high porous saponite (HPS) clay, obtained from Kunimine Kogyo Co. Limited, Japan, was used after calcination at 600 °C for four hours. Direct impregnation of high porous saponite (HPS) into the noble metal solution then ion-exchange with Co(NO₃)₂·6H₂O solution was followed for catalyst preparation, but one catalyst was prepared by reversing the order of metal loading i.e at first ion-exchange with
Co(NO$_3$)$_2$·6H$_2$O solution next impregnation into the noble metal solution and TPR measurement results were compared with the first method catalyst. Experimental results are presented in the following sequence

4.1 Elemental analysis
4.2 Temperature Programmed Reduction (TPR)
4.3 Pulse microreactor evaluation
4.4 Batch reactor evaluation
4.5 Spent catalyst analysis

4.1 Elemental Analysis

Elemental analysis is one of the common methods for the estimation of the different elements on the catalyst. It is very important to balance the amount of different metal loading on the support because the life of the catalyst and desired product distribution are depended with some extant on the amount and type of metal loading. Thus elemental analysis plays an important role during synthesizing the supported catalysts. In this study elemental analysis was carried out mainly to find out the amount of Co loading by ion-exchange method. The loading of Rh and Pd also found from this analysis but Pt loading was not obtained because of insolubility of Pt in the organic solvent (Chloroform) used to facilitate CHNS analysis. Table 4.1.1 lists the elemental analysis of different catalysts. From the table it is noticed that the amount of Rh and Pd loading on the respective catalysts obtained from elemental analysis are almost identical to the calculated (before loading) amount. From the table 4.1.1 it is also observed that the amount of cobalt loading was not constant for all the noble metal promoted catalysts. In case of the unpromoted catalyst cobalt (as CoO) loading was maximum (18.5 wt%) and it was slightly decreased with increasing
Table 4.1.1 Elemental analysis of fresh catalysts for different metal loading

<table>
<thead>
<tr>
<th>No</th>
<th>Group</th>
<th>Catalysts</th>
<th>Metal loaded (wt.%).</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Co</td>
</tr>
<tr>
<td>01</td>
<td>R</td>
<td>Co/HPS (Reference)</td>
<td>18.5</td>
</tr>
<tr>
<td>02</td>
<td></td>
<td>Co-Pt/HPS (H5)</td>
<td>17.5</td>
</tr>
<tr>
<td>03</td>
<td>H</td>
<td>Co-Pt/HPS (H1)</td>
<td>15.0</td>
</tr>
<tr>
<td>04</td>
<td></td>
<td>Co-Rh/HPS (H4)</td>
<td>18.3</td>
</tr>
<tr>
<td>05</td>
<td></td>
<td>Co-Rh/HPS (H2)</td>
<td>16.2</td>
</tr>
<tr>
<td>06</td>
<td></td>
<td>Co-Pd/HPS (H6)</td>
<td>18.3</td>
</tr>
<tr>
<td>07</td>
<td></td>
<td>Co-Pd/HPS (H3)</td>
<td>17.1</td>
</tr>
<tr>
<td>08</td>
<td>A</td>
<td>Co-Pt-Rh/HPS (A4)</td>
<td>18.4</td>
</tr>
<tr>
<td>09</td>
<td></td>
<td>Co-Pt-Rh/HPS (A1)</td>
<td>16.4</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td>Co-Pt-Rh/HPS (A2)</td>
<td>16.6</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>Co-Pt-Rh/HPS (A3)</td>
<td>16.2</td>
</tr>
<tr>
<td>12</td>
<td>B</td>
<td>Co-Pd-Rh/HPS (B1)</td>
<td>18.4</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td>Co-Pd-Rh/HPS (B2)</td>
<td>16.6</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>Co-Pd-Rh/HPS (B3)</td>
<td>16.6</td>
</tr>
</tbody>
</table>

noble metal loading. The occupation of the ion-exchange sites (mainly Na and Mg) on high porous saponite (HPS) by noble metals might be the main reason for decreased Co loading in case of the promoted catalysts.

Reproducibility of the series-A (Pt-Rh promoted) catalysts with respect to metal loading was tested by elemental analysis. Co, Rh and Pt loading for two different batches of catalysts and accuracy of reproducibility are presented in Table 4.1.2. The deviation (error) of Co loading was between 2.45–4.94 (%). Thus this analysis shows that the catalysts are reproducible with reasonable accuracy.
Table 4.1.2 Elemental analysis for two different batches of Pt-Rh promoted fresh catalysts for different metal loading (Reproducibility test)

<table>
<thead>
<tr>
<th>No</th>
<th>Catalyst</th>
<th>Metal loaded (wt.%</th>
<th>Co</th>
<th>Pt</th>
<th>Rh</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Batch-1 Batch-2 Deviation (%)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>01</td>
<td>Co-Pt-Rh/HPS(A4)</td>
<td>18.4     17.8     3.30</td>
<td>1.0</td>
<td>0.10</td>
<td></td>
</tr>
<tr>
<td>02</td>
<td>Co-Pt-Rh/HPS(A1)</td>
<td>16.4     16.8     2.45</td>
<td>1.0</td>
<td>0.18</td>
<td></td>
</tr>
<tr>
<td>03</td>
<td>Co-Pt-Rh/HPS(A2)</td>
<td>16.6     17.2     3.60</td>
<td>1.0</td>
<td>0.48</td>
<td></td>
</tr>
<tr>
<td>04</td>
<td>Co-Pt-Rh/HPS(A3)</td>
<td>16.2     17.0     4.94</td>
<td>1.0</td>
<td>0.78</td>
<td></td>
</tr>
</tbody>
</table>

4.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction (TPR) has been widely used for the investigation and characterization of supported catalysts. In general, all TPR experiments resulted in total hydrogen consumption closed to the values corresponding to total reduction of supported metal oxides. The TPR peak area represents the amount of hydrogen consumption and the peak temperature represents the reducibility of the metal oxide or oxides. Thus TPR results can therefore be interpreted quantitatively as estimates of the distribution of various metal oxide phases as well as the bond strength between the metal and oxygen.

TPR is one of the effective experimental technique have been widely used in the study of hydrogen spillover phenomena. Through hydrogen spillover the supported metal oxides should consume a substantial amount of hydrogen. From the definition of hydrogen spillover, the effect of hydrogen spillover is reflected on the TPR spectra, is to lower the reduction temperature and possibly increase the amount of reduction.
Especially, for zeolite, SiO₂, Al₂O₃ or Clay catalysts TPR technique can show the consumption of hydrogen by supported metal oxides and its participation in the catalytic hydrotreating and hydrocracking reactions. In the literature a lot of works have been reported on supported Co catalysts, therefore the interpretations of TPR results will be based on the published literature to some extent on this subject.

The TPR spectra of the reference Co-Clay (HPS) catalyst and Co-Clay catalysts promoted by different noble metals (Pt, Pd and Rh) with different amounts are shown in figure 4.2.1. For unpromoted Co-HPS, the major peaks were found at 226 °C and 746 °C. The first phase (peak at 226 °C) has been assumed to be highly dispersed cobalt oxide, [53]. The cobalt oxide phase gives rise to TPR peak at 746 °C has been described as amorphous overlayer of cobalt oxide and strongly interacted with the support. The TPR profiles of the noble metal promoted Co/HPS catalysts are similar to the unpromoted catalyst but a third peak also observed. This third peak might be another cobalt oxide phase, which is strongly interacted with the support. The similarities between the TPR profiles of noble metal promoted and unpromoted Co/HPS indicate that hydrogen consumption by the noble metal oxides is negligible compared to the cobalt oxide. This similar profile of the TPR spectra is the further indication of the existence of difference metal oxide phase, and no metal alloy was formed during the reduction [55]. Another important observation was that the peaks of the noble metal catalysts were shifted to the lower temperature. The position of the major peak of unpromoted catalyst was at 746 °C, while it was shifted to around 550 °C with the promoted catalysts by a small amount of noble metal. The shift was more pronounced with rhodium promoted catalysts than Pt.
Figure 4.2.1: TPR spectra of noble metal promoted Co/HPS and unpromoted Co/HPS catalysts.
and Pd promoted catalysts.

