

UNIVERSITY OF CALGARY

Selective Steam Dealkylation of Alkyl aromatic hydrocarbons

by

Abdellatif Abdalla Mohamed Eldood

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

CALGARY, ALBERTA

January, 2008

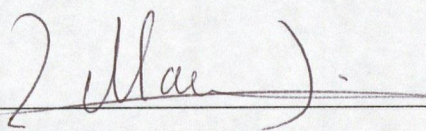
© Abdellatif A. M. Eldood 2008

UNIVERSITY OF CALGARY
FACULTY OF GRADUATE STUDIES


The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Selective Steam Dealkylation of Alkyl aromatic hydrocarbons" submitted by Abdellatif Abdalla Mohamed Eldood in partial fulfilment of the requirements of the degree of Masters of Science.



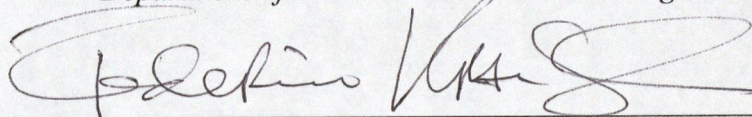
Supervisor, Dr. Pedro Pereira Almas
Department of Chemical and Petroleum Engineering



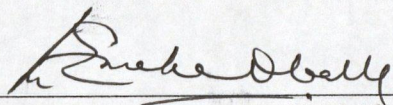
Dr. Maen Husein
Department of Chemical and Petroleum Engineering



Dr. Alex DeVisscher
Department of Chemical and Petroleum Engineering



Dr. Federico Krause
Department of Geoscience



Dr. Mike Oballa
Nova Chemicals

January 18, 2008

Date

Abstract

Existing technologies produce benzene from toluene by consuming hydrogen and using severe reaction conditions. In this work, studies were carried out by performing dealkylation of toluene using water instead of hydrogen in a fixed bed reactor at mild reaction conditions to form benzene, and gaseous by-product containing hydrogen, methane, carbon monoxide and carbon dioxide.

The targeted oil fractions contain impurities such as sulphur, and coke promoters which cause fast deactivation of the catalyst. In this study, rhodium/alumina catalysts reported as the most active catalysts in the literature, were prepared with alumina coated alkali-alkali earth metal. Alkali species are interpreted to interact with the support and the active metal preventing the catalyst from coke deactivation and sulphur poisoning.

The coated catalysts showed an increase in benzene selectivity and improved resistance for coke formation compared to the non-coated catalysts. The steam dealkylation may represent an alternative technology for obtaining benzene from oil fractions rich in alkylaromatic compounds with potential application in petrochemical industry.

Acknowledgements

I would like to thank Dr. Pedro Pereira-Almao for his guidance, support and for the opportunity to work in his research group. Without his patience and encouragement, this research would not have been completed. I really learnt a lot from his exceptional knowledge and rich experience.

Thank you to all members of the Catalysis for Upgrading and Hydrogen Production group for the wonderful and fantastic working environment. I have been really fortunate to closely work with them. My special thanks to Clementina Sosa, Dr. Francisco Lopez, Enzo Peluso and Dr. Azfar Hassan for helping me on different stages of my research.

I am also thankful to the department of Chemical and Petroleum Engineering and NOVA Chemicals for their financial support.

Finally I am grateful to my wife, Petra, for her love, constant support and patience. I can not be thankful enough for my sons Kamal, Yousof, and Amir for all the joy they bring to my life, for the good times and for their pure love.

Dedication.

To my parents, my wife and my sons with love and gratitude

Table of Contents

Approval Page.....	ii
Abstract.....	iii
Acknowledgements.....	iv
Dedication.....	v
Table of Contents.....	vi
List of Tables	ix
List of Figures and Illustrations	xi
List of Symbols, Abbreviations and Nomenclature.....	xiii
 CHAPTER ONE: INTRODUCTION.....	 1
1.1 Background.....	1
1.2 Benzene.....	2
1.3 Hydrogen	2
1.4 Motivation.....	3
1.5 Objectives	4
1.6 Organization of Thesis.....	5
 CHAPTER TWO: LITERATURE REVIEW.....	 6
2.1 Sources of Aromatic hydrocarbons.....	6
2.2 Hydrodealkylation, HDA.....	6
2.3 Steam dealkylation.....	7
2.4 Reactions.....	7
2.5 Mechanism.....	9
2.6 Thermodynamics	10
2.7 Role of reaction conditions	10
2.7.1 Pressure.....	11
2.7.2 Water to Hydrocarbon ratio.....	11
2.8 Activity of alumina-supported catalysts	11
2.9 Selectivity to Benzene	12
2.10 Role of the support in steam dealkylation reaction.....	13
2.11 Steam reforming of other aromatics	13
2.11.1 Alkylbenzenes	13
2.11.2 Condensed hydrocarbons.....	15
2.12 Role of promoters	15
2.13 Possible feedstocks	17
2.13.1 Heavier feedstocks.....	17
2.14 Aquaconversion™	18
 CHAPTER THREE: EXPERIMENTAL.....	 19
3.1 Materials and Equipment.....	19
3.1.1 Materials.....	19
3.1.2 Equipment.....	20
3.2 Catalyst Preparation Procedure.....	20
3.2.1 Support pre-treatment.....	20

3.2.2 Incipient wet impregnation for Rh catalyst	20
3.2.3 Sequential wet impregnation (coating with K and Ca oxides)	21
3.3 Reactivity Measurements	22
3.3.1 Catalyst reduction	22
3.3.2 Catalyst evaluation procedure	22
3.3.3 Experimental setup	24
3.3.4 Experimental conditions	25
3.4 Catalyst and Products Characterization	26
3.4.1 Brunauer–Emmett–Teller (BET) Surface Area Measurement	26
3.4.2 Temperature Programmed Reduction (TPR)	28
3.4.3 Products analysis	29
CHAPTER FOUR: RESULTS AND DISCUSSION	31
4.1 Catalyst Characterization	31
4.1.1 TPR and H ₂ titration	31
4.1.2 BET results	33
4.2 Reactivity tests	34
4.2.1 The 0.6 % Rh Catalysts for Toluene Steam Dealkylation	35
4.2.2 The effect of rhodium loading	39
4.2.3 Effect of the catalyst metal dilution	49
4.2.4 Gas composition	51
4.2.5 Effect of the feed dilution	53
4.3 Influence of time on stream on catalyst deactivation	55
4.4 Other model molecules: Xylene and Ethylbenzene	57
4.5 Using Naphthalene – Toluene mixture, on Rh-4 and Rh-5	59
4.6 Preliminaries of a process for steam dealkylation of pyrolysis gasoline based on the catalyst developed up to now	63
4.6.1 Pyrolysis gasoline	63
4.6.2 Proposed SDA process flow sheet	64
4.6.3 Effect of space velocity on benzene production	66
4.6.4 Mass balance and process description	67
CHAPTER FIVE: CONCLUSIONS AND RECOMMENDATIONS	73
5.1 Conclusions	73
5.2 Recommendations	74
REFERENCES	75
CHAPTER SIX: APPENDIXES	80
6.1 Appendix A	80
6.2 APPENDIX B	81
6.2.1 Calculations	81
6.2.1.1 Mass Balance	81
6.2.1.2 Gases	82
6.2.1.3 Liquids:	83
6.2.1.4 Global mass balance	84

6.2.2 Mass balance correction	84
6.2.2.1 Oxygen balance:	84
6.2.2.2 Difference in oxygen balance	85
6.2.2.3 Reaction rate	87
6.2.2.4 Activation energy:.....	87

List of Tables

Table 2.1: Enthalpy values of some of the reactions involved in toluene steam dealkylation.....	10
Table 3.1: Properties of γ -alumina.....	19
Table 3.2: Type of catalysts	21
Table 3.3: Operating conditions for catalytic evaluation at 440 °C.....	26
Table 3.4: Micro-GC specifications.....	29
Table 3.5: GC-MS conditions, SHIMADZU Model GCMS-QP5000.....	30
Table 3.6: Column temperature ramp for product separation.....	30
Table 4.1: Rhodium Dispersion on the γ -Al ₂ O ₃ support and the catalytic Benzene turnover based on nominal Rh content assuming 100 % dispersion in all cases *	32
Table 4.2: BET Surface Area of calcined catalysts	34
Table 4.3: Conversion and selectivity of different catalysts at 440 °C, WHSV of 1h ⁻¹ ...	41
Table 4.4: Apparent Activation Energy of Rh-Ca:K/ γ -Al ₂ O ₃ Catalysts.....	43
Table 4.5: Summary of standard operating conditions and results: Effect of catalyst dilution	50
Table 4.6: Gas composition and selectivity with benzene as reactant model molecule ...	52
Table 4.7: Gas composition and selectivity with toluene as model molecule	52
Table 4.8: Operation conditions of stability experiment Toluene steam dealkylation	56
Table 4.9: Conversion and benzene selectivity of different model molecules at WHSV of 1h ⁻¹ , and 440 °C	57
Table 4.10: Products comparison of different model molecules at WHSV of 1h ⁻¹ , 440 °C	57
Table 4.11: Gas selectivity of different model molecules at WHSV of 1h ⁻¹ , and 440 °C	58
Table 4.12: Experimental data for Naphthalene–Toluene mixture.....	60
Table 4.13: Typical aromatic composition of pyrolysis gasoline and reformat.....	63
Table 4.14: Products comparison of different model molecules ¹⁾	65

Table 4.15: Aromatic composition of pygas.....	66
Table 4.16: Dependency of benzene yield and productivity on space velocity.....	66
Table 4.17: The mass balance is calculated for the following parameters	67
Table 4.18: Mass balance calculations.....	70
Table 6.1: Results of different catalysts at 440°C and 2bar.....	80
Table 6.2: Selectivity of different compounds.....	83
Table 6.3: Data used for mass balance calculations	86
Table 6.4: Physical properties.....	86

List of Figures and Illustrations

Figure 3.1: Schematic of the SDA experimental apparatus setup	25
Figure 4.1: Effect of temperature on toluene conversion of catalysts Rh-2 and Rh-3 at 420 °C, 430 °C, 440 °C and WHSV of 1h ⁻¹	36
Figure 4.2: Effect of temperature on benzene selectivity at WHSV 1h ⁻¹ for Rh-2 and Rh-3	37
Figure 4.3: Effect of WHSV on toluene conversion for Rh-2 and Rh-3 at 440 °C	38
Figure 4.4: Effect of WHSV on benzene selectivity for Rh-2 and Rh-3 at 440 °C	39
Figure 4.5: Effect of temperature on toluene conversion of Rh-3 and Rh-4 at WHSV of 1h ⁻¹	40
Figure 4.6: Effect of temperature on benzene selectivity for Rh-3 and Rh-4 at 1h ⁻¹ WHSV	42
Figure 4.7: Arrhenius plot for Rh-4	43
Figure 4.8: Effect of WHSV on toluene conversion and benzene selectivity for Rh-4 at 440 °C	44
Figure 4.9 Effect of WHSV on toluene conversion for Rh-4 and Rh-3 at 440 °C	45
Figure 4.10 Effect of WHSV on benzene selectivity for Rh-4 and Rh-3 at 440 °C	46
Figure 4.11: Dependency of benzene selectivity on toluene conversion at different WHSV and 440 °C on Rh-4.....	46
Figure 4.12: Effect of temperature on toluene conversion for Rh-4 and Rh-5 at WHSV 1h ⁻¹	48
Figure 4.13: Effect of temperature on selectivity to benzene at WHSV 1h ⁻¹ for Rh-4 and Rh-5.....	48
Figure 4.14: Selectivity of hydrogen of catalysts Rh-4 and Rh-5 at 420, 430, 440 and WHSV of 1h ⁻¹	49
Figure 4.15: Effect of dilution on Toluene conversion; 440 °C at different WHSV, and TOS of 118 hrs.....	53
Figure 4.16: Effect of dilution on benzene selectivity; 440 °C at different WHSV	54
Figure 4.17: Effect of TOS on toluene conversion at different WHSV and temperatures for Rh-4.....	55

Figure 4.18: Effect of time on stream on toluene-naphthalene conversion at WHSV of 1h^{-1} and $440\text{ }^{\circ}\text{C}$, comparison of Rh4 vs Rh5	59
Figure 4.19: Effect of time on stream on benzene selectivity using toluene-Naphthalene at WHSV of 1h^{-1} and $440\text{ }^{\circ}\text{C}$, comparison of Rh-4 vs Rh-5.....	60
Figure 4.20: Weight loss of Rh-4 using TGA.....	61
Figure 4.21: Weight loss of Rh-5 using TGA.....	61
Figure 4.22: Flow scheme of pygas steam dealkylation.....	69
Figure 4.23: Mass balance chart	70
Figure 6.1: Block diagram of the experimental system	81

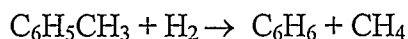
List of Symbols, Abbreviations and Nomenclature

Symbol	Definition
T	Temperature (°C)
R	Gas constant (atm.m ³ /kg.K)
P	Pressure (atm)
τ	Time (min)
S _B	Benzene selectivity
S _x	Xylene selectivity
S _{naph}	Naphthalene selectivity
S _{EtB}	Ethylbenzene selectivity
S _{co}	Carbon monoxide selectivity
S _{co2}	Carbon dioxide selectivity
G _G	Gas match
A _{corr}	Corrected mass (g)
S _G	Gas selectivity
S _H	Hydrogen selectivity
MW _{HC}	Hydrocarbon molecular weight
X _{HC}	Hydrocarbon weight fraction
A _e	Mass of liquid hydrocarbons collected in the outlet (g)
N _{HC}	Moles of liquid hydrocarbons (Toluene; Benzene; Xylene; Naphthalene)
T _{conv}	Toluene conversion (%)
N _T	Converted moles of Toluene
O _e	Oxygen mass Out (g)
O _i	Oxygen mass In (g)
m _e	Total products mass Out (g)
m _i	Total feed mass In (g)
B _e	Benzene outlet mass in the liquid collected (g)
T _e	Toluene outlet mass in the liquid collected (g)
T _i	Toluene inlet mass (g)
W _e	Water outlet mass (g)
W _i	Water inlet mass (g)
W _G	Gas mass (g)
N _B	Moles of Benzene
N _G	Moles of gas species
MW _T	Molecular weight (mol/g)
MW _G	Gas molecular weight
X _G	Gas mole fraction (G=H ₂ ; CO; CO ₂ ; CH ₄)
F _{Gm}	Molar gas flow (mol/min)
F _G	Gas effluent flow (cc/min)

Chapter One: Introduction

1.1 Background

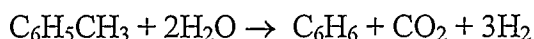
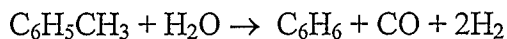
The dealkylation of alkylaromatics in order to produce benzene has been an important process in the petrochemical industry. The production of benzene can be carried out either thermally or catalytically. The main catalytic technology for making benzene from toluene is hydrodealkylation (HDA). Hydrodealkylation of toluene is usually carried out in the presence of hydrogen as shown in the following reaction:



Hydrodealkylation usually occurs at 500-680 °C and 3-6 MPa pressure, whereas thermal processes require relatively higher temperatures (700-800 °C). However, high temperatures may increase the heavy aromatic hydrocarbon content, such as naphthalene and decrease the benzene selectivity [1].

The hydrodealkylation process is a net consumer of the increasingly expensive hydrogen. With environmental legislations that restrict sulphur content in gasoline and other oil products, the demand for hydrogen becomes more and more overwhelming. The high hydrogen consumption as well as the severe conditions, at which hydrodealkylation is carried out, have provided motivation for the development of a process of alkylaromatics dealkylation by steam.

The steam dealkylation (SDA) of alkylaromatics is a catalytic reaction in which the alkyl chain of the molecule is cleaved from the aromatic ring to produce benzene and gases, among them hydrogen. This occurs by the steam reforming of at least one carbon atom of the alkyl chain. The typical SDA reactions of toluene are [2]:



The potential importance of using water in place of hydrogen to convert alkylaromatics into the more valuable benzene in high yield and selectivity has become a subject of extensive research [3]. Steam dealkylation could be an alternative route to

hydrodealkylation for industrial production of benzene from alkylbenzenes, particularly from toluene or BTX fraction.

The main advantages of SDA are the production of hydrogen and mild reaction conditions. While in hydrodealkylation, hydrogen is consumed and it requires more severe reaction conditions. For the SDA process supported catalysts of group VIII metals have been extensively studied by researchers [3], and among them Rh/alumina appears to be the most active and selective catalyst.

1.2 Benzene

Benzene is a valuable raw material in numerous petrochemical industries. Some industries use benzene to make other chemicals which are used to make plastics, resins, nylon and synthetic fibres. Benzene is also used to make some types of rubbers, lubricants, dyes, detergents, drugs, and pesticides.

The demand for benzene is predicted to increase in the future [4]. According to the forecasts [5], the average annual growth rates for demand for benzene during the 2002-2008, is expected to increase by 3.8 %, whereas the production capacity for the same period is expected to increase at an annual average rate of 1.6 %.

Among factors that affect supplies of benzene are the huge investments needed to build new HDA units [6]. Another factor is the high crude oil prices and the shortages of refinery capacity. These factors have pushed gasoline prices to such a high level that it has been more profitable to channel aromatic streams (reformates) into gasoline production [4].