The promotional effect of noble metals would seem to arise in three ways [54]. The first may be by lowering the activation energy of rate determining step of reduction reaction of the metal oxide, the second is by directly increasing the number of nucleation or potential nucleation sites and the third and final is by the spillover hydrogen. In this study only the hydrogen spillover was considered for the reduction of cobalt oxide. Usually it has been believed that cobalt oxide (other less noble metal oxides also) cannot dissociate H₂ at lower temperature, while the noble metals can dissociate H₂ at lower temperature. Thus hydrogen spillover by noble metal can help to decrease the reduction temperature of cobalt oxide. For unpromoted catalysts initially the reduction starts by spontaneous activation of hydrogen, which is usually, occurs at higher temperature. Ones the reduction started the metal particle that is already formed will take the control of the dissociation of H₂. In case of promoted catalysts the picture is totally different, here the promoter aids the initiation of the reduction of cobalt oxide. Initially H₂ is dissociated by adsorption on noble metal sites, then spillover to the cobalt oxide sites. Therefore, cobalt oxides are easier to be reduced on promoted catalysts. A comparison of the TPR peak temperature for the main phase of the promoted and unpromoted Co/HPS catalysts are shown in figure 4.2.2 by bar graphs. This figure shows clearly that the noble metals are promoting the reduction of cobalt oxide and the larger the noble metal content, lower the temperature of the TPR peak observed and Rh was more active as a spillover promoter compared to Pt and Pd for the Co/HPS system.

It is important with respect to the cost of catalysts to reduce the amount of
Figure 4.2.2: TPR peak temperature for different noble metal promoted Co/HPS catalysts.

expensive noble metals in catalysts. One of the main objectives of the present work was to study the effect of bi noble metal promoted Co-Clay catalysts. The order of strength for hydrogen spillover effect is Rh>Pt>Pd>Ru and the price of those precious metals are also the same order. Price of Rh is 10 times higher than Pt and Pd, therefore Rh cannot be used much amount in commercial catalysts. On the other hand Pt and other noble metals can be reduced more easily in presence of Rh. The reduced noble metals thus have the role of porthole for hydrogen spillover toward cobalt oxide part. So some special combination of the precious metals might be effective than single noble metal promoted catalysts.

Figure 4.2.3 and 4.2.4 show the TPR spectra of unpromoted and bi-noble metal
Figure 4.2.3: TPR spectra of Pt-Rh promoted Co/HPS and unpromoted Co/HPS catalysts.
Figure 4.2.4: TPR spectra of Pd-Rh promoted Co/HPS and unpromoted Co/HPS catalysts.
promoted Co/HPS catalysts where Pt-Rh and Pd-Rh combinations were employed as promoter. In both combinations a small amount (0.1-0.8 wt%) of Rh was loaded along with 1 wt% Pt and Pd respectively. The TPR profile of the bi-noble metal promoted catalysts are exactly same as single noble metal promoted catalysts but this time less amount of Rh with 1 wt% Pt or Pd resulted almost same shifting of the TPR peak to the lower temperature. The effect of Rh loading on the peak temperature at constant (1 wt%) Pt and Pd loading are shown in figure 4.2.5 and 4.2.6 respectively. Initially the reduction peak temperature was decreased sharply with the addition of a small amount (0.1 wt% for Pt-Rh and 0.2 wt% for Pd-Rh) of Rh but further increasing the Rh loading it was not decreased significantly. Not only that even with 0.8 wt% Rh the peak temperature was slightly increased. This unexpected tendency was might be due to the deficiency of the impregnation method for catalyst preparation, where a portion of excess Rh might be buried into the support hence could not contribute to the further promotion of cobalt oxide reduction. Large particle of noble metals could also be formed with excess noble metals, which reduced the number of active sites to dissociate hydrogen. Another important point should have to be considered that rhodium chloride salt plus hydrochloric acid (to dissolved rhodium chloride into water) was used for HPS impregnation. Thus higher the Rh concentration means higher chlorine concentration and this excess amount of chlorine has effects to decrease the hydrogen spillover by Rh.

To investigate the effect catalyst preparation method on the reducibility of Rh-Pt promoted catalysts, an attempt was taken by reversing the order of metal loading for catalyst preparation. This time at first Co was loaded on the support by ion-exchange
Figure 4.2.5: Effect of Rh loading on TPR peak temperature on Co-Pt(1 wt%)-Rh/HPS catalysts.

Figure 4.2.6: Effect of Rh loading on TPR peak temperature on Co-Pd(1 wt%)-Rh/HPS catalysts.
Figure 4.2.7: TPR spectra of Co-Pt(1wt%)-Rh(1wt%)/HPS catalyst prepared by two different methods and the spectra of Co/HPS.

R) Co/HPS, A4) Co-Pt(1wt%)-Rh(0.1wt%)/HPS prepared by direct impregnation of noble metals followed by ion-exchange with Co and A4N) Co-Pt(1wt%)-Rh(0.1wt%)/HPS prepared by Co ion-exchange followed by impregnation of noble metals.

technique, after subsequent drying and calcination at 600 °C Pt-Rh were loaded simultaneously by direct impregnation. Finally the catalyst was dried, calcines at 400 °C and pelletized.

TPR spectra of new method catalyst and the previous method for same amount of Pt-Rh loading (1 wt% Pt and 0.1 wt% Rh) are depicted in figure 4.2.7. It is interesting to observe that the TPR profile of the new catalyst was quit different compared to the first method catalyst and the reference catalyst as well. The first peak was observed at the same temperature as it was before but the amount of cobalt oxide in this phase was 5.5 times larger (calculated from the area under this peak) than the previous method and reference catalyst. A clear sharp second peak was found and its temperature was further
shifted by 50 °C compared to the second peak as observed before. Thus different kind of 
Co metal dispersion was noticed by reversing the metal loading order. The peak 
temperature of the main phase was also shifted to the lower temperature by the method of 
catalyst preparation, which indicates that the reducibility of cobalt oxide might be 
enhanced by adopting this method.

4.3 Pulse Microreactor Evaluation

Laboratory scale testing plays an important role during the early stage of heterogeneous 
catalyst development, especially for the catalysts where there is an involvement of 
precious metal as an active component or as a promoter. Commercially available 
catalysts as well as new formulation can be screened rapidly with microreactors. It does 
not only save the cost but also the time and labor with an effective way.

In this study pulse microreactor was employed for the screening of noble metal 
promoted Co-Clay catalysts in the preliminary stage. However, in pulse reactor tests there 
is a little chance to exhibit hydrogen spillover effect but this type of reactor at least can 
tell about the initial activity and the effect of noble metal on it for a proposed catalyst.

Usually model compounds are employed as reactant in this type of reactors. The 
model compounds such as thiophenes, benzothiophenes, dibenzothiophenes etc are the 
representative of sulfur compound and pyridine, quinoline, alkyl-pyridines etc are the 
representative of nitrogen compound in petroleum feed are widely used in pulse reactor 
evaluation. In this work thiophene was chosen as a model compound because of its less 
reactivity of the sulfur compounds participating in HDS reactions and it belongs to the 
family of compounds that comprises the majority of the sulfur content in petroleum feed
stocks. Cumene, the another model compound was also used for the cracking activity test in the pulse reactor. Both of thiophene and cumene have been studied extensively in HDS and cracking reactions respectively is the another added advantage of their use.

A series of experiments were conducted with noble metal promoted Co-Clay catalysts. In fact all proposed catalysts in this work were evaluated in the pulse reactor for hydrodesulfurization (HDS) reaction. Two catalysts were chosen to test the cracking activity, as well as to investigate the effects of noble metals on the acidity of the catalysts. The HDS and cracking activities of the promoted catalysts were also compared with the reference catalyst (Co/HPS). The results are presented and discussed as follows

4.3.1 Hydrodesulfurization (HDS) of Thiophene
4.3.2 Cumene Cracking

4.3.1 Hydrodesulfurization (HDS) of Thiophene

For simplicity the results are grouped as single noble metal promoted catalysts (series-H) and bi-noble metal promoted catalysts (series-A and series-B)

Effect of Single noble Metals

In this series Pt, Pd and Rh were used as a promoter. Initially 2 wt% of Pt, Pd and Rh was loaded in the respective catalysts. The HDS activity of these catalysts is listed in Table 4.3.1. From this table it is observed that Pt promoted catalyst has less activity than the reference catalyst while both Pd and the Rh promoted catalysts have almost same activity as the reference catalyst. Decreased activity of noble metal promoted catalysts was assumed for two reasons. The first reason was due to the decreased amount of Co loading
Table 4.3.1 HDS activity of single noble metal promoted Co-Clay catalyst, evaluated in pulse reactor

<table>
<thead>
<tr>
<th>No</th>
<th>Catalysts</th>
<th>Noble metal loaded (wt%)</th>
<th>HDS activity (Conversion of thiophene at temp. °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>01</td>
<td>Co/HPS ®</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td>Co-Pt/HPS (H1)</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>03</td>
<td>Co-Rh/HPS (H2)</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>04</td>
<td>Co-Pd/HPS (H3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>05</td>
<td>Co-Pt/HPS (H5)</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>06</td>
<td>Co-Rh/HPS (H4)</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>07</td>
<td>Co-Pd/HPS (H6)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(shown in table 4.1.1) in case of noble metal promoted catalysts and the second one might be the excess amount (in this case 2 wt%) of noble metal loading. Because some times an excess amount of promoter can decrease catalytic activity, however it depends on the metals, supports and method of catalyst preparation. To eliminate the effect of the variation of Co loading on the activity of the catalysts and for the purpose of comparison, activity index per atom of Co is plotted as a function of temperature as shown in figure 4.3.1. This figure shows that all promoted catalysts have higher activity index per atom Co compared to the unpromoted catalyst. Therefore, it seems that the activity was decreased because of decreasing the Co loading in case of the noble metal promoted catalysts. Thus to see the noble metal effect on Co-Clay catalysts normalized activity
(activity index per atom Co) will be used for comparisons in the subsequent sections, all calculations and data for activity index are listed in the appendix. To verify the second assumption, (i.e., excess amount of noble metal loading) for the next three catalysts noble loading was reduced to 1 wt%. The results of these catalysts are also presented in the same Table 4.3.1. Figure 4.3.2 shows the comparison of HDS activity index per atom Co as a function of temperature of 1 wt% noble metal promoted and unpromoted catalysts. This time Pt and Pd promoted catalysts have shown slightly higher activity compared to the reference catalyst but Rh promoted catalyst displayed significant higher activity compared to the reference catalyst.

To compare the effect of noble metal loading on HDS of thiophene, activity index per Co atom at different temperature were plotted as a function of noble metal loading as shown in figure 4.3.3, 4.3.4, and 4.3.5. From these figures it is noticed that at 250 °C maximum activity was obtained at 1 wt% noble metal loading after that activity was further decreased with increasing the noble metal loading. This behavior of noble metals is not well understood, at lower temperature the noble metals might be act as dehydrogenation/hydrogenation sites like Co rather than promoting hydrogen spillover so the activity was increased with the addition of noble metals. On the contrary further addition of noble metal beyond 1 wt% the activity was decreased rather increased, this is because of the deposition of the olefins on the catalyst surface formed by excessive dehydrogenation of thiophene by excess amount of noble metal. Another possible reason along with the previous is the blockage of the mouth of the pore structure by the excess metals consequently decreasing the activity.
Figure 4.3.1: Conversion of thiophene per atom-Co as a function of temperature on 2 wt % noble metal promoted Co/HPS catalysts and unpromoted Co/HPS catalyst.

Figure 4.3.2: Conversion of thiophene per atom-Co as a function of temperature on 1 wt% noble metal promoted Co/HPS catalysts and unpromoted Co/HPS catalyst.
Figure 4.3.3: Effect of Pt loading on the catalytic activities of Co-Pt/HPS in the HDS of thiophene.

Figure 4.3.4: Effect of Rh loading on the catalytic activities of Co-Rh/HPS in the HDS of thiophene.
Figure 4.3.5: Effect of Pd loading on the catalytic activities of Co-Pd/HPS in the HDS of thiophene.

At higher temperatures (275 and 300 °C) maximum activity was also observed at 1 wt% noble metal loading but unlike at 250 °C the activity was not decreased with increasing the metal loading as shown in the same figures 4.3.3, 4.3.4, and 4.3.5. With increasing the temperature the hydrogenation rate was also increased consequently the deposition of the olefin was decreased and catalyst retained its activity, furthermore some hydrogen spillover might be taken place at this temperature range, which prevented the deposition of reaction intermediates on the catalyst.

**Effect of bi-noble metals**

One of the main objectives of this study aimed at examining the potential of bi-noble metal promoted Co-Clay catalysts. Pt-Rh and Pd-Rh combinations were selected by
considering the activity and prices of these noble metals as discussed in the previous section. A-series and B-series catalysts represent the combinations of Pt-Rh and Pd-Rh respectively used as promoter.

For the respective series the Pt and Pd loading were kept constant (1 wt%) while the Rh loading was varied from 0.1–0.8 wt%. Table 4.3.2 represents the HDS activity data of both series of catalysts. Figure 4.3.6 shows the comparison of activity index per atom Co of A-series catalysts (Co-Pt-Rh/HPS) and reference catalyst as a function of temperature. This figure shows that the activity index of all Pt-Rh promoted catalysts was higher compared to the reference catalysts. In case B-series (Co-Pd-Rh/HPS) catalysts the activity index of Pd(1)-Rh(0.2) promoted catalyst was almost same while it was higher for the rest of the catalysts in this series compared to the reference catalyst as shown in figure 4.3.7.

Table 4.3.2 HDS activity of bi-noble metal promoted Co/HPS catalyst, evaluated in pulse reactor

<table>
<thead>
<tr>
<th>No</th>
<th>Catalysts</th>
<th>Noble metal loaded (wt%)</th>
<th>HDS activity (Conversion of thiophene at temp. °C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>01</td>
<td>Co/HPS ®</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td>Co-Pt-Rh/HPS (A4)</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>03</td>
<td>Co-Pt-Rh/HPS (A1)</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>04</td>
<td>Co-Pt-Rh/HPS (A2)</td>
<td>1.0</td>
<td>0.5</td>
</tr>
<tr>
<td>05</td>
<td>Co-Pt-Rh/HPS (A3)</td>
<td>1.0</td>
<td>0.8</td>
</tr>
<tr>
<td>06</td>
<td>Co-Pd-Rh/HPS (B1)</td>
<td>-</td>
<td>0.2</td>
</tr>
<tr>
<td>07</td>
<td>Co-Pd-Rh/HPS (B2)</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>08</td>
<td>Co-Pd-Rh/HPS (B3)</td>
<td>-</td>
<td>0.8</td>
</tr>
</tbody>
</table>
Figure 4.3.6: Conversion of thiophene per atom-Co as a function of temperature on Pt-Rh (Pt: 1 wt%) promoted Co/HPS and unpromoted Co/HPS.