1.3 Hydrogen

Hydrogen is an important chemical commodity that is produced and also consumed in a variety of processes. In the oil industry, for instance, hydrogen is used in a number of chemical processes with catalysts to form new compounds. Hydrotreatment in refineries is one example where hydrogen is introduced to oil fractions containing heteroatoms such as sulphur and nitrogen. Hydrogen undergoes numerous chemical

reactions with the heteroatoms at certain conditions resulting in a reduction of heteroatoms content in the oil. This makes hydrogen an essential industrial constituent for heavy end hydrocarbon treatment. Hydrogen offers petroleum refiners the flexibility they need to meet obligations for cleaner products.

The use of hydrogen for petrochemicals and agrochemicals will make rapid advances in the next five years, as even more stringent legislation for environmental protection is enforced. Driven by these environmental legislations for clean transportation fuels, industrial hydrogen demand will increase. According to a report from Business Communications Company, Inc. [7] total US hydrogen demand will increase by a factor of 1.32, from 10977 billion cubic feet (Bcf) in 2002 at an average annual growth rate of 5.5 %.

1.4 Motivation

Heavy oil fractions usually contain aromatic compounds that act as coke precursors as well as sulphur compounds. In order to successfully apply the SDA process to convert such feedstocks into benzene and/or into higher value aromatics such as benzene, toluene, xylene (BTX) and hydrogen, the catalyst must be able to deal with deactivation. Deactivation decreases the activity [8] of the catalyst, and generally has negative impact on catalytic processes. In SDA the deactivation could happen as a result of the following:

Coking:

This is the formation of carbonaceous deposits on the catalyst, and results in blockage of the catalytic pores and active sites.

Poisoning:

Poisoning occurs due to interaction of impurities such as sulphur with the catalytic surface.

This work is part of a broad research program in our group[†] at university of Calgary that investigates possible routes for bitumen upgrading and hydrogen production. This thesis explores an inexpensive alternative to the HDA process for obtaining benzene from aromatic fractions. Some facts that motivate this research are the following:

- Hydrogen which is used in HDA is growing in demand. This suggests that any other, economically acceptable technology to produce benzene without using hydrogen is welcomed.
- The demand for benzene is predicted to increase, suggesting that the supplies from existing HDA facilities may not satisfy the market needs.
- It is predicted that there will be a surplus of aromatic fractions in the market, when environmental legislation that limits aromatic content in gasoline become fully effective [4].

Since the demand for hydrogen is rising and the world wide demand for benzene is also increasing, SDA presents another possible route to the HDA process, for obtaining benzene.

Provided that a proper catalyst is found, the SDA offers a promising direction for industrial applications. The targeted feedstocks for the SDA process could be pygas (co-product of ethylene) which is usually added to the gasoline pool (to boost the gasoline octane number), shale oils, Atmospheric and Vacuum Gas Oils.

1.5 Objectives

There is limited reported work on rhodium catalysts containing alkali metals used for steam dealkylation of alkylaromatics. The main objective of this study is to produce a rhodium based catalyst whose support, in this case gamma alumina, is pre-coated with a

[†] Catalysis for Bitumen Upgrading and Hydrogen Production, Schulich School of Engineering, University of Calgary.
Lead Researcher: Dr. Pedro Pereira-Almao.

layer of alkali metals (calcium and potassium) and evaluate the effect of catalyst with different metal loads on its activity.

Results shown in this work were obtained from tests involving toluene and other model molecules with water. The catalysts used for the purposes of this thesis are formulations containing 0.3 % and 0.6 % of Rhodium impregnated or not on top of 3 % of Ca:K on top of alumina, $\gamma\text{-Al}_2\text{O}_3$.

The ultimate goals of the research program are:

- 1- To select the most suitable formulation or formulations based on reactivity results,
- 2- To evaluate the effect of operating variables on the conversion as well as on the benzene,
- 3- To design and develop catalysts formulations with high resistance for carbon and sulphur deactivation and,
- 4- To apply the know-how gained from testing model molecules on reactivity experiments using real world feedstocks on a continuous experimental setup.

In the present thesis results are presented for the goals 1, 2 and 3 using the most active metal reported in the literature, rhodium.

1.6 Organization of Thesis

This thesis is organized as follows: Chapter 1 describes the background and objectives of the present study. Chapter 2 presents the literature relevant to the present study. Chapter 3 describes the experimental setup used during this research, including, materials, experimental methodologies. Chapter 4 shows the results obtained from catalyst characterization, reactivity tests and their discussion. Chapter 5 includes conclusions and recommendations for future work. The appendices present examples of calculations, and mass balances for the catalyst reactivity unit.

Chapter Two: Literature review

2.1 Sources of Aromatic hydrocarbons

Aromatics are an important raw material for the production of monomers for polyesters and phthalates, engineering plastics, detergents, and pharmaceuticals. Among them, benzene, toluene, and xylenes (BTX) are the basic aromatic starting reactants.

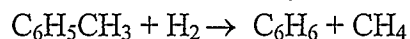
Catalytic reforming (reformate 68 %) and naphtha pyrolysis (pygas 29 %) are the main sources of BTX production [9]. A significant quantity (47 %) of benzene is commercially obtained from pyrolysis gasoline (pygas) as a by-product [9, 10]. The worldwide production capacity ratio for B:T:X obtained from the two above mentioned processes is 32:36:32. However, toluene which has the lowest market demand (11 %) is always in surplus from the production of reformate and pyrolysis gasoline, whereas benzene and xylenes are in strong demand (55 % and 34 % respectively) with the average annual growth rates of around 10 % [11, 12]. Thus the conversion of dispensable toluene into the more valuable benzene therefore has an economic importance.

2.2 Hydrodealkylation, HDA

Hydrodealkylation of alkylaromatics is a common route in the petrochemical industry. Benzene for example, is produced from pyrolysis gasoline or pure alkylaromatic hydrocarbons, mainly toluene, thermally or catalytically by using the hydrodealkylation process. Typically nickel, chromium, molybdenum, or platinum oxide catalysts are used commercially [2].

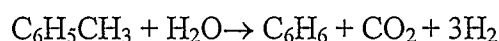
It is well known [1, 13, 14], that thermal processes require relatively high temperatures 700 to 800 °C as compared to catalytic ones which are usually accomplished at temperatures of about 600 °C under hydrogen pressures of 3-6 MPa. The commercial processes have high selectivity, and the benzene yield normally exceeds 95 %. In the toluene hydrodealkylation process a considerable quantity of hydrogen is required, which makes the benzene quite expensive.

Under these conditions, toluene undergoes dealkylation according to the following reaction:



2.3 Steam dealkylation

There is considerable interest in accomplishing the dealkylation process of toluene and other alkylbenzenes fractions by an alternative path, such as the reaction of these hydrocarbons in presence of steam [1, 13, 14]. In such chemical process, benzene is mostly formed by the following reaction:

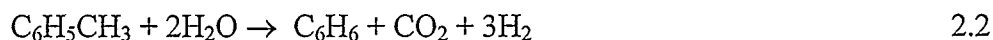
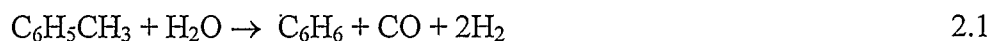


The advantage of this reaction route is that by the interaction of toluene with water benzene is formed and moreover, hydrogen is not consumed, rather produced in the process. In addition, this reaction is accomplished at lower temperatures 400-500 °C and atmospheric pressures compared to the hydrodealkylation.

2.4 Reactions

The steam dealkylation of toluene yields: benzene, hydrogen, carbon oxides, methane as main products, and traces of xylenes. The dealkylation proceeds through parallel and consecutive reactions:

Steam dealkylation, SDA:



Side reactions lead to nonselective conversion of aromatic hydrocarbons such as:

Hydrodealkylation, HDA:



Toluene and benzene can undergo a degradation of the nucleus or total steam reforming,

DN:



Hydrogenolysis:



Coking:



The composition of gaseous products from the process is determined not only by the transformations listed above; but also by the occurrence of the fast equilibrium reactions:



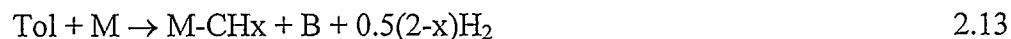
2.5 Mechanism

It is reported in the available literature [15], that the mechanism and particularly the kinetic pathway of the oxygenated species produced during the SDA should differ according to the group of the metal. On the least oxidizable metals such as Rh, the presence of oxide or hydroxyl species on the metal is almost negligible. The support, therefore acts as a primary adsorbent for the water molecule where activation occurs [16, 17]. Based on these conclusions, the mechanism for a supported Rhodium catalyst in the steam dealkylation reactions is suggested to follow a noncompetitive mechanism, i.e. toluene and water do not compete for the active sites of the metal, and it can be written as follows:

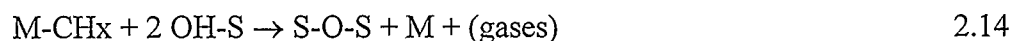
The activation of water takes place on the support sites



Adsorption and reaction of toluene on the metal site



Migration and reaction of the surface species



Where: S-O-S is the support surface; M is the metal sites; Tol is toluene; B is benzene

As shown here, toluene steam dealkylation reactions are said to occur bi-functionally in the sense that the metal activates hydrocarbon whereas, support sites are the principal sites for water activation. Both Grenoble et al. and Duprez et al. [3, 17] followed the above reaction scheme and derived kinetic expressions with similar results. Beltrame et al. [18] suggested several kinetic models, and indicated that the best fit was obtained based on reaction of toluene and water on different type of sites.

2.6 Thermodynamics

The steam dealkylation of toluene is an endothermic reaction. Usually carried out between 400-500 °C, using water to a hydrocarbon molar ratio in a range of 4 to 8. Under these conditions the toluene steam dealkylation is thermodynamically favored as reported in [3, 19].

Table 2.1: Enthalpy values of some of the reactions involved in toluene steam dealkylation

Reaction	ΔH (kJ mol ⁻¹)	ΔH at 500 °C (kJ mol ⁻¹)
2.1	+164	+176
2.2	+123	+137
2.3	-42	-46
2.4	+869	+923
2.5	+581	+656
2.8	-574	-631
2.9	-50	-23

Ref: [3, 19]

From the work of Maslyanskii et al. [2] at 350 °C to 550 °C temperature range on a Ni/Al₂O₃ catalyst, it is clear that the final composition of the reaction products is determined basically by the chemical equation 2.2.

2.7 Role of reaction conditions

The steam dealkylation reaction is usually carried out at 400-500 °C, using water to hydrocarbon molar ratio in a range of 4 to 8, and at atmospheric pressure. This section of the literature review will explore the reported effects of changing some of these conditions.

2.7.1 Pressure

Rabinovich et al. [20] have studied the steam dealkylation of toluene using an alumino-rhodium catalyst at pressures of 500 kPa and 1000 kPa. According to his work a variation of pressure between 500 and 1000 kPa has little effect on the degree of toluene conversion. Nevertheless at conversions higher than 60 % they observed that pressure has a negative effect on conversion. A similar finding is related to the selectivity, for instance, at the same degree of conversion the selectivity at 500 kPa is higher than that at 1000 kPa. Another interesting observation is the proportional relation between the pressure and the composition of methane and carbon dioxide.

2.7.2 Water to Hydrocarbon ratio

The most used ratio falls in the range of 6 to 8, and not many studies have been done regarding the role of water:hydrocarbon ratio in steam dealkylation reactions. Treiger [21] investigated the effect of the molar ratio of water/toluene on the degree of conversion and benzene selectivity at different molar ratios from 2 to 16 on rhodium catalyst. An important finding to point out is that, the optimal water/toluene ratio seems to be 6 to 8. At this water:toluene ratio, a maximum of toluene conversion 45 % was observed. The selectivity to benzene is the highest when the water:toluene ratio is very low [3]. Generally the selectivity to benzene declines with the ratio, the conversion on the other hand reaches its maximum at 8, and decreases slightly as the ratio increases. It is interesting that a similar effect of the water/hydrocarbon ratio on the selectivity of dealkylation of toluene was also observed when this reaction was carried out with a nickel catalyst [22].

2.8 Activity of alumina-supported catalysts

The role of the support is a significant one in steam reactions. For instance, Rostrup-Nielsen [23] studied the effect of support for total steam reforming of ethane. He concluded, based on activity measurements and partial-pressure dependencies, that the support was the activation site for water. Rabinovich et al. [24] observed that by changing

the type of alumina they can alter the activity of rhodium for the steam dealkylation of toluene. The majority of this research has been done on group VIII metal catalysts. The activity of these metals in the steam dealkylation reaction was studied by numerous researchers [3] who reached similar conclusions about the activity of alumina-supported group VIII metals, when used for toluene conversion. Their observations regarding the metal activity can be listed in the following sequence: Rh, 100; Pd, 28; Pt, 18; Ni, 17; Co, 15; Ru, 14; Ir, 13. All have agreed on that the rhodium (Rh) is the most active metal in the steam dealkylation reaction of toluene in spite of the different experimental conditions. Another important conclusion is that the activity of rhodium is highly independent of the support type.

In the present thesis work, the focus will be only on rhodium, thus other metals will not be mentioned in detail.

2.9 Selectivity to Benzene

The selectivity in steam dealkylation appears to be essentially a function of the metal especially for those of group VIII. The available literature shows Pt, and Pd to be highly selective towards benzene in a range of 95-100 %. Whereas other metals such as Ni, Co, and Ru have significantly lower selectivity in the range of 50-60 %. rhodium, which is the most active metal, has reported benzene selectivity ranging between 81 and 86 %. Duprez [3] has associated the selectivity to benzene of the catalyst to the properties of certain metals. According to his results, it is clear that metals such as Pt, Pd and Rh are more selective than Ni, Co, or Ru because of their low affinity to oxygen. In other words the higher the affinity of the metal for oxygen species, the lower its selectivity. It is generally known that the variations of selectivity are also related to the lifetime of the primary species leading to benzene on the metal. For a metal to be selective, it is crucial that desorption of these species to be faster than the surface reaction. Furthermore, Duprez [25] reported that metals supported on alumina or, generally speaking, metals which are well dispersed are more selective than poorly dispersed metals. This is particularly the case of Rh, Ir, Pd and Pt catalysts which can reach high dispersion values.

2.10 Role of the support in steam dealkylation reaction

Duprez et al. [25] investigated several metals on different supports, and classified metals into two groups: One comprising Pt, Rh, and Pd that are support-sensitive and the other comprising Ni, Ru, Co, and to a lesser extent Ir that are support-insensitive. It is worth also noting that the metals of the second group are the most oxidizable metals of group VIII.

As reported by McNaught [26], metals of the first group could be considered as relatively inert towards water and the strength of metal-H₂O interaction is fairly weak. Ferino et al. [27] studied alumina supported rhodium catalysts and correlated the behaviour of these catalysts to surface acidity of these supports. Their results showed that coke or tar deposition is essentially due to the presence of stronger surface acid sites. On the other hand, weaker surface acid sites of the support have positive role on activity and selectivity. This confirms clearly that the support does not act just as a carrier for the metal, but it has direct intervention in the reaction pathway [17, 18].

2.11 Steam reforming of other aromatics

Most of the research on steam reactions with aromatic hydrocarbons has been mainly conducted on toluene as a model compound. This section will be devoted to show the general features of the steam reforming of hydrocarbons other than toluene.

2.11.1 Alkylbenzenes

The main reactions that occur in steam processing of alkylbenzenes are the cleavage of C-C bond in the side chain (dealkylation), the dehydrogenation of the side chain, and the total reforming of the nucleus (breaking of the C-C bond in aromatic ring). Ethylbenzene transformation for example gives the following reactions [3]:

Dealkylation of Ethylbenzene, DA, :



Dehydrogenation, DH:

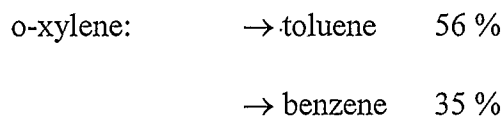


Total steam reforming, DN:

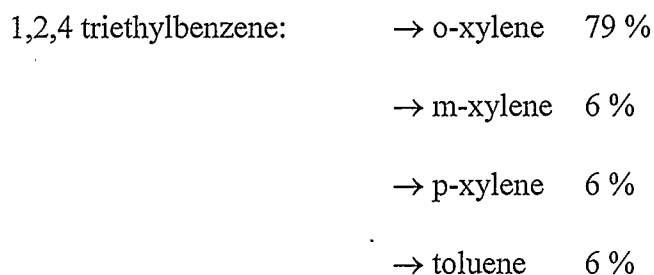


Where: C_8H_8 is styrene

Balandin et al. [28] studied the steam reforming of several alkylbenzenes on a nickel-chromium catalyst and reported that polymethylbenzenes react more readily than toluene when the methyl groups are not present on adjacent positions of the aromatic ring. However, Maslyanskii et al. [29, 30] showed that the rates of reaction decreased in the series: ethylbenzene > cumene > tertbutylbenzene. It seems that the size of the attached alkyl group affects the rate of dealkylation. For instance ethylbenzene is much more reactive than toluene. For the selectivity, Balandin [28] showed the following schemes of steam dealkylation of o-xylene and 1,2,4 triethylbenzene:



A total of 91 % from dealkylation reaction



A total of 97% from dealkylation reaction

Duprez et al. [31, 32] studied the conversion with steam of several alkylbenzenes such as ethylbenzene, cumene, tertbutylbenzene, o-xylene and n-propylbenzene on rhodium, nickel and platinum catalysts. They concluded that rhodium is the most active

metal and platinum is the most selective for preserving the aromatic nucleus while nickel shows the lowest selectivity to liquid hydrocarbons.

2.11.2 Condensed hydrocarbons

This group of hydrocarbons is commonly represented by naphthalene, tetralin or decalin as model molecules [33]. The types of reactions involved in condensed hydrocarbons-steam dealkylation are similar to those of toluene-steam dealkylation. For example, steam dealkylation of naphthalene on Rh:V/Al₂O₃ gives about 68 % of combined selectivity to toluene and benzene and 30 % of selectivity towards total steam reforming. Thus suggesting the following reaction path:



Meanwhile the reaction of tetralin and decalin with steam is mainly dehydrogenation which leads to naphthalene. This is in agreement with the results obtained by Yamamoto et al. [34].

2.12 Role of promoters

Promoters are additives which, although themselves inactive, improve the activity, the selectivity, or the stability of the unpromoted catalysts. Improvement of the catalyst selectivity, activity, and stability is critical for the catalyst's industrial application.

The factors that impact the performance of the catalyst in steam reforming are, formation of coke, sulphur poisoning, and sintering of the active metal. For instance, Duprez [3] has summarized several solutions to prevent catalyst deactivation:

- Additives to rhodium such as UO₃ increase the water-gas shift reaction (equation 2.10), since CO is considered to be a coke precursor.

- Addition of alkali to inhibit the acidic polymerization of olefinic compounds.
- Reaction under pressure and hydrogen recycling to decrease the amount of alkenes and to prevent metal oxidation.
- Increase of the water-to-toluene ratio.
- Additives to the support inhibiting the ionic diffusion of rhodium into alumina and stabilizing the support.
- Use of a two-zone reactor, with the noble metal catalyst being loaded in the second zone.

In a study by Yamamoto et al. [34], where he investigated the steam reforming of coal liquids and toluene on potassium-doped $\text{NiO-Fe}_2\text{O}_3$ catalysts and were able to show that the selectivity for the demethylation of toluene is drastically improved. They also reported that a further effect of the addition of potassium was the improvement in catalyst lifetime. In support of this point Chen et al. [35] found that nickel catalysts promoted by Li, Na, K, or Ca could be prevented from sulphur poisoning.

Alkali species are generally interpreted in terms of electronic effects [36, 37]. For example, Ertl et al. [38] have suggested, from studies of alkali promoted Fe single crystals, that the promoter species act to enhance the electron density of the metal. As a result the adsorption energy of N_2 is increased by the presence of K. According to his theory a similar effect is to be expected for the adsorption of CO. Lang et al. [39], in agreement with this, have observed that the enhanced metal-adsorbate interaction, when CO, H_2 , or N_2 are adsorbed on alkali promoted surfaces, occurs because of an electrostatic interaction between the adsorbate and the alkali metal. They showed that this electrostatic interaction results in an increase in the population of the anti-bonding orbitals of adsorbates such as CO.

CO adsorption and H_2 desorption studies led to the suggestion that some alkali (Cs) species interact directly with the Al_2O_3 support [40]. Unlike Lang et al. [39], Blackmond et al. [40] found little evidence for a significant electronic effect of the Rh-Cs interaction. They attributed this fact to the tendency of Cs to interact preferentially with

the support and not with metal. Blackmond et al. also indicated that the degree of interaction between the alkali species and the catalyst depends on the method of preparation of the catalyst. Changes in preparation procedures may result in changes in the state of the alkali species. Thus, the interaction between Cs and Rh described here might be a unique case. For example other researchers [36, 41] found no differences in CO hydrogenation activity or selectivity between Ni/SiO₂ catalysts prepared by two different methods.

Another important effect of alkali species is a geometric one; in which the added alkali may dilute the metal surface. The result of this might be to suppress certain types of adsorption of reactants that requires ensembles of neighbouring metal sites or, to a certain degree, prevent coupling interactions between adsorbed molecules [42-44]. In accordance with this, McClory et al. [45] reported geometric effects as a major factor of alkali promotion on Ru/SiO₂ from their studies of CO hydrogenation.

2.13 Possible feedstocks

2.13.1 Heavier feedstocks

Eventual application of the steam dealkylation on heavier feedstocks, such as pygas, Light cycle oil (LCO) or Vacuum Gas Oil (VGO), is feasible provided that a good catalyst is available. All these oil fractions contain hydrocarbons that can be processed in order to obtain lighter fractions with high content of valuable hydrocarbons, and that can be processed further into pure compounds.

The available literature lacks any information about the application of this process to real oil fractions. Nevertheless, Rabinovich et al. [46] claimed a successful long experiment (10 to 40 days between reactivation) with toluene conversions of 48 – 60 % and benzene selectivity about 50 %. The feedstocks used were hydrotreated naphtha cuts from pyrolysis and reforming containing C7-C8 or C7-C9 aromatics and up to 30 % nonaromatic hydrocarbons on group VIII catalysts.

2.14 Aquaconversion™

An example of implementing catalytic steam processing is the Aquaconversion™ technology that was developed in the early 90's by INTEVEP, Venezuela [47] . This technology is a version of the steam dealkylation, in terms of using a similar catalyst and steam instead of hydrogen, to produce lighter hydrocarbons and hydrogen. Aquaconversion™ is applied to residuals of heavy crude oil with low API (10° to 15°), at mild conditions using steam and a modified catalyst of a similar type to the one used in this study, to produce synthetic crude with a considerably improved API gravity. Aquaconversion™, which produces significantly lower coke yield, is considered to be a substitute to visbreaking units for naphthenic oils or could operate along side a delayed coking unit to stabilize its products and reduce coke yields.

Chapter Three: Experimental

3.1 Materials and Equipment

In this section all materials and equipment used in the catalyst development and the experimental evaluation are described.

3.1.1 Materials

The selected catalyst precursor for this study is rhodium chloride $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (from Sigma-Aldrich, Rh: 38-40 wt %). As promoters we used KNO_3 and $\text{Ca}(\text{NO}_3)_2$ (both from Sigma-Aldrich, with > 98 % purity). The properties of the $\gamma\text{-Al}_2\text{O}_3$ support are shown in Table 3.1.

Table 3.1: Properties of γ -alumina

Shape	sphere
Diameter, mm	1
Surface area (BET), m^2/g	160
Pore Volume, cc/g	0.43
Maker	Sasol, Germany

Other essential chemicals used in this study are as follows: Toluene, Benzene, Ethylbenzene, and Xylene (HLPC purity >99.8 % from Sigma-Aldrich). Naphthalene used was obtained from Merck KGa, Germany (99.6 % pure). Reverse osmosis water was used for the reactivity tests and to make an aqueous solutions when required. The hydrogen and helium used, were of ultra high purity grade and were obtained from Praxair.

3.1.2 Equipment

The steam dealkylation of alkyl aromatics took place in a laboratory experimental apparatus that consists of the following equipment and parts (see Figure 3.1: schematic of the SDA laboratory apparatus setup)

The reactor was made of stainless steel 3/8" in diameter surrounded by a heating element, 1/16" stainless steel steam generator, and two condensers. Gas supplies for the setup used were helium, hydrogen, and air/nitrogen. Glass vessels with capacities of 500 ml and 100 ml burettes were used as liquids tanks. Two pumps each with a capacity of 10 cc/min were used to introduce the hydrocarbon and water to the reaction system. Controllers from Brooks instruments were also used to control the flow of reactants, temperature, and system pressure. The reaction unit is attached to a data acquisition system.

3.2 Catalyst Preparation Procedure

3.2.1 Support pre-treatment

There is a previous know-how [47] that a mild acid pretreatment on the alumina can eliminate support contaminations and enhance the dispersion of rhodium. Therefore, this concept was used in this research work. The support, $\gamma\text{-Al}_2\text{O}_3$ was placed in a 250 ml beaker and a 0.1 M HCl solution was then added to it. The resulted mixture was kept at room temperature for 12 hrs in the hood. The beaker was then transferred to a muffle furnace and dried at 120 °C for 12 hrs. The resulting support was stored in a desiccator.

3.2.2 Incipient wet impregnation for Rh catalyst

This method was used to deposit the active metal (Rh) either on the blank support or on pre-coated support (by Ca and K layer) and it is described as follows:

First a known amount of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ was dissolved in pure water. Then the activated γ -alumina was placed in a glass dish and the aqueous solution of rhodium chloride, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, was added to it. This mixture is then covered and stored in a dark

place at room temperature for 12 hrs. The initial dark orange solution gradually turned into light yellow, while the solid became orange. This change in colour was a visual indication that impregnation was completed. Following this step the catalyst was transferred to the muffle furnace and dried at 120 °C for 3 hrs. The catalyst was then calcined in air at 450 °C for 12 hrs. Thus the resulting orange solid was transferred to a bottle, sealed and kept for later use. This procedure was used to prepare catalysts Rh-2 and Rh-5 containing 0.6 Rh and 0.3 Rh wt %, respectively.

3.2.3 Sequential wet impregnation (coating with K and Ca oxides)

This method was used to deposit a layer of the desired potassium and calcium oxides on the support prior to the impregnation with rhodium. The procedure is described below.

A known amount of the activated γ -alumina was placed in a glass dish. An aqueous solution of the desired concentration of $\text{Ca}(\text{NO}_3)_2$ and KNO_3 (each of 0.57 g) was then added slowly to the dish containing the activated $\gamma\text{-Al}_2\text{O}_3$. After 12 hrs of standing in the hood, the coated $\gamma\text{-Al}_2\text{O}_3$ was transferred to the muffle furnace for drying at 120 °C for 3 hrs. After drying, the catalyst was calcined at 650 °C for 12 hrs under air flow. The resulting white solid was transferred to a glass dish and impregnated with an aqueous solution of $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$, following the same procedure described in the previous section. This procedure was used to prepare catalysts Rh-3 and Rh-4 containing 0.6 Rh and 0.3 Rh wt %.

Table 3.2: Type of catalysts

Cat.	Support	Rh (wt. %)	K (wt. %)	Ca (wt. %)	Ca+K (wt. %)	Surface area (m ² /g)
Rh-2	γ -alumina	0.6	-	-	-	174.5
Rh-3	γ -alumina	0.6	1.02	1.04	3.28	144.5
Rh-4	γ -alumina	0.3	1.66	1.63	3.28	165.4
Rh-5	γ -alumina	0.3	-	-	-	174.8

3.3 Reactivity Measurements

Before the catalyst was subjected to a reactivity test it was pretreated and reduced. The details of the catalyst pretreatment procedure and reactivity tests are described as follows.

3.3.1 Catalyst reduction

In order to generate the catalytic active phase for these reactions all tested catalysts were reduced in situ, prior to the reactivity experiments. This process was carried out in a stepwise manner under a hydrogen atmosphere for about 14 hrs. The details are the following:

1. The charged reactor was flushed with an inert gas at room temperature for 30 min,
2. Flow H_2 at room temperature for 15 min.
3. While flowing H_2 (at 50 cc/min) the reactor temperature is increased as follows:
 - a. From room temperature to 150 °C where it was kept for 20 min,
 - b. Then the temperature is increased to 480 °C at a rate of about 2 °C/min, and kept at 480 °C with the H_2 flowing for 8 hrs,
 - c. Next the temperature is reduced to the desired reaction temperature, and
4. Hydrogen was subsequently purged out from the experimental setup with helium and then all reaction conditions were set at the desired values in order to start the catalyst evaluation experiments.

3.3.2 Catalyst evaluation procedure

A required amount of catalyst was placed in the stainless steel reactor. The reactants were fed to the reactor after the catalyst reached the set reaction temperature. Toluene (or any other model molecule) was introduced to the reactor typically about 30 min after water was injected. All reactivity measurements were performed at least 30-60 min after the commencement of the reaction, to ensure that the system was under the

steady state conditions, using the online MS. Since the experimental setup used in this work operated in a continuous manner it was necessary to understand the following terms.

Experiment: An experiment is considered as a reactivity test for a single load of a catalyst. It is composed of series of consecutive runs and, depending on the reaction conditions experiment is denoted as R1, R2, etc. Each run contains several material or mass balances.

Material or mass balance: This is done by comparing the amount going in and the corresponding amount coming out for a certain period of time. Each mass balance period lasts at least 1 hr. In all runs the mass balance was about 95-100 % closed (the mass balances were about 95-100 % satisfied). A correction of the mass balance was performed in order to obtain a 100 % recovery. Calculations of selectivity and conversion were then made for each mass balance and average results were reported in this work.

Sampling: the samples of effluent gas-stream were taken online during the mass balance period. Samples of liquid products were taken at the end of the mass balance period. These samples were either analyzed immediately or stored in the refrigerator for later analysis.

Selectivity:

- a) For gases the selectivity is expressed as number of gas moles formed per mole of toluene consumed:

$$S_G = \frac{N_G}{N_T}$$

- b) The selectivity to benzene is expressed as number of benzene moles formed during the reaction per moles of toluene consumed:

$$S_B = \frac{N_B}{N_T}$$

Weight hourly space velocity, WHSV:

Is obtained from the toluene mass flow per mass of the catalyst load per time:

$$\text{WHSV (h}^{-1}\text{)} = \frac{\text{Tol}_{\text{mass flow}}}{h} * \frac{1}{\text{mass of catalyst}}$$

Conversion: Toluene molar conversion, T_{conv} , is defined as moles of toluene reacted per mole of toluene initially fed to the reaction system:

$$T_{\text{conv.}} = \frac{N_T}{T_i} * 100$$

Calculated examples of selectivity and conversion are provided in appendix B.

3.3.3 Experimental setup

The flow reactor with a fixed-bed catalytic system was operated at 400-480 °C and at a slightly higher pressure than atmospheric pressure. The fixed bed was loaded with approximately 1.6 g of catalyst (2 cc). The reactor was placed in an electrically heated oven.

Toluene and water were pumped separately at a specified flow rate in order to achieve the required weight hourly space velocity, WHSV. Both reactants were vaporized in a preheater. The toluene vapours then mixed with steam and entered the fixed-bed catalytic reactor. The reactor, as well as, the oven walls, were equipped with thermocouples in order to control the temperature inside the reactor and the preheater. In all the experiments, the reactor and preheater temperatures were controlled within an accuracy of ± 2 °C.

The gaseous products leaving the reactor were passed through two attached condensers, where the unconverted feed, liquid products and steam were collected in the operated condenser. The non-condensable gases which contained methane, carbon

monoxide, carbon dioxide and hydrogen passed through to the online gas chromatography instrument for analysis. The apparatus setup used in this work is shown in Figure 3.1.

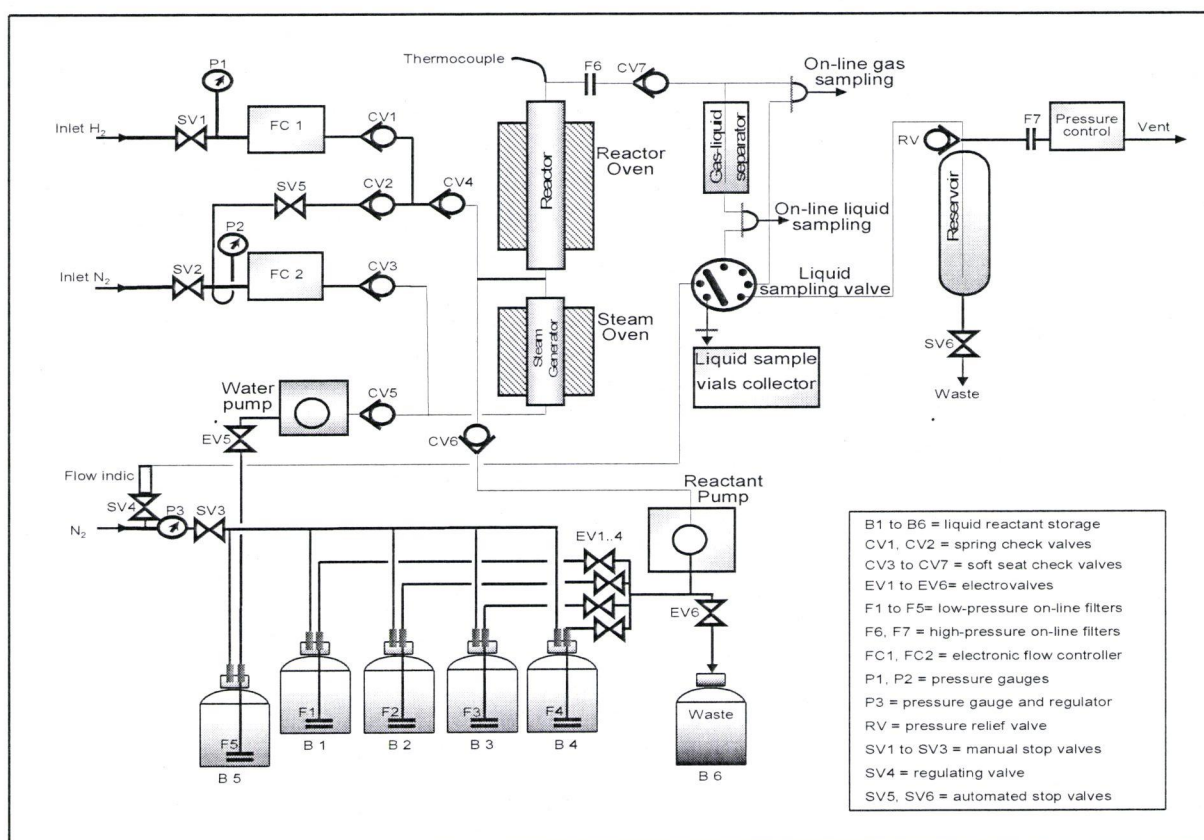


Figure 3.1: Schematic of the SDA experimental apparatus setup

3.3.4 Experimental conditions

The catalysts were tested under experimental conditions with different temperatures and flow rates. Table 3.3 shows the experimental conditions at 440 °C and WHSV of $1h^{-1}$. For all the evaluated catalysts runs at 440 °C and WHSV of $1h^{-1}$ were considered as standard operating conditions for steam dealkylation of toluene. Other operating conditions will be mentioned in later sections.