Figure 4.3.7: Conversion of thiophene per atom-Co as a function of temperature on Pd-Rh (Pd: 1 wt%) promoted Co/HPS and unpromoted Co/HPS.
These results strongly agreed with the investigations by Song and coworkers [56] that the noble metals have higher HDS and cracking activities at lower temperature compared to the other transition metals.

Like before, the activity index per atom of Co was plotted as a function of Rh loading to show the effect of Rh loading at constant Pt and Pd loading for the respective catalysts, as shown in figure 4.3.8 and 4.3.9. It is interesting to see that a trace amount of Rh (0.1–0.2 wt%) can increase the activity of Co/HPS significantly. After that no considerable increment was observed by further addition of Rh, even the activity was little bit decreased at lower temperature (250 °C) with increasing the Rh loading beyond 0.2 wt% at constant Pt loading. This might be the same reason as it was discussed for single noble metal promoted catalysts. Where an excess amount can increase the dehydrogenation rate consequently increasing the deposition of unsaturated products on the catalysts at lower temperature on the other hand at higher temperature hydrogen spillover eliminated the deposition and retained its activity.

In summary of this section it can be concluded that noble metal can increase the HDS activity of Co/HPS but after certain degree of metal loading the activity was not further increased with increasing the noble metal loading. Rh promoted catalysts have shown higher activity than Pt and Pd promoted catalysts. For bi-noble metal promoted catalysts a small amount of Rh with 1 wt% Pt or Pd exhibits higher activity compare to the single noble metal promoted catalysts as well as the reference catalyst.
Figure 4.3.8: Effect of Rh loading on the catalytic activities of Co-Pt(1 wt%)-Rh/HPS in the HDS of thiophene.

Figure 4.3.9: Effect of Rh loading on the catalytic activities of Co-Pd(1 wt%)-Rh/HPS in the HDS of thiophene.
4.3.2 Cumene Cracking

The overall performance of a hydrocracking catalyst normally depends on the constructive combination of an acidic and a hydrogenation/dehydrogenation function. In such a bi-functional catalyst the acid function is usually a support material for example zeolite, silica-alumina or clay while the type and amount of the material (usually a transition metal) determine the hydrogenation/dehydrogenation function supported on the acidic surface. Thus an appropriate balancing of these functions plays an important role on the performance consequently the successes of the catalyst for the practical application.

In this work cumene cracking was conducted in pulse microreactor to get the information about the cracking activity of the noble metal promoted catalysts. Only two bi-noble metal promoted catalysts were chosen for cumene cracking test, the results are presented in Table 4.3.3. Cracking activity index per atom Co also plotted in figure 4.3.10. From the figure it is noticed that cumene-cracking activity index of the promoted catalyst was less than the reference catalyst. Ahmed and coworkers [18] investigated the effect of Co loading on Mo/Y-zeolite catalysts. They measured the total acidity by temperature programmed desorption (TPD) method and tested the cumene cracking activity by pulse reactor and found that both acidity and cumene cracking activity was decreased with increasing the Co loading. From their investigations and this present study it can be interpreted that noble metals (Pt-Rh) are interacting with the acid sites and blocking them so that the total acidity consequently the cumene cracking activity was decreased. However this requires further investigations in terms of metal-acid-sites interaction of the present catalysts.
Table 4.3.3 Cumene cracking activity of bi-noble metal promoted Co-Clay catalyst, evaluated in pulse reactor

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Noble metal loaded</th>
<th>Cumene cracking activity at temp. °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>Co/HPS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>1.0</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 4.3.10: Cumene cracking activity per atom Co as a function of temperature on Pt-Rh (Pt: 1 wt%) promoted Co/HPS catalysts and unpromoted Co/HPS catalyst.
4.4 Batch Evaluation

In this section batch reactor evaluation results of the promising catalysts are presented and discussed. Promising catalysts were selected from the temperature programmed reduction (TPR) measurements and the pulse reactor evaluation results. From the observation in two previous sections it is clear that a small amount of noble metal/metals on supported Co/HPS catalysts markedly influence the catalytic activity. The TPR study shown that the presence of noble metal/metals on Co/HPS strongly influences the reducibility of the catalysts, by shifting the TPR peak to lower temperature. The reduction temperature peak of both single and bi-noble metal promoted catalysts were observed between 530~615°C, while it was 746°C for unpromoted catalyst. Therefore the peak has been shifted to lower temperature by 150~200°C. Rh promoted catalysts have shown lowest temperature peak which was 532°C, while for 1 wt% Pt promoted catalysts it was 615°C. When 0.1~0.2 wt% Rh loaded with 1 wt% Pt the reduction peak temperature was 560°C. Thus a small amount of Rh with Pt could change comparable activity as 1 wt% Rh promoted catalysts. These results have been presented through figures 4.2.1-4.2.6 and discussed in detailed in section 4.2.

From pulse evaluation results it was observed that 1 wt% Rh promoted catalyst shown highest activity, on the other hand bi-noble metal promoted catalysts with 0.1~0.2 wt% Rh and 1 wt% Pt shown comparable HDS activity with the highest activity as 1 wt% Rh promoted catalyst.

So, from the TPR study and pulse evaluation results two bi-noble metal promoted catalysts were selected which are Co-Pt(1wt%)-Rh(0.1wt%)/HPS and Co-Pt(1wt%)-
Rh(0.2wt%)/HPS. These selected catalysts were evaluated in a batch autoclave reactor by using vacuum gas oil (VGO) as a feed.

For each catalyst three runs were carried out with different reaction time, i.e., 30 mins, 60 mins and 90 mins. For each run 100 gm of feed and 3 gm of sulfided catalysts was used. The reaction temperature was 400°C and the pressure were 140 kg/cm² (H₂). Experimental details and the operating conditions have been given in chapter 3. After completion of the reaction for specified time, gas and liquid product were collected. The gas product was analyzed by the gas chromatograph and the liquid product was analyzed for the composition of carbon, hydrogen, nitrogen and sulfur by CHNS analyzer and product distribution by simulated distillation, raw data and sample calculations are presented in the appendix.

Table 4.4.1 represents the activity data of Pt-Rh promoted Co-Clay and plain Co-Clay catalyst itself. From the above table it is noticed that in case of promoted catalysts the total amount of gas product was less than the unpromoted catalyst. One of the possible reasons of this less amount of gas product is due to higher hydrogenation activity of the noble metal promoted catalyst comparative to the unpromoted catalyst. Higher and sustained hydrogenation activity of the Pt-Rh promoted catalysts is further noticed from H/C ratio, as plotted in figure 4.4.1. This figure shows that in case of unpromoted catalyst the H/C ratio was increased from 30 mins to 60 mins after that it was sharply decreased with 90 mins reaction time. Therefore, it seems that with increasing the reaction time the dehydrogenation rate of the unpromoted catalyst was increased severely which produced large number of unsaturated reaction intermediates that deposited on the catalyst surface and decreased active surface for further reaction. On the other hand H/C ratio was incr-
Table 4.4.1 Batch reactor evaluation results using VGO feed, at 400°C reaction temperature and 140 kg/cm² pressure.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction time (min.)</th>
<th>Cracking (%)</th>
<th>Conversion in HDS (%)</th>
<th>H/C Ratio</th>
<th>Total gas products</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/HPS</td>
<td>30</td>
<td>12.22</td>
<td>49.00</td>
<td>1.735</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>14.10</td>
<td>51.00</td>
<td>1.740</td>
<td>2.50</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>15.00</td>
<td>58.60</td>
<td>1.712</td>
<td>2.28</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>11.50</td>
<td>40.00</td>
<td>1.697</td>
<td>0.36</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>16.45</td>
<td>57.30</td>
<td>1.721</td>
<td>1.60</td>
</tr>
<tr>
<td>0.1wt%Rh</td>
<td>90</td>
<td>25.00</td>
<td>69.60</td>
<td>1.733</td>
<td>1.51</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>11.50</td>
<td>51.40</td>
<td>1.704</td>
<td>1.01</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>15.10</td>
<td>59.30</td>
<td>1.711</td>
<td>1.13</td>
</tr>
<tr>
<td>0.2wt%Rh</td>
<td>90</td>
<td>24.50</td>
<td>62.30</td>
<td>1.722</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Figure 4.4.1: H/C ratio in the product as a function of reaction time in batch autoclave reactor.
 eased with increasing the reaction time for the promoted catalysts. Thus the hydrogenation activity of the promoted catalysts was sustained with increasing the reaction time. For the purpose of comparison, hydrocracking activity index per atom Co was plotted in figure 4.4.2 by bar graphs. It is noticed that the conversion (per atom Co) with unpromoted catalyst after 30 mins run was little bit higher than the promoted catalysts. But the picture was totally different after 60 and 90 mins run. This time no further significant increment of activity index per atom Co was observed with unpromoted catalyst, while with promoted catalysts activity index per atom Co was increased significantly. To show the trends of the hydrocracking activity with batch reactor results are also plotted against time in a same graph paper as shown in figure 4.4.3. From figure it can easily observed that in case of the promoted catalysts the activity index per atom Co was sharply increased with increasing the reaction time. On the other hand with unpromoted catalyst it was not significantly increased with the increase of reaction time. Among the two bi-noble promoted catalysts 0.1 wt% Rh promoted catalyst has shown little bit higher activity than 0.2 wt% Rh promoted catalyst (for both cases Pt loading was 1 wt%).

The HDS activity data in batch reactor was calculated from CHNS analysis results (sample calculation shown in the appendix) also presented in table 4.4.1. Figure 4.4.4 shows the HDS activity index per atom Co by bar representation for all catalysts. After 30 mins reaction time HDS activity index per atom Co of unpromoted catalyst was more or less same as Pt(1wt%)-Rh(0.2wt%) promoted catalyst but it was higher than Pt(1wt%)-Rh(0.2wt%) promoted catalyst. Like cracking activity both noble metals promoted catalysts have shown higher HDS activity than the unpromoted catalyst after
Figure 4.4.2: Hydrocracking (VGO) activity per atom Co of Pt-Rh promoted Co/HPS and unpromoted Co/HPS catalyst in batch autoclave reactor.

Figure 4.4.3: Hydrocracking (VGO) activity per atom Co as a function of reaction time in batch autoclave reactor for Pt-Rh promoted Co/HPS and unpromoted Co/HPS catalyst.
Figure 4.4.4: Hydrodesulfurization (HDS of VGO) activity per atom Co of Pt-Rh promoted Co/HPS and unpromoted Co/HPS catalyst in batch autoclave reactor.

60 mins in reaction compared to the reference catalyst. After 90 in reaction the HDS activity of 0.1 wt% Rh promoted catalyst shown highest activity but unlike cracking activity the HDS activity of 0.2 wt% Rh promoted catalyst did not show significant higher activity than the reference catalyst. For clear distinction of HDS activity index per atom Co of all catalysts the results are also plotted in a same graph paper as function of time, as shown in figure 4.4.5. The tendency of 0.1 wt% Rh promoted catalyst was increasing but this time the activity of 0.2 wt% Rh promoted catalyst was unexpectedly not increased.

From last two paragraphs it can be concluded that the unpromoted Co/HPS catalyst was deactivated within the first 30~45 mins in reaction while Pt-Rh promoted catalysts have shown a high and sustained activity. These results are well correlated to
Figure 4.4.5: Hydrodesulfurization (HDS of VGO) activity per atom Co as a function of reaction time in batch autoclave reactor for Pt-Rh promoted Co/HPS and unpromoted Co/HPS catalyst.

the TPR measurement results, where hydrogen spillover was demonstrated by lowering the reduction temperature by the noble metals. This high and sustained activity was attributed to an enhanced acidity due to hydrogen spillover from noble metal to the acidic sites. This phenomenon can be explained reasonably by acidic function of spillover hydrogen. It have been suggested that hydrogen spillover can give rise to protons, which can spillover to give rise to Brønsted acid sites on the supported metal oxides [7,52,53]. Thus it is quit logical to interpret for the present work that H₂ from gas phase at first activated on noble metal, dissociate on it and spillover to the support surface and create active sites or reacts with coke that was generated by cracking reaction and removed it. Hence the catalyst remained active. The phenomenon of coke removal by hydrogen
spillover will be further clarified in the next section by the elemental analysis of spent catalysts.

When a noble metal/metals used as an active component or promoter in a catalyst the sulfur poisoning question frequently arises. On the other hand recent studies have shown that the addition of another suitable transition metal with the noble metal or a proper combination of two noble metals can improved the resistance of the noble metal. Another possible way of increasing the sulfur tolerance of noble metals is attributed to the electron deficiency of noble metals when supported on an acidic surface. The term electron deficiency refers to the electron transfer from the noble metal to the acidic support [56]. It has considered that the closed contact between the acid site and the noble metal atom makes it possible to withdrawn from the noble metal, thus creating an electron deficient metal particle. It has been suggested that the resistance to sulfur poisoning arises from the smaller bonding energy of the electron acceptor sulfur atoms with the electron deficient noble metal species [56]. During this study no sulfur poisoning was observed in the batch autoclave evaluation of the noble metal promoted catalysts. Addition to the published data described above, the sulfur tolerance on the noble metal catalysts can be explained by the spillover view point, if the catalyst configuration can be prepared to enhance hydrogen diffusion, sulfur might preferentially be removed by vigorous hydrogen transfer, consequently sulfur poisoning rather prevented.

Reproducibility run was carried out for Co-Pt(1)-Rh(0.2)/HPS catalyst in the batch autoclave reactor for 30, 60 and 90 mins reaction time. Hydrocracking activity index per atom Co for two different runs is presented in same figure 4.4.6 by bar graphs. The results were reproducible within an accuracy of 6.0% for 30 mins reaction time.
Figure 4.4.6: Hydrocracking of VGO over Co-Pt(1)-Rh(0.2)/HPS catalyst in batch autoclave reactor for two different runs.

0.67% for 60 min reaction time and 3.0% for 90 min reaction time. This result proves the reproducible activity of the bi-noble metal promoted Co/HPS catalysts.

4.5 Spent Catalyst Analysis

It has been believed that the deactivation of acidic catalysts are mainly due to the formation of carbonaceous products, which formed during the acid catalyzed transformation of heavy constituents of heavy oils. However, the poisoning effect also cannot be excluded for deactivation but its contribution far smaller compared to the coke deposition.