Table 3.3: Operating conditions for catalytic evaluation at 440 °C

Conditions	
Pressure, kPa	200
Flow of water, cc/min	0.04
Flow of toluene, cc/min	0.03
Molar Ratio H ₂ O:C ₇ H ₈	6 - 8
Hourly weight space velocity, h ⁻¹	1
Catalyst charge, g	1.5 – 1.6

3.4 Catalyst and Products Characterization

The techniques and methods that were used to characterize the catalysts, as well as the products obtained in the reactivity experiments, are described as follows.

3.4.1 Brunauer–Emmett–Teller (BET) Surface Area Measurement

The standard method for measuring surface area is based on the physical adsorption of a gas on a solid surface. Usually the amount of nitrogen adsorbed at equilibrium at its normal boiling point (-196 °C) is measured over a range of nitrogen pressures below 1 atm [48]. Several layers of molecules may be adsorbed on top of each other on the surface under these conditions. Therefore the amount adsorbed when one molecular layer is obtained must be identified in order to determine the surface area. The method to determine the surface area of the catalysts is the widely used Brunauer-Emmett-Teller (BET) method [49], which is based on the following equation:

$$\frac{1}{W((P_o/P)-1)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_o} \right) \quad 3.1$$

Where:

W is the weight of the gas adsorbed at relative pressure,

P/P_0 is the relative pressure,

P is the measured pressure,

P_0 is the saturation or vapour pressure,

W_m is the weight of adsorbate constituting a monolayer of surface coverage,

C is BET constant, it is related to the energy of adsorption in the first adsorbed layer and therefore it is an indication of the magnitude of the adsorbent-adsorbate interaction.

The surface area data in the present work are gathered based on the multipoint BET method. The BET equation yields a straight line when $\frac{1}{W((P_0/P) - 1)}$ is plotted against P/P_0 . The relative pressure P/P_0 for accurate surface measurements is usually found in a range of 0.05 to 0.35.

The weight of a monolayer of adsorbate W_m can then be obtained from the slope s and intercept i of the BET plot.

Slope:

$$s = \frac{C-1}{W_m C} \quad 3.2$$

Intercept:

$$i = \frac{1}{W_m C} \quad 3.3$$

$$W_m = \frac{1}{s+i} \quad 3.4$$

Then the surface area can be calculated. The molecular cross sectional area \hat{A}_{CS} of the adsorbate molecule has to be known before this can be calculated. The A_{CS} of nitrogen is 16.2\AA^2 [49]. The total surface area S of a sample is obtained thus:

$$S_t = \frac{W_m N A_{CS}}{M} \quad 3.5$$

Where:

N is Avogadro's number, 6.023×10^{23} molecules/mol,

M is the adsorbate molecular weight, MW of N_2 28 g/mol,

The specific surface area S (area per gram) of the solid can be calculated from:

$$S = \frac{S_t}{\text{Mass of sample}}, \quad S = \frac{S_t}{W} \quad 3.6$$

The samples from this study were characterized on ChemBET 3000 from Quantachrom Instruments.

3.4.2 Temperature Programmed Reduction (TPR)

In order to determine the rhodium distribution over the $\gamma\text{-Al}_2\text{O}_3$, temperature programmed reduction was performed with the ChemBET 3000. This instrument is attached to a Pfeiffer OmniStar mass spectrometer to analyse the gases produced during the TPR. Hydrogen titration was performed following TPR. The method consists of the reduction of the catalyst under a hydrogen atmosphere in parallel with a precise temperature ramping [48]. Hydrogen consumption and eventual reduction products released are measured, in our case with a Thermal Conductivity Detector (TCD), all along the temperature ramp. This procedure allows a quantitative determination of hydrogen adsorption, distinction of the different reducible metal sites present on the catalyst surface and their relative abundance.

3.4.3 Products analysis

The products of the experiments that contained liquids and gases were analyzed by gas chromatography. The effluent gas mixtures which contained hydrogen, carbon monoxide, carbon dioxide, and methane were characterized using a Micro-GC 3000A, from Agilent. This instrument is equipped with two columns. The Micro-GC specifications are summarized in table 3.4.

Table 3.4: Micro-GC specifications

	A	B
Column type	Molecular sieve	Plot Q
Carrier gas	Helium	Helium
Detector type	TCD	TCD
Inlet temperature (°C)	45	55
Column temperature (°C)	100	60
Run time (s)	240	240

The hydrogen in the product gases was determined by the molecular sieve column. The rest of the gases were quantified using the Q column.

The liquid products consisted practically of a mixture of benzene and toluene. Hence, the analyses were carried out by using a GS/MS from SHIMADZU, model: GCMS-QP5000. Analysis conditions and temperature program used for this purpose are shown in Table 3.5 and Table 3.6.

Table 3.5: GC-MS conditions, SHIMADZU Model GCMS-QP5000

Injector temperature	250 °C
Inlet temperature	250 °C
Column flow	1 ml/min
Split ratio	197
Total flow	207.5 ml/min
Detector conditions	
Temperature	250 °C
He flow	207 ml/min
Voltage	0.15 kV

Table 3.6: Column temperature ramp for product separation

Temperature ramp		
Rate (°C/min)	Temperature (°C)	Hold (min)
0	38	16.5
3.1	100	0
10	200	10

Chapter Four: Results and Discussion

The results of the work accomplished are presented in this chapter and are divided into two sections.

The first comprises all the results of catalysts characterization and the second contains the reactivity test results. The catalysts were compared based on active metal content and alkali metal content.

4.1 Catalyst Characterization

4.1.1 TPR and H₂ titration

In order to determine the rhodium distribution over γ -Alumina, TPR followed by H₂ titration was performed. The method consisted of reduction of the catalyst under hydrogen atmosphere followed by titration with hydrogen. The reactions expected to take place are described as follows:

Reduction of the Rh:



Titration of the reduced Rh, with H₂:



Based on these reactions and measurement of the conductivity difference between the inlet gas and the outlet of the gas passing through the system where the titration takes place, the hydrogen uptake is quantified and the rhodium dispersion over the γ -Alumina is determined.

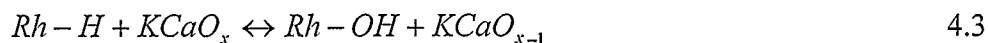
Table 4.1: Rhodium Dispersion on the γ -Al₂O₃ support and the catalytic Benzene turnover based on nominal Rh content assuming 100 % dispersion in all cases*

Catalyst	Rh Content (%)	Rh dispersion (D)	Benzene Yield per Rh content (X•S _B /%Rh/h)	Benzene Yield per Rh per disp. (X•S _B /%Rh•D/h)
Rh-2 (non-coated)	0.6	90	70	78
Rh-3 (K:Ca coated)	0.6	21	75	357
Rh-4 (K:Ca coated)	0.3	34	109	321

*Reaction conditions: 440 °C, WHSV of 1h⁻¹

Table 4.1 presents the results obtained for distribution of active metal on catalysts. Further the table contains what could be called the nominal turnover rate, i.e. benzene yield per Rh content (X•S_B/%Rh) per unit of time for the different rhodium catalysts. The dispersion of rhodium, for the catalyst Rh-2 is high and reproduces the values found in the literature [19, 50, 51]. The dispersion of Rh-3 was unexpectedly low despite its 0.6 % rhodium content. Also, a catalyst with lower content of rhodium as in Rh-4 (0.3 %) should have rhodium dispersion similarly or even better than the 90 %. On the other hand Rh-4 with 0.3 % Rh showed a surprisingly low dispersion. The common factor between Rh-3 and Rh-4, besides the poor dispersion of rhodium measured, is that both catalysts Rh-3 and Rh-4 were prepared with alumina pre-coated with 3 % Ca:K oxides. The possible reason for these results could be explained in two ways. The first relates to the oxygen-donor ability of potassium and calcium binary oxides on the catalyst surface. Hydrogen titration was performed at room temperature. Thus, the reduction of the oxidic species will not take place significantly. These oxides could provide oxygen to Rh and Rh-H species; re-establishing equilibrium with additional different species such as Rh-O, and Rh-OH. Consequently this would alter the active metal dispersion results. The chemical change that might be occurring is shown in equations 4.3 and 4.4.

Oxygen transfer to Rh-H:



Oxygen transfer to reduced Rh:



The second reason might be the migration of some Ca and K or their lower labile oxides, which results in covering the top of the Rh metal, hiding it from the reach of hydrogen. This also, will affect the active metal dispersion results. Further surface investigation needs to be conducted to clarify which mechanism is predominant. To achieve this, a technique such as X-ray Photoelectron Spectroscopy can be extremely useful, but it is not available at this time at the University of Calgary. Upward migration of alkali metals from deep internal layers of transition metals has been extensively studied and reported for ammonia synthesis catalysts. Nevertheless, whichever mechanism exists, the outcome is not affecting the activity rate per atom of Rh in the catalyst as the reactivity results clearly show. This fact prejudices against the migration of oxidic species from K and Ca on top of Rh, since they would prevent the access of the reactants to the active Rh. The third column (from left to right) in Table 4.1 shows that if we considered 100 % dispersion for the three catalysts the turnover would anyway be higher for Rh-3 and Rh-4 than for Rh-2 despite its higher metal dispersion. Last column of Table 4.1 points out that assuming these dispersion results were correct, then the nominal turnover frequency as expressed in the table by benzene yield per Rh content and per hour would be enormously different, which would also be difficult to explain.

4.1.2 BET results

The BET surface area results obtained for the support and for the prepared catalysts are presented in Table 4.2. These surface area results are obtained from catalysts after the calcinations step.

Table 4.2: BET Surface Area of calcined catalysts

Catalyst	γ -Al ₂ O ₃ type	Rh wt. %	Ca + K wt. %	Surface area m ² /g
γ -Al ₂ O ₃	fresh	0	0	168.1
γ -Al ₂ O ₃	Activated	0	0	178.0
Rh-0	Activated	0	3.28	174.4
Rh-1	fresh	0.6	0	133.5
Rh-2	Activated	0.6	0	168.3
Rh-3	Activated	0.6	3.28	144.5
Rh-4	Activated	0.3	3.28	165.4
Rh-5	Activated	0.3	0	174.8

Note:

1) Since Rh-0 does not contain active sites, Rh, it was tested for reactivity.

2) Rh-1 was prepared on fresh alumina, i.e. without acid treatment, thus was not tested for reactivity.

The activated γ -Al₂O₃ was selected to prepare all the tested catalysts. It was mentioned elsewhere [52] that the acid treatment of the fresh γ -Al₂O₃ support proved to benefit the catalyst's activity. It is evident from the above table that the surface area of the fresh alumina has increased after the acid treatment.

Also it can be noticed that the impregnation of the active metal, rhodium, as well as the coating by alkali metals, has caused a reduction in surface area of the support. The surface area of the catalyst samples decreased after coating with Ca and K (Rh-0) compared with the activated alumina. If the surface areas of Rh-2 and Rh-5 were compared to those of Rh-3 and Rh-4 we could observe that there is a decrease in surface area corresponding to the amount of rhodium impregnated on the alumina support. Likewise, catalyst Rh-3 shows smaller surface area than Rh-4. This is to be expected since Rh-3 contains a higher metal load.

4.2 Reactivity tests

The reactivity tests which consisted of evaluating rhodium catalysts represent an important part of this study. The impact on the different selectivities and on reaction

conversion of the catalysts was studied by using model molecules and varying the reaction conditions. Toluene is used as the key model molecule to evaluate the catalyst reactivity. Other model molecules such as benzene, ethylbenzene, xylenes and naphthalene were also used for evaluation purposes of selected catalysts.

The different catalysts developed for this research, were prepared as described previously in the experimental section. Following the previously mentioned method, these catalysts were prepared in batch mode in the required amount, and then stored to be used in the reactivity tests later.

In order to assess the reproducibility between repeated experiments for the different tested catalysts, the standard deviation of the average values were determined. For all catalysts the standard deviation was found to be within an acceptable range. Table 6.1 in Appendix A shows results and standard deviations for different catalysts at 440 °C. Also, a sample of the mass balance calculations is available in Appendix B.

4.2.1 The 0.6 % Rh Catalysts for Toluene Steam Dealkylation

The impact of alkali metals introduction to the catalyst was assessed on Rh-2 (without coating) and Rh-3 (with coating). Mainly the conversion and selectivity results of SDA reactions of toluene are presented for each catalyst.

4.2.1.1 Effect of temperature on conversion

The toluene conversions for Rh-2 and Rh-3 are shown in Figure 4.1. The conversion is represented in percentage of moles of toluene converted per moles of toluene injected to the reaction system. For both catalysts, the values of conversion and selectivity presented here are obtained from experiments with comparable time on stream, which ranges between 120 min to 400 min.

As expected, the conversion increased with temperature for both catalysts. This increase in conversion is more pronounced for Rh-2. While Rh-3 (with coating of calcium and potassium) has higher conversion at all temperatures compared to Rh-2, its conversion seems to change only slightly with reaction temperature.

In the range of 420 to 440 °C the molar conversion of toluene increased from 40 % to 60 % for Rh-2, whereas molar conversion values for Rh-3 has changed from 60 % to 64 %. This increase in toluene conversion is attributed to the addition of alkali metals together with the effect of acid pre-treatment of the support. One could advance a mass transfer control as the reason, which could be the consequence of a drastic increase in the activity of the catalyst. The unexpected small change in conversion in the case of Rh-3 (which always has higher conversion with respect to the non coated catalyst) with reaction temperature could be related to the dispersion of rhodium as discussed previously in the catalyst characterization section.

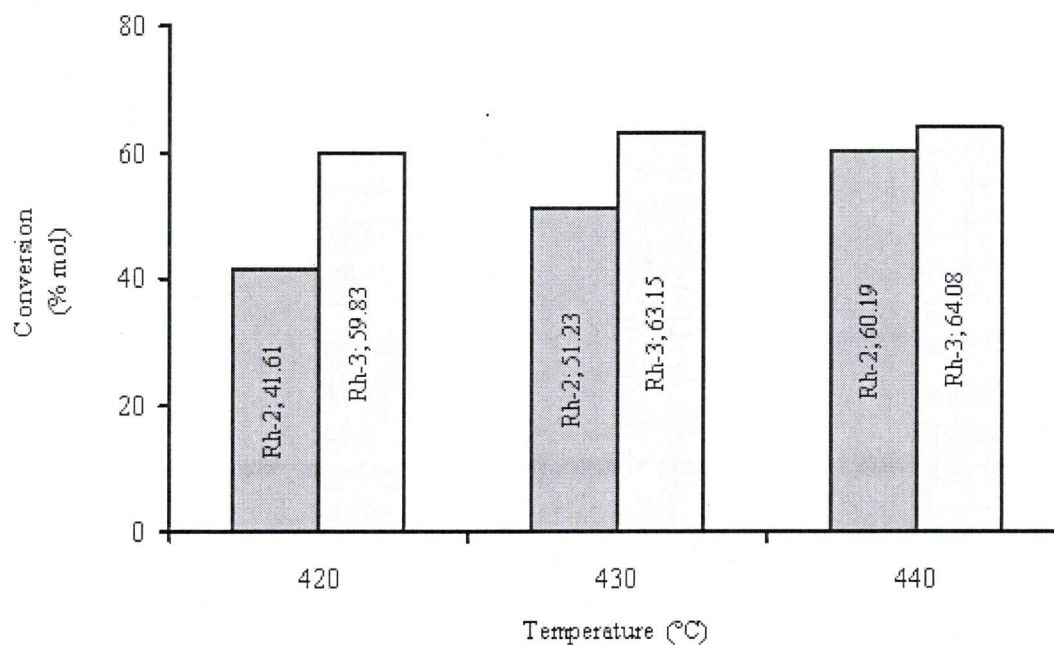


Figure 4.1: Effect of temperature on toluene conversion of catalysts Rh-2 and Rh-3 at 420 °C, 430 °C, 440 °C and WHSV of 1h^{-1}

It is worth noting that the toluene conversion results of Rh-2 and Rh-3 at 440 °C obtained in this study are higher than the values presented in the literature for rhodium catalyst (0.6 % Rh). Rhodium catalyst was reported to have toluene conversion of about 40 % [19]. The reason for these results could be in the type of $\gamma\text{-Al}_2\text{O}_3$ used as support

and in the catalyst pre-treatment or preparation method used. The alumina used in this research is spherical in shape and underwent an acidic pre-treatment prior to its use in the preparation steps. Figure 4.2 demonstrates the change in selectivity to benzene with regard to temperature. The effect of temperature on benzene selectivity on Rh-3 is more visible than for Rh-2.