Elemental analysis of spent catalysts is a useful and one of the simplest methods to calculate the amount of coke deposition on the catalysts during reaction. In this study
the increased and sustained activity of noble metal promoted Co/HPS catalysts for the hydrocracking of heavy oils was possibly be attributed to the effect of hydrogen spillover on suppressing the coke deposition on the catalyst surface. For further verification the spent catalysts from batch autoclave reactor after different time exposed to the reaction was analyzed CHNS analyzer, and the results are reported in table 4.5.1. Carbon deposition on commercial catalyst (Co-Mo/Al₂O₃) for same reaction conditions obtained from KFUPM-RI are also presented in the same table for the purpose of comparison.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Time (Min)</th>
<th>Wt. % of Carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Commercial</td>
<td>30</td>
<td>2.8</td>
</tr>
<tr>
<td>Co-Mo/Al₂O₃</td>
<td>60</td>
<td>2.6</td>
</tr>
<tr>
<td>Co/HPS</td>
<td>30</td>
<td>6.5</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>6.2</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>5.4</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>4.9</td>
</tr>
<tr>
<td>0.1wt%Rh</td>
<td>90</td>
<td>4.9</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>5.4</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>5.0</td>
</tr>
<tr>
<td>0.2wt%Rh</td>
<td>90</td>
<td>4.7</td>
</tr>
</tbody>
</table>
Figure 4.5.1: Weight percent of carbon deposited on different catalysts from batch reactor.

Figure 4.5.2: Weight percent of carbon deposited on different catalysts for different time reaction in batch reactor.
After 30 mins reaction amount of coke deposition on the Pt-Rh promoted Co/HPS was substantially less (17 %) than the unpromoted Co/HPS, as shown in figure 4.5.1 by bar graphs but still it higher than the commercial catalyst. After 60 mins and 90 mins in reaction the coke deposition on both promoted and unpromoted catalysts were slightly decreased. Figure 4.5.2 plotted the weight percent of carbon deposition on the spent catalysts as a function of time in reaction. From figure it is noticed that the tendency of coke deposition was decreasing with increasing the reaction time for all catalysts. This less amount of coke deposition of the noble metal promoted Co/HPS can be explained reasonably by the hydrogen spillover effect. Hydrogen in the gas phase chemisorbed and dissociate on noble metal (for this study bi-noble metals i.e, Pt-Rh) sites to produce reactive hydrogen species [55]. The reactive hydrogen species spillover from Pt-Rh sites to the hydrogenation sites as well as to the support surface and react with the reaction intermediates from acidic sites (which are deposited on the active sites as coke), hence the surface remain clean and active. Hosoi and coworkers found that when Pt promoted ZrO₂ catalyst exposed for skeletal isomerization of n-pentane in hydrogen environment, it showed both high and persistence activity for a long period, more than 1000 hours. They explained that the hydrogen had the effect on the removal of coke formed during the reaction by hydrogenating [57]. Another explanation can be noted by using the term remote control, where hydrogen generated on Pt/Rh spilt over to the acidic surface and influenced reaction (remote control) by controlling the concentration of the reaction intermediates carbonium ions, finally prevent the deposition by hydrogenating them.

Reproducibility data for carbon deposition on the spent catalysts for two different
Figure 4.5.3: Carbon deposition of spent catalyst (Co-Pt(1)-Rh(0.2)/HPS) for different runs are presented in figure 4.5.3. The results were reproducible within an accuracy of 7%.
Chapter 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

From this study the following conclusions are drawn:

1. The maximum amount of Co loading on the noble metal promoted catalysts by ion-exchange with the high porous saponite (HPS) was only 18.5 wt%, and cobalt loading was slightly decreased with increasing the noble metal loading.

2. The addition of small amount of noble metal/metal (Pt, Pd and Rh) significantly increases the reducibility of cobalt oxide supported on clay surface, which is indicated by shifting the TPR peak to the lower temperature.

3. The higher the amount of noble metal the lower the reduction temperature observed, but this is true up to a certain mount of noble metal loading after that no significant shifting was not noticed, specially for Rh promoted catalysts. The TPR peak temperature of 1 wt% and 2 wt% Rh promoted was almost identical.
4. Among the noble metals used as a promoter Rh has shown superior activity for hydrogen spillover compared to Pt and Pd. The order of activity is Rh>Pt>Pd.

5. Combination of two noble metals (Pt-Rh and Pd-Rh) can minimize the use of more precious metal Rh without losing promotional effect.

6. Pt-Rh combination is more active than Pd-Rh to promote the reduction of Co/HPS.

7. In pulse microreactor 2 wt% Pt promoted Co/HPS catalyst has shown less HDS activity compared to the unpromoted Co/HPS while Rh promoted Co/HPS have shown almost same HDS activity as Co/HPS. Reducing the noble metal loading has increased these activities. 1 wt% Rh loaded Co/HPS has shown significantly higher HDS activity but 1 wt% Pt/Pd promoted Co/HPS have shown slightly higher activity than the unpromoted catalyst. Thus the HDS activity has been affected by the excess amount of noble metal loading.

8. Rh promoted Co/HPS catalysts have shown higher HDS activity compared to the Pt and Pd promoted Co/HPS catalysts.

9. All bi-noble promoted catalysts have shown higher HDS activity compared to the unpromoted Co/HPS catalyst but the Pt-Rh combination displayed significantly higher activity than the Pd-Rh combination.
10. Among Pt-Rh promoted Co/HPS catalyst 0.1 wt% Rh (1 wt% Pt) promoted catalyst has shown highest activity.

11. For cumene cracking in pulse microreactor the activity of Pt-Rh promoted catalysts have been shown less compared to the reference catalyst (Co/HPS). Higher the amount of Rh (at constant amount of Pt, 1 wt%) lower the cumene cracking. Thus with the addition of Rh to Co/HPS the acidity of the catalyst has been decreased consequently the cracking activity decreased.

12. Hydrogen spillover effect has been clearly observed when the Pt-Rh promoted Co/HPS catalysts were exposed for the cracking of the practical feed (VGO) in a batch autoclave reactor. The cracking activity of the promoted catalysts increased with the increase of the reaction time, however the initial activity of the promoted catalysts was slightly less than the unpromoted Co/HPS catalyst. On the contrary the activity of unpromoted catalyst was not increased further with the increases of the reaction.

13. Hydrogen spillover effect on Co/HPS further reconfirmed by spent catalyst analysis, which shows the amount of carbon deposition on the promoted catalysts has been found less than the unpromoted Co/HPS after exposing same reaction time.
5.2 Recommendations

After conducting detail experimental investigations of the hydrogen spillover effect on Co-Clay hydrotreating catalysts the following recommendations for future research are presented

1. Morphological characterizations like transmission electron microscopy (TEM) and x-ray photoelectron spectra (XPS) can be conducted by to observe the noble metal and cobalt ionic state and dispersion of the same on the support.

2. Different techniques can be adapted for catalyst preparation.

3. For Pt and Rh metal loading other than chloride salts can be used during catalyst preparation because Cl$_2$ also can be spilt over and may compete with hydrogen, hence can reduce effective hydrogen spillover. Nitrate salts of the respective metals can be used for this purpose.

4. In this study batch autoclave reactor was employed for catalysts evaluation due to its simplicity and short time required conducting the experiments. A microflow reactor can be used for further studies. Such a reactor will enable a steady state operation and catalyst deactivation and studies for long time.
APPENDICES
[A] TPR MEASUREMENT

\[
\begin{align*}
(1) \ \text{DATA NAME} & \quad = 200212 \\
(2) \ \text{INITIAL TEMP (°C)} & \quad = 30 \\
(3) \ \text{INITIAL TEMP HOLDING TIME (min)} & \quad = 1 \\
(4) \ \text{TIME BY TARGET TEMP (min)} & \quad = 100 \\
(5) \ \text{FINAL TEMP (°C)} & \quad = 1030 \\
(6) \ \text{FINAL TEMP HOLDING TIME (min)} & \quad = 10 \\
(7) \ \text{CALIBRATION} & \quad = \text{-----} \\
\hspace{1cm} \text{(COUNT)} & \quad = 1 \\
(8) \ \text{SAMPLE WEIGHT (g)} & \quad = 1 \\
(9) \ \text{MEMO} & \quad = HS \\
(10) \ \text{X-AXIS (TIME: '0' / TEMP: '1')} & \quad = 1
\end{align*}
\]

\[
\text{NO= 1 PEAK= 226°C AREA= 12043 %12042.60 \mu mol} \\
\text{NO= 2 PEAK= 615°C AREA= 104967 %104967.00 \mu mol} \\
\text{NO= 3 PEAK= 854°C AREA= 3876 3876.09 \mu mol}
\]

Figure A-1: Sample TPR spectra.
[B] CALCULATION OF ACTIVITIES IN PULSE REACTOR

B.1 Sample calculation for hydrodesulfurization (HDS) activity of thiophene

\[
\% \text{ conversion} = \frac{A_{GC} - A_{Reactor}}{A_{GC}} \times 100 \quad \ldots \quad \text{(B.1a)}
\]

Where,

\(A_{GC}\) = Area under the peak when thiophene was injected into GC

\(A_{Reactor}\) = Area under the peak when thiophene was injected in the reactor

For example, from figure B-1, at temperature 300 °C

\(A_{GC} = 1697883\)

\(A_{Reactor} = 33241\)

Substituting into equation (B.1a)

\[
\% \text{ conversion} = \frac{1697883 - 33241}{1697883} \times 100
\]

\[= 80.4\]

Activity index per atom - Co = \[
\frac{x}{\text{atom - Co}} = \frac{100 \times x \times MW_{CoO}}{M \times MW_{CoO} \times N} \quad \ldots \quad \text{(B.1b)}
\]

Where \(x\) = Conversion

\(M\) = Weight of catalyst loaded into the reactor

(For HDS of thiophene 0.05 gm, for cumene cracking 0.02 gm and for hydrocracking of VGO in batch autoclave reactor 3.00 gm catalysts was used)

\(W_{CoO}\) = Weight percent of CoO on the catalyst

\(MW_{CoO}\) = Molecular weight of CoO
\[ N = \text{Avogadros number} \]
\[ = 6.023 \times 10^{23} \text{ mole}^{-1} \]

For conversion, \( x = 0.804 \)

\[ M = 0.05 \text{ gm (for HDS of thiophene 0.05 gm catalyst was loaded into the reactor for reaction)} \]

\[ W_{CoO} = 18.3 \% \text{ (for 1 wt\% Pd promoted catalyst)} \]

Substituting these values into equation (B.1b)

\[ \text{Activity index per atom} - Co = \frac{100 \times 0.804 \times 74.93}{0.05 \times 18.3 \times 6.023 \times 10^{23}} \]
\[ = 1.13 \times 10^{-20} \]

**Table B-1** HDS activity index per atom-Co of single noble metal promoted Co-Clay catalyst, evaluated in pulse reactor.

<table>
<thead>
<tr>
<th>No</th>
<th>Catalysts</th>
<th>Noble metal loaded (wt%)</th>
<th>HDS activity index per atom-Co at different temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>01</td>
<td>Co/HPS ®</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>02</td>
<td>Co-Pt/HPS (H1)</td>
<td>2.0</td>
<td>-</td>
</tr>
<tr>
<td>03</td>
<td>Co-Rh/HPS (H2)</td>
<td>-</td>
<td>2.0</td>
</tr>
<tr>
<td>04</td>
<td>Co-Pd/HPS (H3)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>05</td>
<td>Co-Pt/HPS (H5)</td>
<td>1.0</td>
<td>-</td>
</tr>
<tr>
<td>06</td>
<td>Co-Rh/HPS (H4)</td>
<td>-</td>
<td>1.0</td>
</tr>
<tr>
<td>07</td>
<td>Co-Pd/HPS (H6)</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
### Figure B-1: Sample chromatogram for products of hydrodesulfurization (HDS) of thiophene in pulse reactor.

<table>
<thead>
<tr>
<th>PKNO</th>
<th>TIME</th>
<th>AREA</th>
<th>MK</th>
<th>IDNO</th>
<th>CONC</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.672</td>
<td>169783</td>
<td></td>
<td>100</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TOTAL** 169783 100

START

0.832

2.027

5.5

---

CHROMATOPAC C-R6A

FILE 0

SAMPLE NO 0

METHOD 41

REPORT NO 2112

<table>
<thead>
<tr>
<th>PKNO</th>
<th>TIME</th>
<th>AREA</th>
<th>MK</th>
<th>IDNO</th>
<th>CONC</th>
<th>NAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.832</td>
<td>195</td>
<td></td>
<td>0.1095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>2.027</td>
<td>114</td>
<td></td>
<td>0.1095</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2.49</td>
<td>113</td>
<td></td>
<td>0.1091</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>2.628</td>
<td></td>
<td></td>
<td>2.628</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2.395</td>
<td></td>
<td></td>
<td>46.7083</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>3.342</td>
<td></td>
<td></td>
<td>3.9554</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>3.0773</td>
<td></td>
<td></td>
<td>3.0773</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5.9003</td>
<td></td>
<td></td>
<td>5.9003</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1.6603</td>
<td></td>
<td></td>
<td>1.6603</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.3494</td>
<td></td>
<td></td>
<td>0.3494</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>1.3863</td>
<td></td>
<td></td>
<td>1.3863</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.6387</td>
<td></td>
<td></td>
<td>0.6387</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.5733</td>
<td></td>
<td></td>
<td>0.5733</td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.2927</td>
<td></td>
<td></td>
<td>0.2927</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>31.9343</td>
<td></td>
<td></td>
<td>31.9343</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**TOTAL** 164032 100
B.2 Sample calculation for cumene cracking activity

\[
\% \ \text{conversion} = \frac{0.52}{A_{GC}} \times A_{\text{Reactor}} \times 100 \quad \text{(B.2)}
\]

Where,

- \( A_{GC} \) = Average area under the peak when benzene injected into the GC
- \( A_{\text{Reactor}} \) = Area under the peak of benzene when cumene injected into the reactor

From figure (B-2), at temperature 250 °C

\[
A_{GC} = 47460, \quad A_{\text{Reactor}} = 20747
\]

Therefore,

\[
\% \ \text{conversion} = \frac{0.52}{47460} \times 20747 \times 100
\]

= 22.73

From equation (B.1b)

\[
\text{Activity index per atom} - Co = \frac{100 \times 0.2273 \times 74.93}{0.02 \times 18.5 \times 6.023 \times 10^{23}} = 7.64 \times 10^{-21}
\]

Table B-2 Cumene cracking activity index per atom-Co of bi-noble metal promoted Co-Clay catalyst, evaluated in pulse reactor.