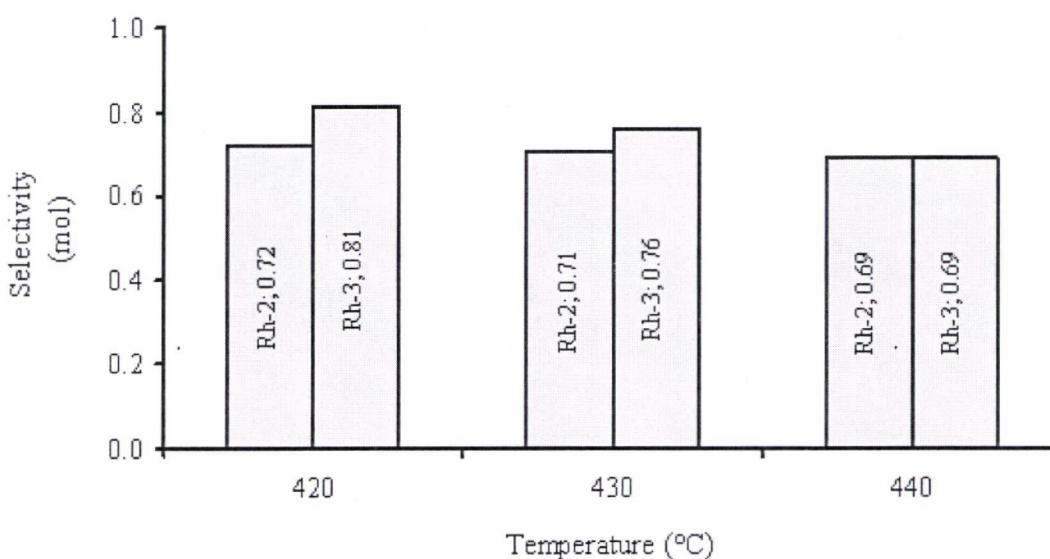


Figure 4.2: Effect of temperature on benzene selectivity at WHSV 1h^{-1} for Rh-2 and Rh-3

It is interesting that the addition of alkali metal improved the toluene conversion (see Figure 4.1) but only slightly the selectivity to benzene in the lower temperature range investigated and it did not affect the benzene selectivity at high temperature. Specifically at 440 °C both Rh-2 and Rh-3 exhibit the same benzene selectivity. Such results have not been reported in the literature for Rh based catalysts. It can be speculated that the binary oxides addition do not change the characteristics of the metal active sites of the catalyst, but perhaps displaces the equilibrium of species that are responsible for the reaction.

4.2.1.2 Effect of space velocity on conversion

The effect of space velocity on the conversion of toluene is shown on Figure 4.3. As expected for both catalysts, the highest toluene conversion was obtained at the lowest space velocity, which means longer residence time. Both catalysts displayed a decrease in toluene conversion with increase in the space velocity of the reaction. The decrease in conversion in the case of Rh-2 with the increase of WHSV is more rapid than with Rh-3.

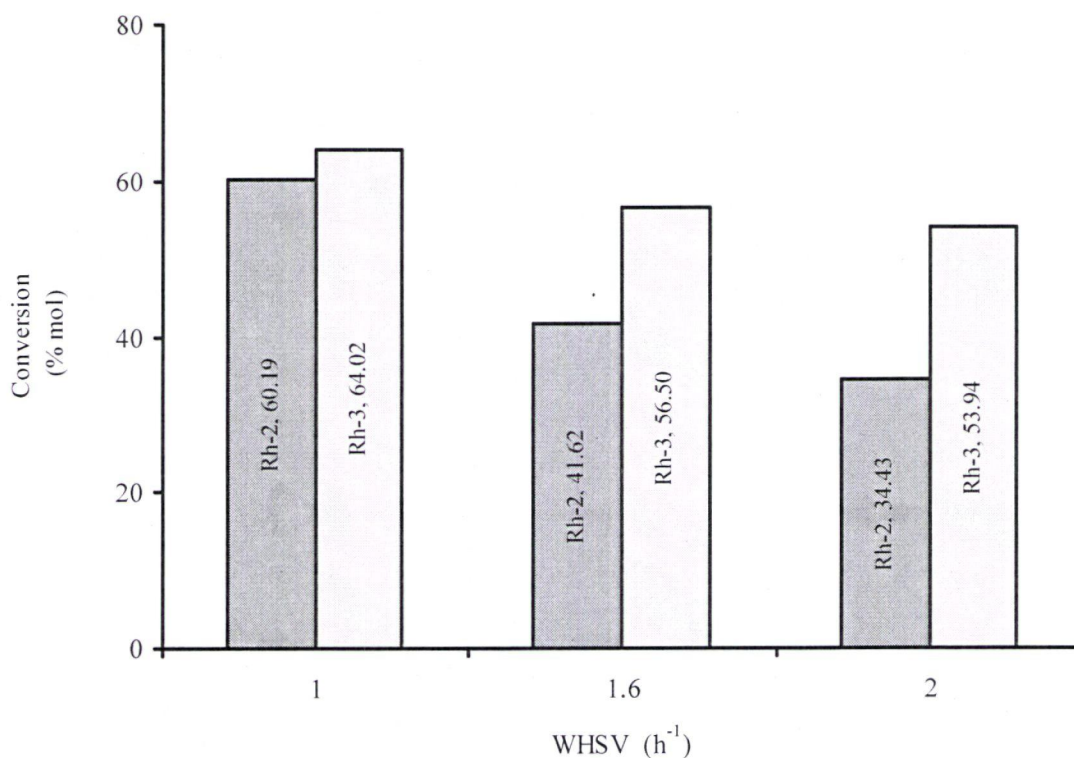


Figure 4.3: Effect of WHSV on toluene conversion for Rh-2 and Rh-3 at 440 °C

This change in toluene conversion can be associated with the addition of alkali metals to the $\gamma\text{-Al}_2\text{O}_3$ support. Regarding Rh-3, the alkali metals seem to have stabilized the toluene conversion.

4.2.1.3 Effect of space velocity on selectivity

The relationship between selectivity to benzene and space velocity is shown in Figure 4.4. Rh-2 and Rh-3 both increase their selectivity to benzene with the rise of the

space velocity. It can be seen that the higher the WHSV the higher is the selectivity to benzene; this is a common trend for both catalysts regardless whether the catalyst is coated with alkali metals or not.

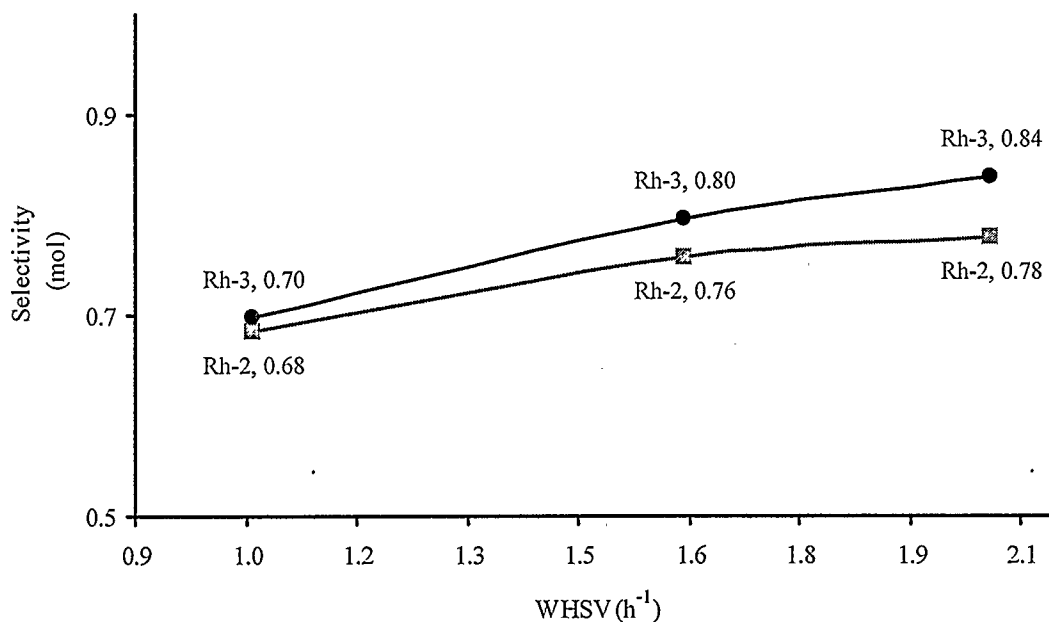


Figure 4.4: Effect of WHSV on benzene selectivity for Rh-2 and Rh-3 at 440 °C

4.2.2 The effect of rhodium loading

In this section two catalysts are compared in terms of their active metal loading and its effect on conversion and selectivity. Rh-3 and Rh-4 are both coated with the same amount of alkali metals. The difference between them is in the content of rhodium (see Table 4.1). Rh-4 contains a reduced amount of rhodium.

4.2.2.1 Effect of temperature on conversion

In order to compare the effect of the temperature at different rhodium loads, two different catalysts, Rh-3 and Rh-4, were evaluated at the same operating conditions.

Figure 4.5 shows the effect of temperature on the conversion of Rh-3 and Rh-4. Toluene conversion for Rh-3 as well as for Rh-4 increases with increase in temperature. This was expected to happen, since it is commonly known that when reaction temperature rises, the catalyst becomes more active and as a result the conversion of the reactants is boosted.

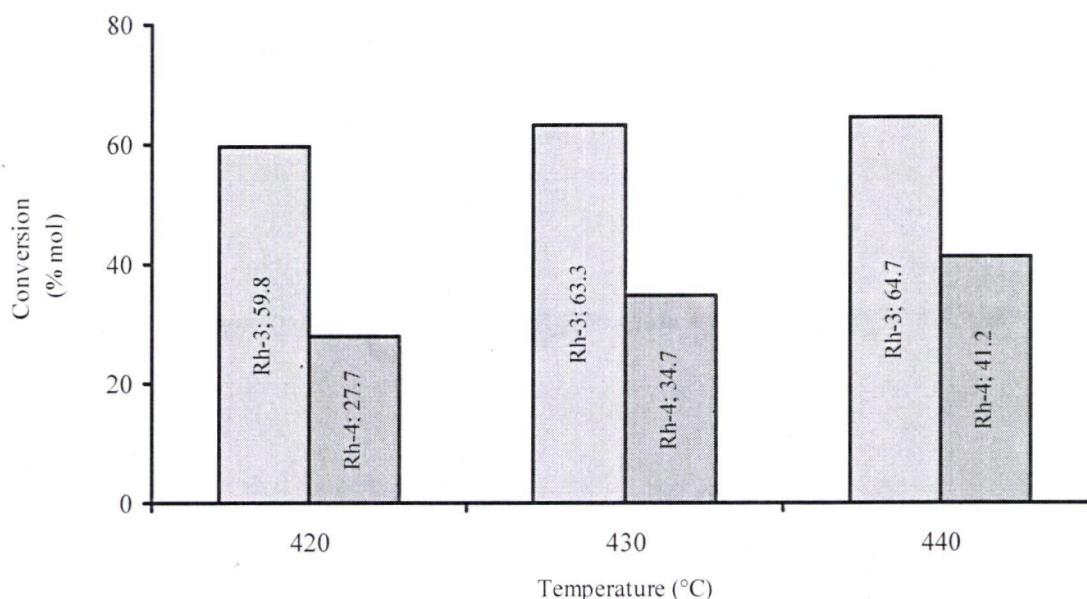


Figure 4.5: Effect of temperature on toluene conversion of Rh-3 and Rh-4 at WHSV of 1h^{-1}

Assuming that the reaction mechanism does not change with Rh load, the dependence of conversion on temperature should be the same for both catalysts. The fact that Figure 4.5 shows a difference between the two, can be explained by diffusion steps that become more relevant when passing from a catalyst with small metal load Rh-4 to one with a larger metal load Rh-3. It may be suspected that internal diffusion plays a more relevant role in Rh-3 than in Rh-4, thus reducing the activation energy of the process. The calculated activation energy was found to be 63 kJ/mol for Rh-3 and 92 kJ/mol for Rh-4.

Now, by comparing Rh-2 with Rh-3 which at 440 °C, it is apparent tat they do not differ much in conversion and selectivity. Thus, it becomes clear that perhaps 0.6 % metal load is excessive and implies that part of the metal is of limited access for the

reactants. The activity per atom of Rh is higher for Rh-4 than for Rh-3 and Rh-2 (see Table 4.3), if we assume that rhodium is similarly dispersed on the support in all three catalysts. Results and operating conditions of Rh-3 and Rh-4 are presented in Table 5.1 of Appendix A. Since rhodium is an expensive metal these results are of much applied interest.

Table 4.3: Conversion and selectivity of different catalysts at 440 °C, WHSV of 1h⁻¹

Catalyst	Rh-2	Rh-3	Rh-4
Rh content, (%)	0.6	0.6	0.3
Toluene conversion, (%)	60	64	41
Benzene selectivity, (%)	70	70	80
Yield per Rh content, (X•S _B /%Rh)	70	75	109

4.2.2.2 Effect of temperature on selectivity

Figure 4.6 provides the effect of temperature on benzene selectivity for Rh-3 and Rh-4. This is an interesting result as both catalysts contain the same amount of alkali metals. The 10 % gain in the selectivity to benzene is probably caused by the lower rhodium content in Rh-4. The rhodium content in the case of Rh-4 is 50 % less than in Rh-3. Lower rhodium content combined with addition of alkali metals has granted an interaction between the alkalis and the metal that contributed to the increase in benzene selectivity. This type of interaction is likely preceded by providing Rh with abundant hydroxyl and oxygen radicals resulting from the dissociation of water on the K-CaOx coating. This oxygen-pump insures not only the oxidation of methyl radicals, but also saturation of the most active sites of Rh responsible of over-cracking the aromatic rings of benzene and toluene.

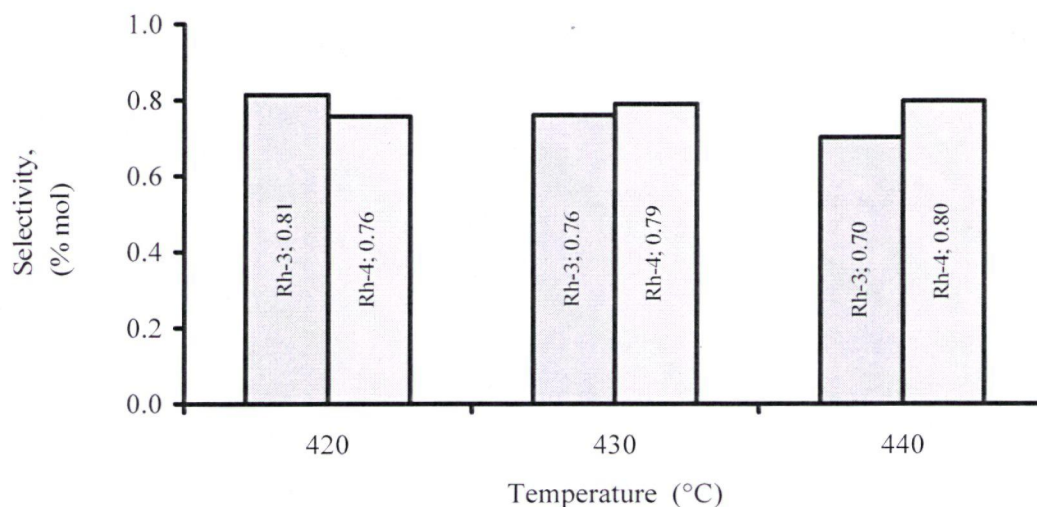


Figure 4.6: Effect of temperature on benzene selectivity for Rh-3 and Rh4 at 1h^{-1} WHSV

For comparison Table 4.3 presents the selectivity together with conversion values obtained at reaction temperature $440\text{ }^{\circ}\text{C}$ for the different catalysts. The table reveals, in row 4, the enhancement in production of benzene achieved by catalyst Rh-4. Multiplying conversion by selectivity, the yield of benzene is found. Furthermore if we divided the yield by the rhodium content we would find that Rh-4 is a much more efficient catalyst than the other two catalysts, i.e. Rh-2 and Rh-3 as shown in Table 4.3.

All the data shown so far is indicative that a more careful study of the proportions of $\text{Rh/KCaO}_x/\text{Al}_2\text{O}_3$ is needed for future work on these types of catalysts.

4.2.2.3 Apparent Activation Energy

The apparent activation energy of the process was calculated for catalyst Rh-4, assuming a kinetic order of zero, which means we can plot the logarithm of the reaction rate (mmol of toluene converted /h*cat mass) against $1/T$ (K). A kinetic order zero is at least within the range of conditions of this work, is a reasonable approximation based on the literature [3].

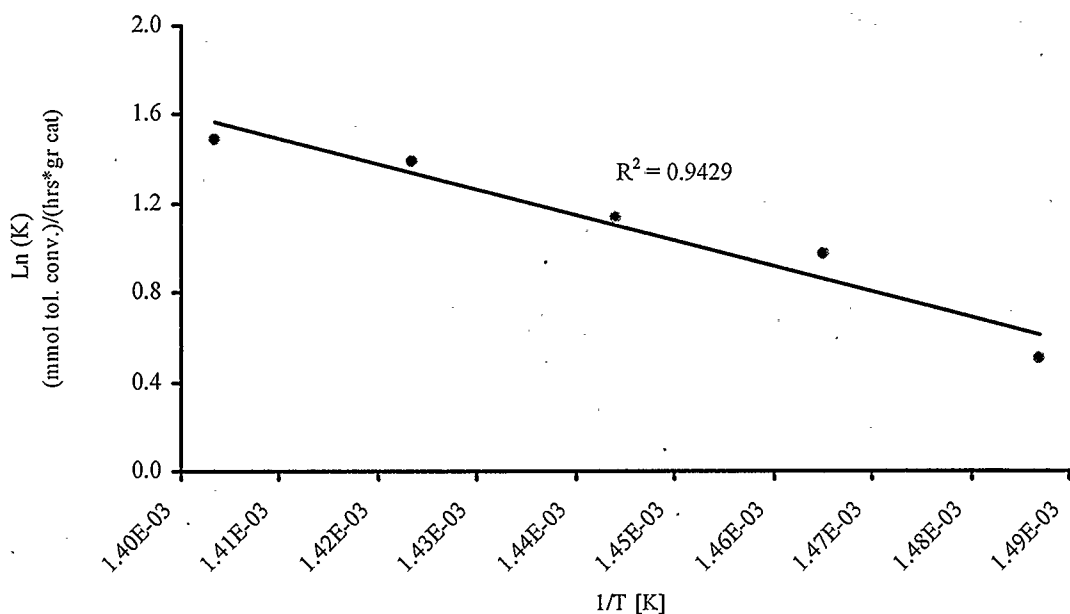


Figure 4.7: Arrhenius plot for Rh-4

The activation energy value obtained from Figure 4.7 is compared with results found in the literature [19] for 0.6 % Rh/ γ - Al_2O_3 catalyst see Table 4.4. Calculation example is shown in appendix B. The activation energy value reported here was determined from runs completed at different reaction temperatures ranging from 400 °C to 440 °C.

Table 4.4: Apparent Activation Energy of Rh-Ca:K/ γ - Al_2O_3 Catalysts

Catalyst	Ref. [20]	Rh-3	Rh-4
Activation energy, kJ/mol	101	63	92

4.2.2.4 Effect of space velocity on toluene conversion and selectivity to benzene of Rh-4

The effect of space velocity, WHSV, on conversion of Rh-4 is shown on Figure 4.8. As expected, the maximum toluene conversion was reached at the lower value of WHSV. At low space velocity the catalyst has longer residence time to complete the chemical transformation on the toluene reactant.

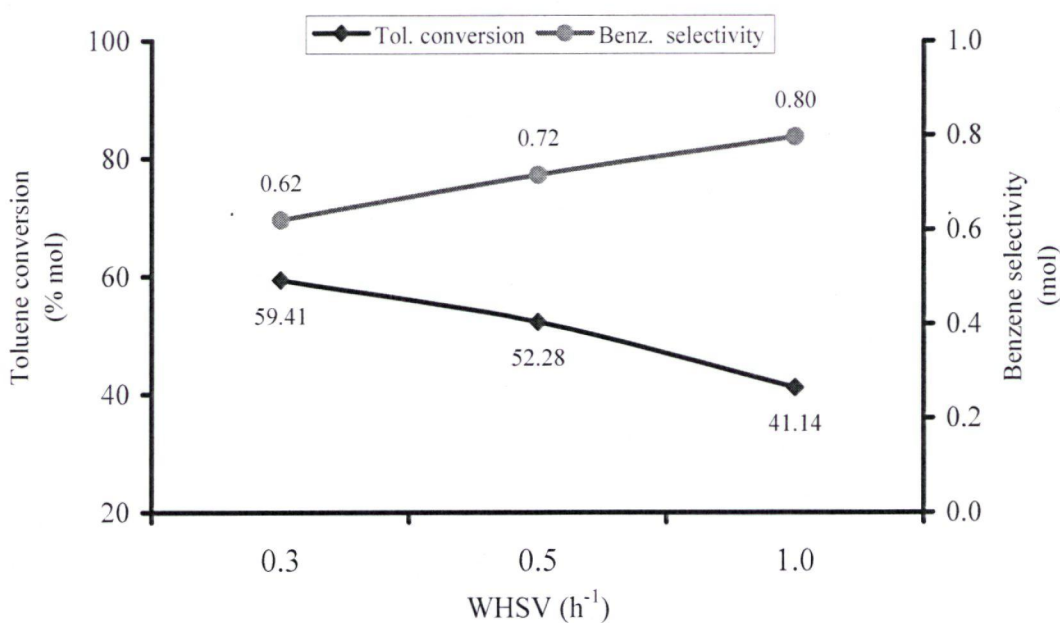


Figure 4.8: Effect of WHSV on toluene conversion and benzene selectivity for Rh-4 at 440 °C

Similar trends were seen with catalyst Rh-2 and Rh-3 (refer to Figure 4.4) which have similar and higher content of rhodium (0.6 %), respectively. It is possible to say that this behaviour is related neither to the active metal content in the catalyst nor, to the coating of the catalysts.

Also in Figure 4.8 we can see the effect of space velocity on benzene selectivity for Rh-4 at 440 °C. The selectivity increases with the increase in space velocity. As mentioned earlier, a shorter residence time seems to further limit reforming of the aromatic ring by steam.

4.2.2.5 Effect of WHSV on toluene conversion and selectivity to benzene for Rh-4 and Rh-3 at 440 °C

The overall tendency of selectivity to benzene for catalysts with lower content of rhodium (Rh-4) is comparable to that with higher content of rhodium (Rh-3), as can be noticed in Figure 4.9 and Figure 4.10. The two figures show the effect of WHSV on toluene conversion and benzene selectivity for both catalysts Rh-4 and Rh-3, respectively at 440 °C.

However, it is significantly important here to see that Rh-4 produces more benzene than catalyst Rh-3. This is despite the fact that catalyst Rh-4 has 50 % less rhodium content. This improvement in selectivity to benzene is much better reflected in Figure 4.10, where the two catalysts are compared at 440 °C and different space velocities.

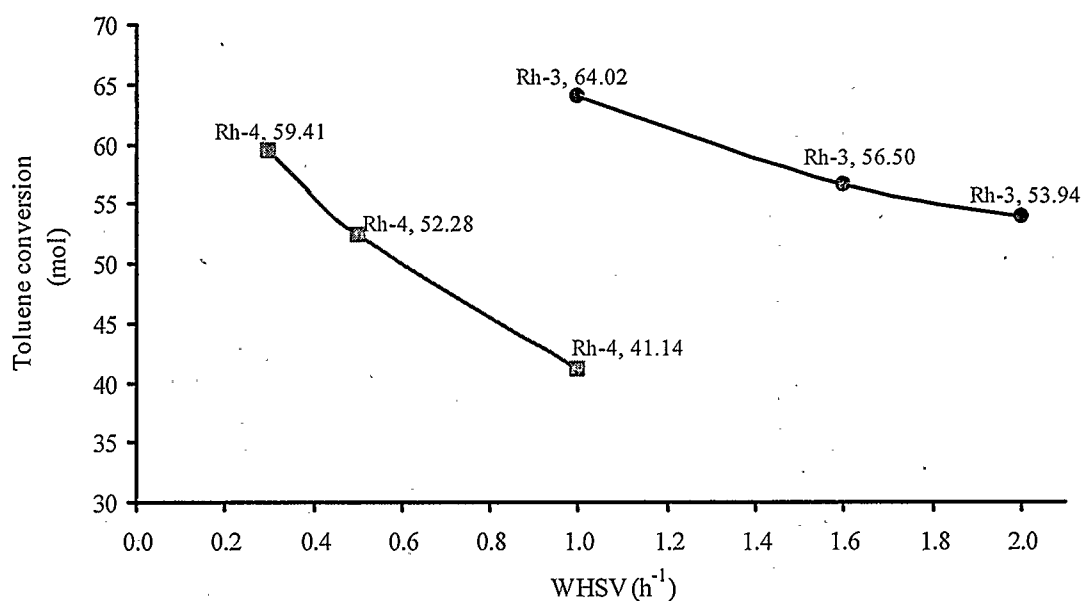


Figure 4.9 Effect of WHSV on toluene conversion for Rh-4 and Rh-3 at 440 °C

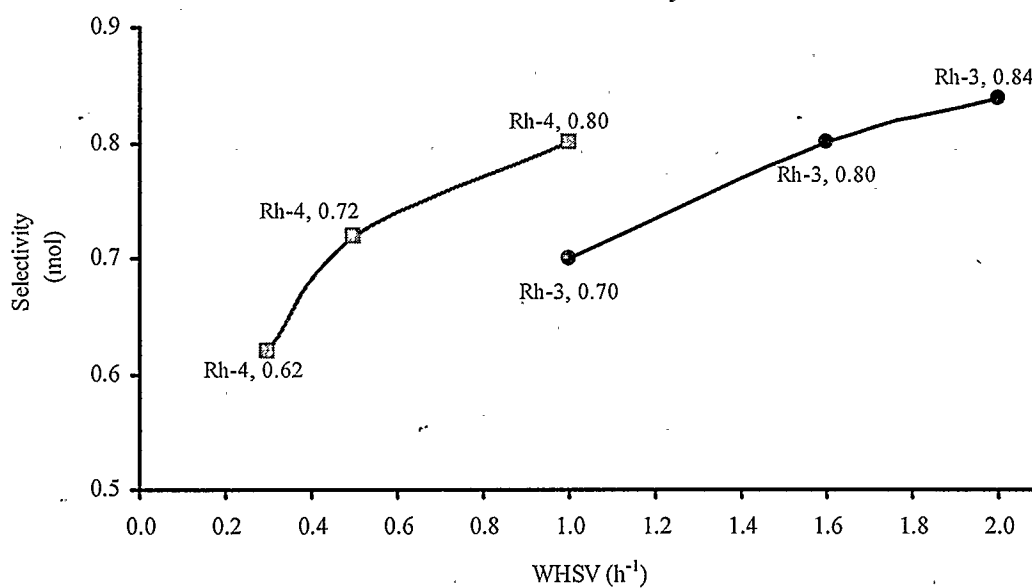


Figure 4.10 Effect of WHSV on benzene selectivity for Rh-4 and Rh-3 at 440 °C

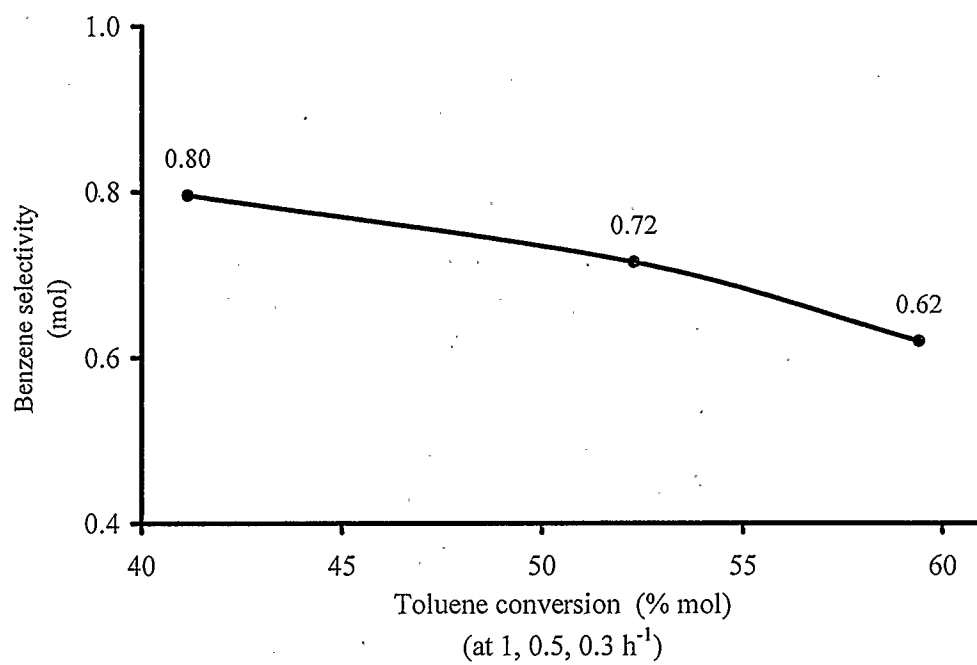


Figure 4.11: Dependency of benzene selectivity on toluene conversion at different WHSV and 440 °C on Rh-4.

Figure 4.11 shows the selectivity to benzene plotted against toluene conversion at fixed temperature and different WHSV. When toluene conversion is high, the selectivity to benzene decreases. An analogous dependency between conversion and selectivity is reported in the literature [20, 21]. The explanation of this behaviour could be that at low space velocity the reactants spend longer time on the surface of the catalyst which enables slower undesired reactions to occur. Also benzene, which at low conversion is maintained at low concentration, would become a reactant with significant concentration at higher toluene conversion, thus increasing its chances of degradation. The consequence of this fact is that more destruction of the benzene molecule happens with longer contact time, resulting in less benzene production.

4.2.2.6 Effect of alkali metals

Catalysts Rh-4 and Rh-5 have the same rhodium content, but catalyst Rh-5 does not contain any alkali metals. When comparing the two catalysts in Figure 4.12, it is evident that the alkali metals addition has not enhanced the toluene conversion much as was the case in catalysts with higher rhodium content (Figure 4.1). Particularly when the temperature rises, no significant increase in toluene conversion was noticed. In the case of Rh-2 and Rh-3 addition of the alkali had a more pronounced effect on toluene conversion. This may be attributed to a higher active metal load of catalyst Rh-3 (0.6 % Rh) compared to catalyst Rh-4 (0.3 %Rh) and their contact with the alkali metals. A reduction and variation in the proportion of alkali metals would be needed to complete an assessment on the facts shown in Figure 4.12.

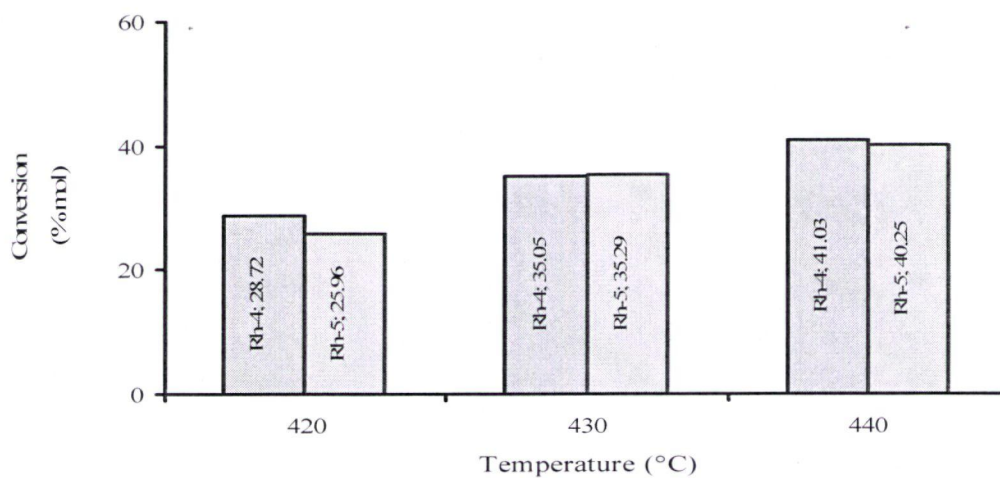


Figure 4.12: Effect of temperature on toluene conversion for Rh-4 and Rh-5 at WHSV 1h^{-1}

In Figure 4.13 we can see the impact that alkali addition has on selectivity to benzene at different temperatures. With the alkali metals addition Rh-4 has an improved benzene selectivity compared to Rh-5.

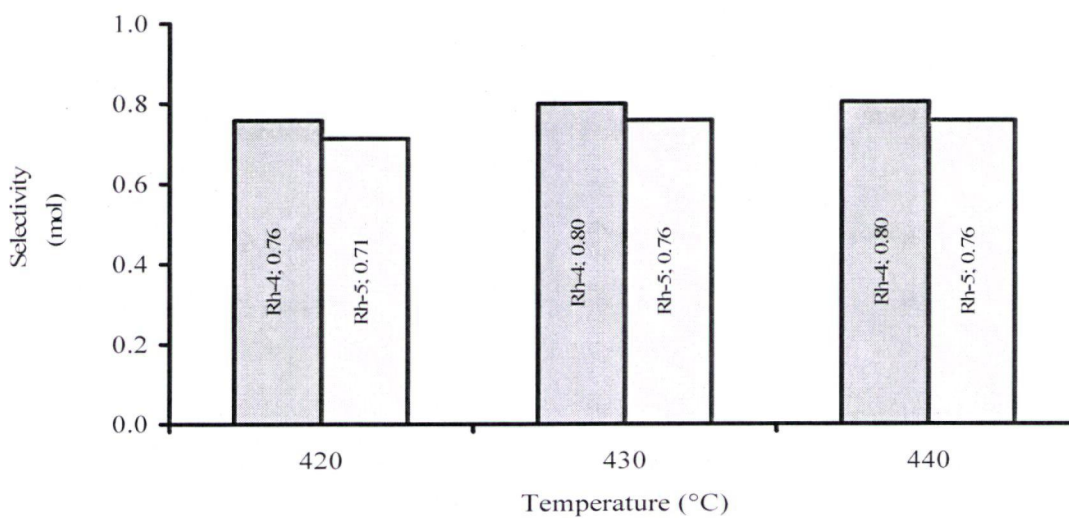


Figure 4.13: Effect of temperature on selectivity to benzene at WHSV 1h^{-1} for Rh-4 and Rh-5

Another impact of the presence of alkali metals is on the production of hydrogen. It could be noticed from Figure 4.14 that the selectivity to hydrogen is higher at all temperatures for Rh-5 catalyst than for Rh-4 catalyst. This may be explained by the fact that Rh-4 is more selective towards benzene producing reactions than is Rh-5. From reactions 2.5-2.7, it can be extracted that non selective reactions (aromatic ring reforming) contribute to an excess of hydrogen production and depletion of benzene production.