<table>
<thead>
<tr>
<th>Name of the catalysts</th>
<th>Noble metal loaded</th>
<th>Cumene cracking activity index per atom-Co at different temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Rh</td>
</tr>
<tr>
<td>Co/HPS</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>1.0</td>
<td>0.1</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>1.0</td>
<td>0.2</td>
</tr>
<tr>
<td>PKNO</td>
<td>TIME</td>
<td>AREA</td>
</tr>
<tr>
<td>------</td>
<td>-------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>3.257</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>3.725</td>
<td>7641</td>
</tr>
<tr>
<td>3</td>
<td>4.62</td>
<td>188</td>
</tr>
<tr>
<td>4</td>
<td>4.682</td>
<td>147</td>
</tr>
<tr>
<td>5</td>
<td>4.747</td>
<td>133</td>
</tr>
<tr>
<td>6</td>
<td>4.897</td>
<td>129</td>
</tr>
<tr>
<td>7</td>
<td>4.865</td>
<td>108</td>
</tr>
<tr>
<td>8</td>
<td>5.927</td>
<td>20747</td>
</tr>
<tr>
<td>9</td>
<td>9.24</td>
<td>151</td>
</tr>
<tr>
<td>10</td>
<td>10.862</td>
<td>104197</td>
</tr>
<tr>
<td></td>
<td>TOTAL</td>
<td>133555</td>
</tr>
</tbody>
</table>

Figure B-2: Sample chromatogram for products of cumene cracking in pulse reactor.
[C] CALCULATION OF ACTIVITIES IN BATCH REACTOR

C.1 Sample calculation for H/C ratio of the liquid product using vacuum gas oil (VGO) as feed

\[ \frac{H}{C} = \frac{\text{Wt. of hydrogen in liquid product}}{\text{Wt. % of carbon in liquid product}} \times 12 \]

From table C.2 (Catalyst: Co-Pt(1)-Rh(0.1)/HPS, Feed: VGO, 90 min. reaction time)

\[ \frac{H}{C} = \frac{12.47}{86.38} \times 12 = 1.7323 \]

C.2 Sample calculation for hydrocracking activity using vacuum gas oil (VGO) as feed

Hydrocracking activity of catalysts was obtained from the boiling point distribution of the liquid product by simulated distillation (SIMDIST). Table C.1 shows a sample fractional distribution of boiling points of simulated distribution products. The calculation was done on the basis of the boiling point of diesel (343 °C) cut. At 343 °C temperature the weight percent of diesel was zero for the feed (VGO), so at the same temperature weight percent of diesel cut has been taken the conversion in the batch autoclave reactor.

For example, from table C.1 at 343 °C weight percent of the product is 25

So, % conversion = 25
From equation (B.1b), \[ Activity\ index\ per\ atom\ Co = \frac{100 \times 0.25 \times 74.93}{3.0 \times 18.4 \times 6.023 \times 10^{21}} \]
\[ = 5.635 \times 10^{-21} \]

**Table C-1** Boiling point distribution of products from batch autoclave reactor

Catalyst: Co-Pt(1)-Rh(0.1)/HPS (3 gm sulfided catalysts) 
Feed: VGO

Sample: Liquid product from batch autoclave reactor

<table>
<thead>
<tr>
<th>% OFF</th>
<th>DEG. C</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>43</td>
</tr>
<tr>
<td>1</td>
<td>84</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
</tr>
<tr>
<td>3</td>
<td>114</td>
</tr>
<tr>
<td>4</td>
<td>116</td>
</tr>
<tr>
<td>5</td>
<td>121</td>
</tr>
<tr>
<td>6</td>
<td>139</td>
</tr>
<tr>
<td>7</td>
<td>158</td>
</tr>
<tr>
<td>8</td>
<td>174</td>
</tr>
<tr>
<td>9</td>
<td>190</td>
</tr>
<tr>
<td>10</td>
<td>203</td>
</tr>
<tr>
<td>11</td>
<td>214</td>
</tr>
<tr>
<td>12</td>
<td>226</td>
</tr>
<tr>
<td>13</td>
<td>237</td>
</tr>
<tr>
<td>14</td>
<td>249</td>
</tr>
<tr>
<td>15</td>
<td>259</td>
</tr>
<tr>
<td>16</td>
<td>270</td>
</tr>
<tr>
<td>17</td>
<td>279</td>
</tr>
<tr>
<td>18</td>
<td>287</td>
</tr>
<tr>
<td>19</td>
<td>298</td>
</tr>
<tr>
<td>20</td>
<td>307</td>
</tr>
<tr>
<td>21</td>
<td>315</td>
</tr>
<tr>
<td>22</td>
<td>323</td>
</tr>
<tr>
<td>23</td>
<td>331</td>
</tr>
<tr>
<td>24</td>
<td>338</td>
</tr>
<tr>
<td>25</td>
<td>345</td>
</tr>
<tr>
<td>26</td>
<td>351</td>
</tr>
<tr>
<td>27</td>
<td>357</td>
</tr>
<tr>
<td>28</td>
<td>363</td>
</tr>
</tbody>
</table>
Table C-2 CHNS results of the liquid products from batch autoclave reactor

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Reaction time</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(min.)</td>
<td>N</td>
</tr>
<tr>
<td>Co/HPS</td>
<td>30</td>
<td>0.095</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.092</td>
</tr>
<tr>
<td>Co-Pt(1)-Rh(0.1)/HPS</td>
<td>30</td>
<td>0.081</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.070</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.081</td>
</tr>
<tr>
<td>Co-Pt(1)-Rh(0.2)/HPS</td>
<td>30</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.094</td>
</tr>
</tbody>
</table>

C.3 Sample calculation for hydodesulfurization (HDS) activity using vacuum gas oil (VGO) as feed

Hydodesulfurization (HDS) activity of catalysts in batch autoclave reactor was calculated form the CHNSH results as shown in table C-2. The calculation was as follows

\[
\% \text{ conversion} = \frac{\text{Wt.} \% \text{ of sulfur in the liquid product}}{\text{Wt.} \% \text{ of sulfur in the feed}} \times 100 \quad \text{(C.3)}
\]

For example,

From table 1.1.1 (page 2) the weight percent of sulfur in the feed (VGO) = 2.66

From table C-2 the weight percent of sulfur in the product (Catalyst: Co-Pt(1)-Rh(0.1)/HPS, Feed: VGO, 90 min. reaction time) = 0.809

Substituting into equation (C.3)
\[ \% \text{ conversion} = \frac{2.66 - 0.808}{2.66} \times 100 \]

= 69.5

From equation (B.1b),

\[
\text{Activity index per atom - Co} = \frac{100 \times 0.695 \times 74.93}{3.0 \times 18.4 \times 6.023 \times 10^{23}}
\]

= $1.5663 \times 10^{-22}$

**Table C-3** Activity indexes per atom-Co for batch autoclave reactor.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction Time (Min)</th>
<th>Hydrocracking activity index per atom-Co</th>
<th>HDS activity index per atom-Co</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co/HPS</td>
<td>30</td>
<td>2.73480E-23</td>
<td>1.09840E-22</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.16073E-23</td>
<td>1.14324E-22</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>3.36247E-23</td>
<td>1.31361E-22</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>2.59190E-23</td>
<td>9.01530E-23</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>3.70755E-23</td>
<td>1.29145E-22</td>
</tr>
<tr>
<td>0.1wt%Rh</td>
<td>90</td>
<td>5.63458E-23</td>
<td>1.56867E-22</td>
</tr>
<tr>
<td>Co-Pt-Rh/HPS</td>
<td>30</td>
<td>2.74090E-23</td>
<td>1.22500E-22</td>
</tr>
<tr>
<td>1wt%Pt</td>
<td>60</td>
<td>3.59888E-23</td>
<td>1.41333E-22</td>
</tr>
<tr>
<td>0.2wt%Rh</td>
<td>90</td>
<td>5.83924E-23</td>
<td>1.48484E-22</td>
</tr>
</tbody>
</table>
LITERATURE CITED


VITA

Mohammad Mozahar Hossain.

Born in Baradad Pur, Bangladesh on the 21\textsuperscript{th} of April, 1971

Received Bachelor’s Degree in Chemical Engineering from Bangladesh University of Engineering & Technology (BUET), Dhaka in July, 1996.

Completed Master’s Degree in Chemical Engineering from King Fahd University of Petroleum & Minerals, Dhahran, Saudi Arabia in April, 1998.