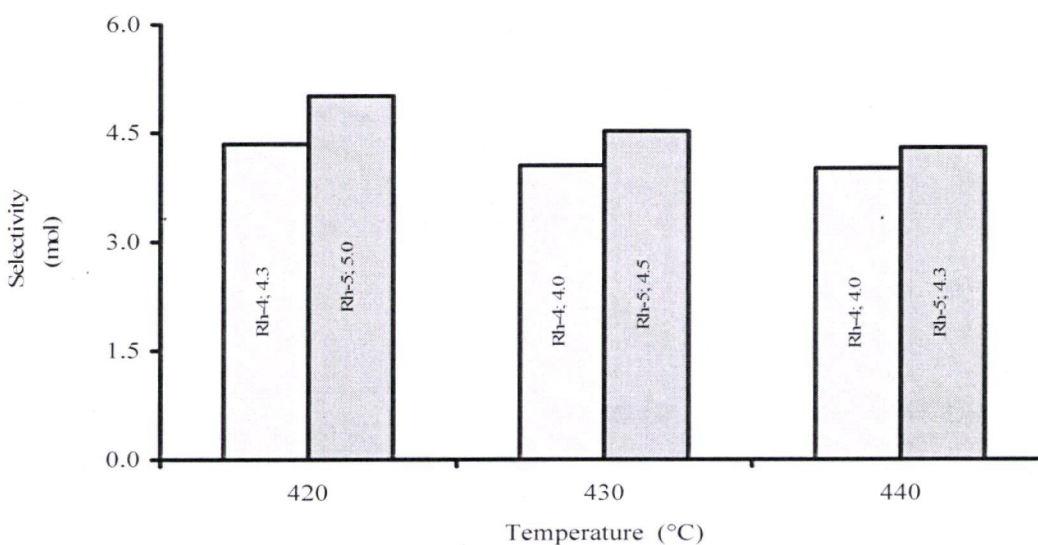


Figure 4.14: Selectivity of hydrogen of catalysts Rh-4 and Rh-5 at 420, 430, 440 and WHSV of 1h^{-1}

4.2.3 Effect of the catalyst metal dilution

Given the enhancement in terms of activity per unit mass of Rh achieved with the reduction of metal loading (see catalysts Rh-3 and Rh-4 in Table 4.5) it becomes important to determine the source of this benefit. The objective was to find out whether the increase in catalyst activity (expressed in moles of toluene converted per unit time per mass of rhodium loaded) was due to dilution of the catalyst or whether it was due to a more intrinsic interaction between the alkaline coating and the active metal Rh. Moreover the importance of this investigation seemed to have an economic significance. For this

reason a new catalytic bed, denoted as Rh-X, was prepared. This new catalytic formulation consisted of a mixture of 50 wt. % of Rh-3 catalysts and 50 wt. % of Rh-0 (pure γ -alumina), as per Table 4.2. The total metal content in this catalytic bed should be very similar to the bed formed with pure Rh-4 catalyst. The catalytic results obtained from Rh-3 and Rh-4 catalysts were used as references.

From the results presented in Table 4.5, it can be seen that Rh-X has no effect on toluene conversion when compared to Rh-4 catalyst. On the other hand a decrease in benzene production was observed. Comparison between catalysts Rh-X and Rh-3 reveals that Rh-X has higher reaction rate and benzene production than Rh-3.

It was demonstrated that the incorporation of 3 wt. % K and Ca into the catalytic preparation enhanced the conversion of toluene (Rh-2 and Rh-3). In the case of Rh-X, the dilution of the catalytic bed with 50 wt. % of 3 wt. % K:Ca- Al_2O_3 was not able to enhance the water dissociation and thus it was not able to increase the toluene conversion.

The evaluation experiment for Rh-X was performed using the same operating conditions as for Rh-3 and Rh-4 catalysts, i.e. at 440 °C and WHSV of 1h^{-1} .

Table 4.5: Summary of standard operating conditions and results: Effect of catalyst dilution

Catalyst	Rh-3	Rh-X	Rh-4
Rhodium content, %wt	0.6	0.6/2	0.3
Temperature, °C	440	440	440
Pressure, Bar	2	2	2
Molar ratio H_2O :Toluene	6-8	6-8	6-8
WHSV, h^{-1}	1	1	1
Toluene conversion, mol. %	64	41	41
Reaction rate, (Mol. tol. consumed/ hr.% Rh)	0.93	1.51*	1.48*
Benzene selectivity, mol/mol	0.70	0.75	0.80

* Standard deviations of these values are 0.04 and 0.05 for Rh-X and Rh-4 respectively.

4.2.4 Gas composition

Reactions of toluene with water produced gases H_2 , CO , CO_2 , and CH_4 . Other gases like ethylene, propane, and butane were not detected in the effluent gas and this stands in contrast to the work of Rabinovich et al. [20]. They have reported that C2-C3 compounds were formed, perhaps due to bond scission on acidic sites, whereas methane was formed via hydrogenolysis on the metal. Our results may be explained in light of the nature of active sites in the catalyst. Since the presence of hydroxyl sites plays a major role in the reforming of hydrocarbons, this suggests early steam reforming into CO , CO_2 , and hydrogen of the initial CH_x species formed from the cracking of toluene prevents the growth of paraffinic chains.

Selectivity to different gases is shown in Table 5.2 in Appendix B. The provided values were obtained for Rh-4 at 440 °C and space velocity of $1h^{-1}$. The gas selectivity is calculated from: $S_{gas} = \frac{N_{gas}}{N_T}$, see Appendix B for a calculation example.

4.2.4.1 Gasification of the aromatic ring during Steam Dealkylation of Toluene

The reaction of pure benzene with steam was studied on Rh-4 to assess the benzene contribution to the degradation of the aromatic nuclei. These tests were carried out using the standard reaction conditions as with toluene, i.e. WHSV of $1h^{-1}$ and 440 °C.

Table 4.6 and Table 4.7 show the results obtained from these reactivity tests. By comparing the values, it can be seen that the effluent gas flow and the gas composition are very similar. Hence this suggests that decomposition of the aromatic cycle most likely occurs on the fresh formed benzene and, that this benzene, is the main source of the decomposition products. Therefore it might be anticipated that the significance of such a transformation, the rate of decomposition, increases with an increase in the toluene conversion and that this takes place at low space velocities or, perhaps, at high experimental temperatures. This response explains the decline in benzene selectivity with the increase in conversion of steam dealkylation reaction of toluene, Figure 4.11.

Table 4.6: Gas composition and selectivity with benzene as reactant model molecule

Gas	Gas Composition (mol. %)	Gas selectivity (mol. %)
H ₂	63.41	11.21
CO	1.30	0.23
CH ₄	6.30	1.11
CO ₂	28.99	5.11

Reactant: Benzene; Gas Flow: 20.98 cc/min on Rh-4.

Table 4.7: Gas composition and selectivity with toluene as model molecule

Gas	Gas Composition (mol. %)	Gas selectivity (mol. %)
H ₂	63.50	5.11
CO	1.99	0.16
CH ₄	8.51	0.68
CO ₂	25.99	2.09

Reactant: Toluene; Gas Flow 21.80 cc/min on Rh-4.

4.2.5 Effect of the feed dilution

In some of the experiments on Rh-4, the feed (toluene and water) was subjected to an additional flow of 9.5 cc/min of helium. This allows us to study the effect of feed dilution, on the performance of the catalyst. In this case the dilution of the reactants was about 10 % in comparison to experiments without dilution. Previously we discussed the results of the 50 % catalyst bed dilution (see section 4.2.3) which, seems a less important condition than the reactants dilution.

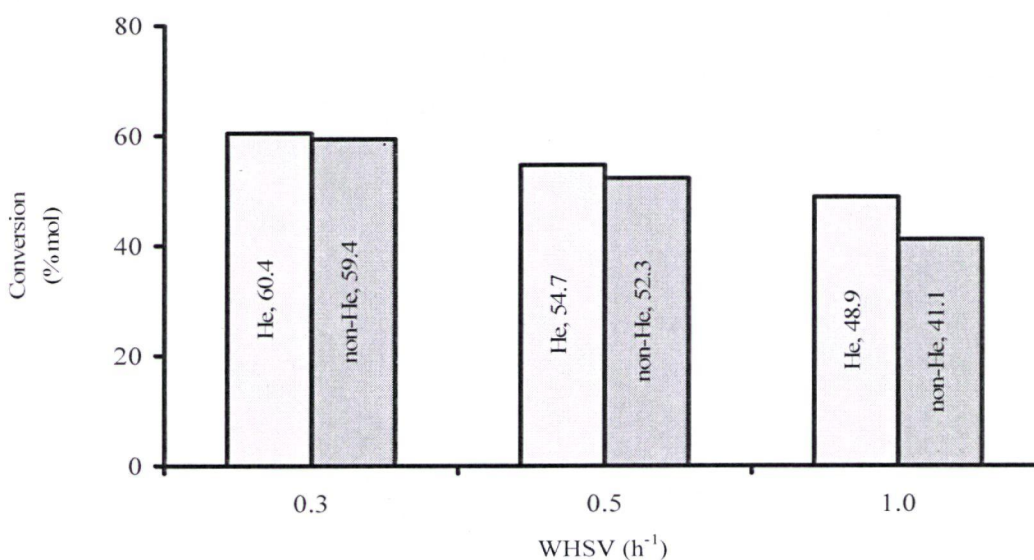


Figure 4.15: Effect of dilution on Toluene conversion; 440 °C at different WHSV, and TOS of 118 hrs

Figure 4.15 shows the feed dilution effect over toluene conversion by Rh-4 during a period of time of about 100 hours. The same effect was reported elsewhere for catalysts with the same composition as Rh-2 [47]. It can be observed that the dilution of feed has caused the conversion of toluene to rise. This is an important finding, since it might have an industrial application if an alkyl aromatic stream was to be processed via steam dealkylation. The presence of non-reactive components might have a favourable effect.

With regard to the products of interest, specifically the production of benzene, this is summarized in Figure 4.16. It can be observed that the dilution of feed did not create any improvement in benzene selectivity and, on the contrary, it reduced the benzene selectivity.

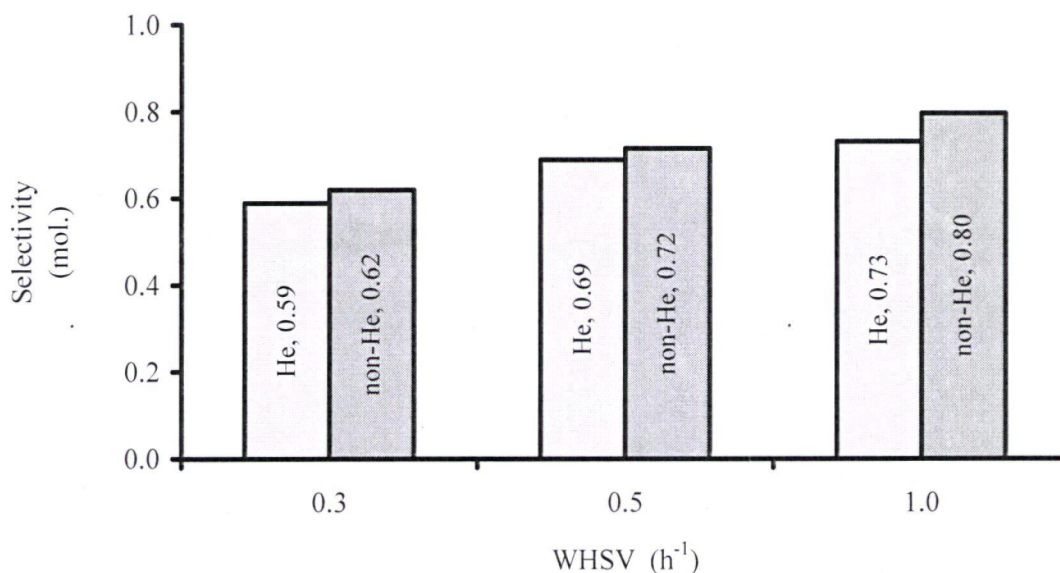


Figure 4.16: Effect of dilution on benzene selectivity; 440 °C at different WHSV

It seems that dilution of the feed enhances global conversion of toluene by reducing an overpopulation of adsorbed toluene species on the catalyst (lower toluene partial pressure), but that the non-selective reactions are also beneficiaries of that low surface concentration. This behaviour occurs, perhaps because the stronger catalytic sites are the ones that are first covered by toluene or, because, water partial pressure is also depleted. A more detailed study would need to be accomplished on this matter to clearly discern the contribution of this dilution effect.

4.3 Influence of time on stream on catalyst deactivation

The stability tests were conducted on the coated catalyst, Rh-4, using toluene for an extended period of time. During this experiment different runs were conducted on the catalyst, (see Table 4.8, for experiment details).

The most important difference between these runs was the change of the reaction conditions such as space velocity and temperature. The goal was to determine how time on stream, TOS, affects the reactivity of this catalyst. The decline in the catalytic activity

during extended runs was expressed as:
$$\frac{(y_i - y_f)}{(y_i * \text{Exp. time})}$$

where: y_i and y_f are the initial and end toluene conversions.

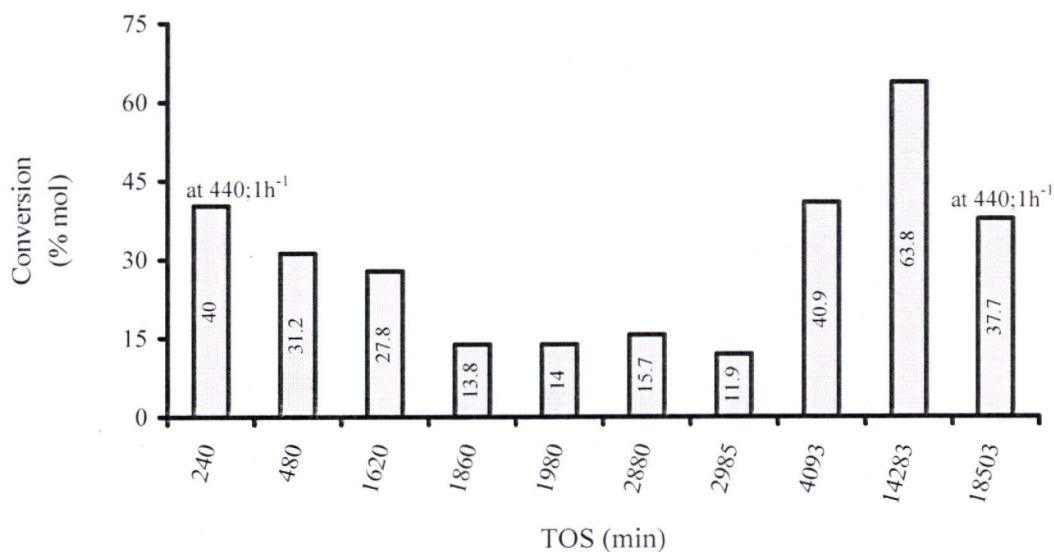


Figure 4.17: Effect of TOS on toluene conversion at different WHSV and temperatures for Rh-4.

Figure 4.17, shows the effect of time on stream on toluene conversion for an extended experiment. The calculated value of the activity loss for the entire experiment

time is very low, 3.5×10^{-4} % per hr. This suggests that this catalyst can maintain its original activity measured at 440 °C and 1 h^{-1} space velocity with insignificant deactivation due to coke deposition. Similar minor deactivation rate was observed with Rh-3, [47].

Table 4.8: Operation conditions of stability experiment Toluene steam dealkylation

Experiment runs	Temperature °C	WHSV h^{-1}	Time on stream min
R1	440	1	240
R2	430	1	480
R3	420	1	1620
R4	410	1	1860
R5	410	2	1980
R6	400	1	2880
R7	400	2	2985
R8	440	1	4093
R9	440	0.3	14283
R10	440	1	18503

4.4 Other model molecules: Xylene and Ethylbenzene

In order to further evaluate the reactivity of Rh-4 we used other model molecules that commonly exist in monoaromatic rich streams.

Table 4.9 compares data for toluene with data obtained using xylene or ethylbenzene. For comparison, these runs were conducted at the same standard conditions as with toluene. The main objective was to evaluate the performance of Rh-4 and using C8 aromatics.

Table 4.9: Conversion and benzene selectivity of different model molecules at WHSV of 1h^{-1} , and $440\text{ }^{\circ}\text{C}$

	Toluene	o-Xylene	Ethylbenzene
Conversion, mol.%	41	31	55
Benzene selectivity	0.80	0.51	0.30

For all reactants the liquid products were benzene, toluene and traces of naphthalene, xylene and ethylbenzene. The gaseous products were methane, carbon monoxide, carbon dioxide and hydrogen. These are the same products as in the case when the reactant is toluene.

Table 4.10 presents the different products obtained for these experiments. And Table 4.11 shows gas selectivity of all model molecules used in this study.

Table 4.10: Products comparison of different model molecules at WHSV of 1h^{-1} , $440\text{ }^{\circ}\text{C}$

Liquid products (wt. %) ¹⁾	Toluene	o-Xylene	Ethylbenzene	Naphthalene ²⁾
Benzene	32.0	12.1	13.3	14.2
Toluene	-	9.9	29.5	77.9
Xylene	0.6	-	3.4	0.8
Ethylbenzene	0.03	0	-	1.6
Naphthalene	0.10	0.4	0.3	-

1) The balance to 100 % represents the unreacted model molecule.

2) Mixture of 7.24 wt. % naphthalene in toluene.

Table 4.11: Gas selectivity of different model molecules at WHSV of 1h^{-1} , and $440\text{ }^{\circ}\text{C}$

Model molecule:	Toluene	o-Xylene	Ethylbenzene	Naphthalene
Gas selectivity, mol. %				
H_2	5.11	5.55	3.61	4.07
CO	0.16	0.11	0.20	0.09
CH_4	0.68	0.39	0.34	0.32
CO_2	2.09	2.10	1.27	1.63

4.5 Using Naphthalene – Toluene mixture, on Rh-4 and Rh-5

Two different experiments were conducted on the coated rhodium catalyst (Rh-4) and on the non-coated rhodium catalyst (Rh-5), respectively. The target was to evaluate the effect of alkali metal addition by comparing the two catalysts reactivity. The activity measurement for these experiments was performed using 9 wt. % naphthalene-toluene mixture at 440 °C and space velocity 1h^{-1} . Table 4.12 includes the runs data and results obtained from these experiments. Figure 4.18 and Figure 4.19 show the influence of time on stream on toluene conversion and selectivity to benzene for the two catalysts.

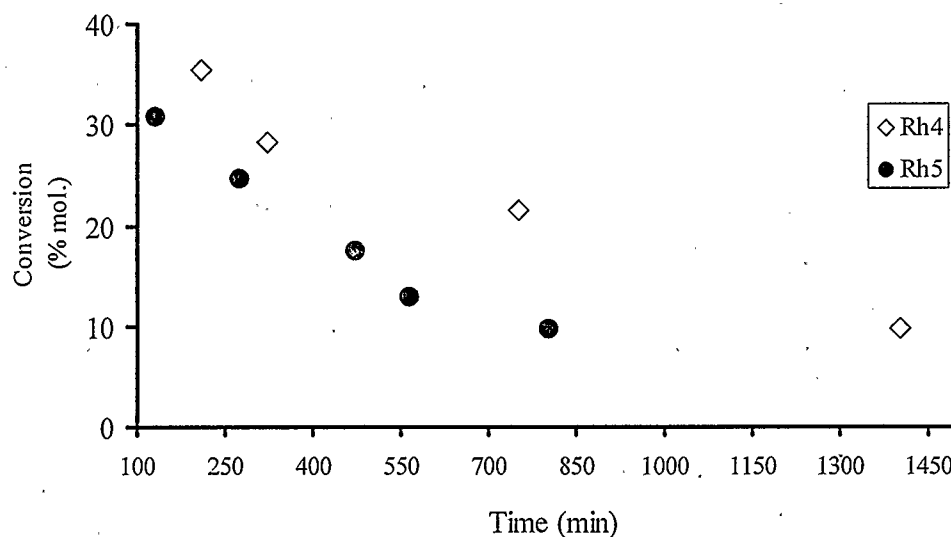


Figure 4.18: Effect of time on stream on toluene-naphthalene conversion at WHSV of 1h^{-1} and 440 °C, comparison of Rh4 vs Rh5

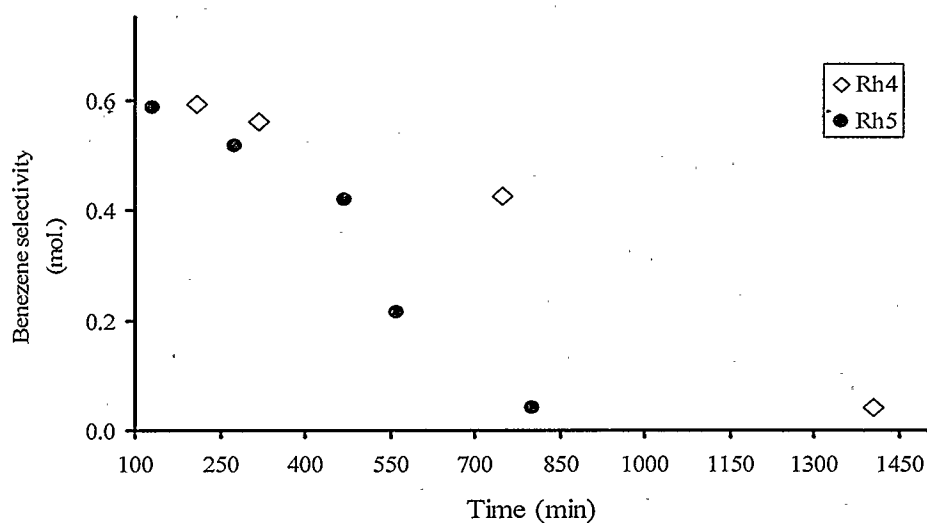


Figure 4.19: Effect of time on stream on benzene selectivity using toluene-Naphthalene at WHSV of 1h^{-1} and $440\text{ }^{\circ}\text{C}$, comparison of Rh-4 vs Rh-5

Table 4.12: Experimental data for Naphthalene-Toluene mixture

Catalyst	Rh-4	Rh-5
Pressure, Bar	2	2
Molar ratio $\text{H}_2\text{O}:\text{HC}$	7.9	7.5
Experiment time, hr	23	23
Toluene conversion, mol.%*	35.50	30.80
Benzene selectivity, mol.*	0.59	0.59
Carbon content, wt. %	2.90	5.25

TGA** technique was used to measure the carbon deposits on the catalyst surface after the experiments were completed (after 23hrs on stream). The results obtained are expressed as per cent of carbon content in Table 4.12. The introduction of alkali metals proved to be useful in preventing carbon formation on the catalyst's surface. The catalyst

* Maximum obtained values

** measuring the weight loss before and after burning carbon deposits

with alkali metals coating (Rh-4) has 80 % less carbon content than the catalyst without alkali metals coating (Rh-5). Thermograms of Rh-4 and Rh-5 are shown in Figure 4.20 and Figure 4.21.

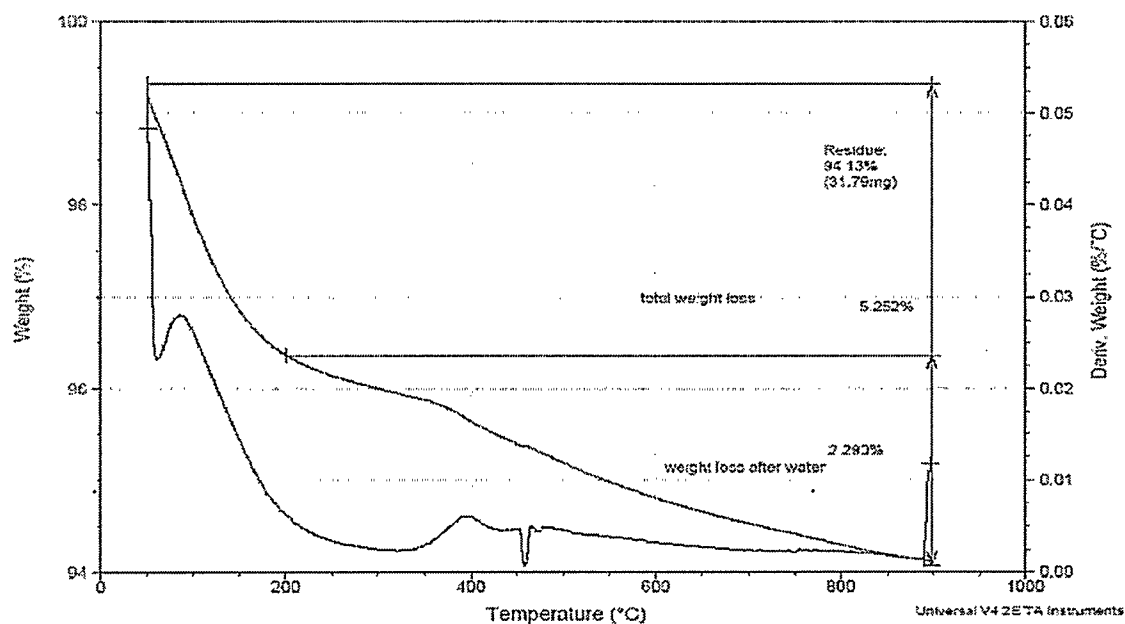


Figure 4.20: Weight loss of Rh-4 using TGA

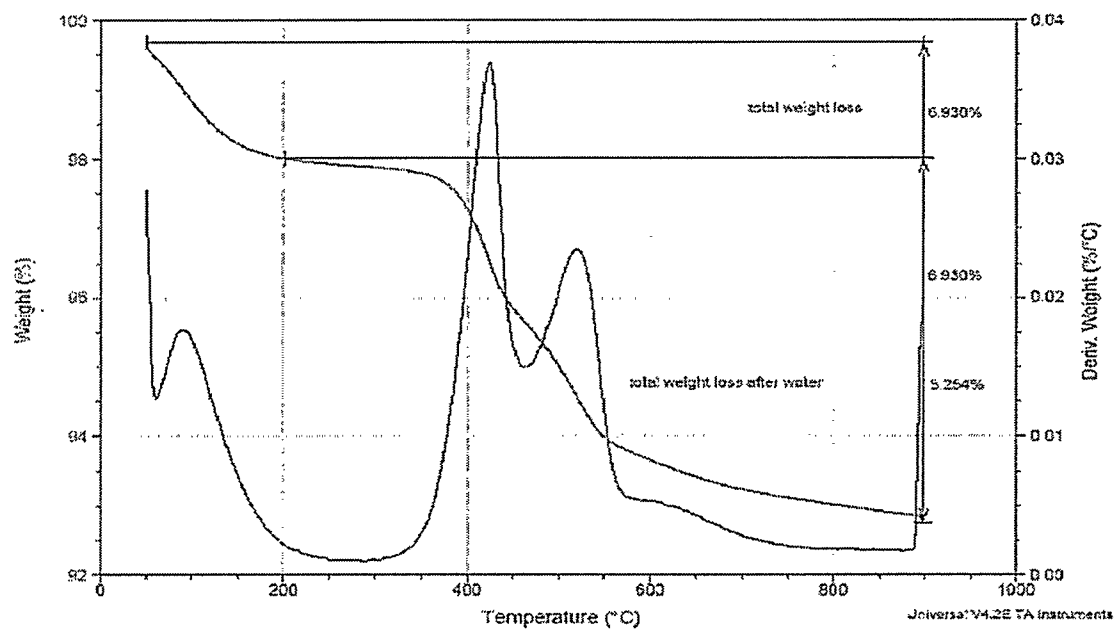


Figure 4.21: Weight loss of Rh-5 using TGA

It is a well known fact that coke and tar depositions are essentially due to the presence of stronger surface acid sites [27]. However, the definitive effect observed was a loss in activity of the catalyst a fact which might be attributable to coke formation.

The delay in coke formation could be related to the neutralization of strong acidic (strong acid centers are undesired) sites by alkali metals or, also, it could be related to the dispersion of crystallites (cluster of Rh sites) of Rh that are responsible for the adsorption of coke precursors. As a result the introduction of alkali metals leads to a decrease in coke deposition. The positive role of alkali and alkaline-earth metals on the resistance to coke formation fact is reported by Chen et al. [37].

4.6 Preliminaries of a process for steam dealkylation of pyrolysis gasoline based on the catalyst developed up to now

4.6.1 Pyrolysis gasoline

The Pyrolysis gasoline (pygas) is a by-product from steam cracking process of naphtha to produce ethylene. Pyrolysis gasoline is a rich source of aromatic hydrocarbons (contains about 70 % aromatics) from which benzene can be obtained. Table 4.13 shows the aromatic content of pygas compared to naphtha from reforming. Pygas is perhaps the richest industrial source of naphtha range aromatics.

Table 4.13: Typical aromatic composition of pyrolysis gasoline and reformat

	Pygas, wt. %	Reformat, wt. %
Benzene	40	3
Toluene	20	13
Xylenes	4	18
Ethylbenzene	3	5
C9+ aromatics	3	16
Total aromatics	70	55
Naphtenes, Paraffins, Olefins	30	45

Several processes exist to obtain aromatic hydrocarbons from the aromatics-rich raw pygas, which also contains non-aromatics. A very common method is extraction by using a solvent to separate the aromatic fraction from non-aromatic hydrocarbons. Among traditional solvents are furfural, tetramethylene sulfone, dimethyl sulfoxide, sulphur dioxide, sulfolane, diethylene glycol and tetraethylene glycol [53, 54]. Benzene is usually removed from aromatic-rich fractions by distillation, extractive distillation, or, by fractional distillation.

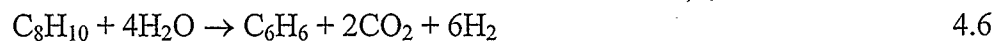
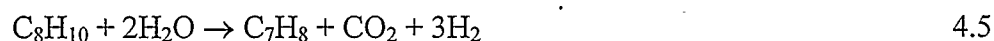
4.6.2 Proposed SDA process flow sheet

The results obtained from testing other model molecules, heavier than toluene, such as ethylbenzene, naphthalene, and xylene on 0.3 Rh-Ca:K/Al₂O₃ catalyst (Rh-4) indicate that these aromatic hydrocarbons transform to benzene in the steam dealkylation by following, generally two routes. They convert directly to benzene or/and to toluene and then to benzene, this can be expressed as follows:

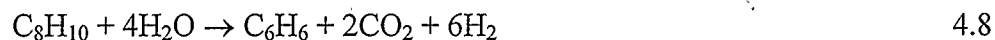
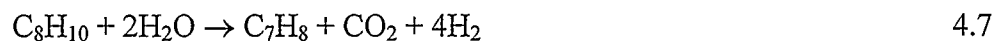
HC: → benzene

→ toluene → benzene

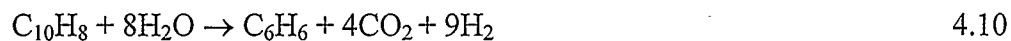
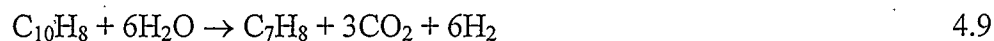
Ethylbenzene:



Xylene:



Naphthalene:



The composition of the liquid products obtained from testing different model molecules are shown in Table 4.14. For instance when ethylbenzene is treated with steam on Rh-4, the dealkylation proceeds to produce about 82 % of liquid and 18 % gases. The liquid product composition for ethylbenzene contains 13.3 % benzene, 29.5 % toluene, 3.4 % xylene, and 0.3 % naphthalene as shown in Table 4.14 for other model molecules as well.

Table 4.14: Products comparison of different model molecules¹⁾

Liquid (wt. %)	Toluene	o-Xylene	Ethylbenzene	Naphthalene ²⁾
Benzene	32.0	12.1	13.3	14.2
Toluene	-	9.9	29.5	77.9
Xylene	0.6	-	3.4	0.8
Ethylbenzene	0.03	0	-	1.6
Naphthalene	0.10	0.4	0.3	-

¹⁾ Data were collected from experiments conducted on Rh-4 at 440 °C, 2bars, HC/H₂O: 6-8 and WHSV of 1h⁻¹. The balance to 100 % represents the unreacted model molecule.

²⁾ Mixture of 7.24 wt. % naphthalene in toluene.

Based on the presented results a process concept for the steam dealkylation process could be suggested in order to process even heavier feedstock consisting of poly alkyl aromatics. One possible feedstock that could be considered in this case is the pyrolysis gasoline fraction, as well as reformat, which is an aromatic stream from naphtha's catalytic reforming. Since the catalyst was not evaluated for sulphur resistance, and given that benzene could be easily isolated from the raw pygas, the following is assumed:

- The catalyst Rh-4 is sulphur resistant and deactivation via coke deposition can be overcome.
- The pygas considered for the SDA has already been freed of saturated hydrocarbons as well as benzene, by using one of the well known extraction process already mentioned at the introduction of this section.

Now that pygas, after benzene removal, predominantly contains toluene it is possible to expect about the same conversion as in the case of pure toluene SDA i.e. 40 % at space velocity of 1 h^{-1} . Higher pygas conversion is expected at lower space velocity than 1 h^{-1} . Table 4.15 shows the normalized pygas composition after the benzene elimination from raw pygas.

Table 4.15: Aromatic composition of pygas

	wt. %
Toluene	66.7
Xylene	13.3
Ethylbenzene	10
C9+ aromatics	10

4.6.3 Effect of space velocity on benzene production

The table below contains data obtained from steam dealkylation of toluene at different space velocities.

Table 4.16: Dependency of benzene yield and productivity on space velocity

WHSV, h^{-1}	0.3	0.5	1
Toluene conversion, %	59.4	52.2	41.1
Benzene, %	62	72	80
Yield, %	36.8	37.6	32.9
Productivity	11.0	18.8	32.9

By calculating the yield and productivity to benzene it can be noticed that the space velocity of 1 h^{-1} (see Table 4.16) will more likely offer the best benzene productivity and therefore it is used for the mass balance calculations. It is also assumed that the pygas conversion at the space velocity of 1 h^{-1} is similar to that of toluene and that this is the same for both reactors, i.e. 41 %. The yield and productivity to benzene are found from the expressions 4.11 and 4.12:

$$\text{Yield} = X \cdot S_B \quad 4.11$$

$$\text{Productivity} = X \cdot S_B \cdot WHSV \quad 4.12$$

4.6.4 Mass balance and process description

Table 4.17: The mass balance is calculated for the following parameters

Ratio, H ₂ O:HC	6.00
Pygas, kmol/h	1
H ₂ O, kmol/h	5.9
H ₂ O, kg/h	105.9
Pygas feed, kg/h	100
Conversion, %	41

The suggested steam dealkylation of pygas consists primarily from two fixed bed reactors connected in series (see Figure 4.22). The first reactor (R-1) is used to treat the fresh refined pygas (the refined pygas represents a pygas without benzene) which contains mainly toluene, ethylbenzene, xylene, and C9+. This feedstock will be fed to (R-1) and converted in to a mixture of benzene, toluene, and xylene (BTX), but will also contain naphthalene and other heavier aromatic hydrocarbons.

The reaction conditions for the proposed SDA of pygas may be adopted from the results of toluene steam dealkylation at different space velocities. This is 440 °C and pressure of 2 bars. It is clear from Table 4.16 that WHSV 1 h⁻¹ offers the highest productivity rate.

The first reactor outlet is fed to a distillation column (C-1) to get benzene from the top. The bottom of the column, which will contain unconverted pygas and heavier compounds, is passed to the next reactor R-2, where the reaction may be carried out at higher severity compared to the first reactor. The reason for increasing the reaction temperature in R-2 is that the SDA of heavier aromatic hydrocarbons is favoured at higher temperatures. The expected temperature increase is about 50 °C in the second reactor R-2 against the first reactor. In comparison this reaction temperature is still in the

low range of the hydrodealkylation process [55]. Reactor R-2 will operate at different temperature, but the other reaction parameters are same as in reactor R-1.

The purpose of the separators is removing aromatics from the water phase. Based on our practice with pure aromatics, it is anticipated that these separators would be highly efficient. The water is then vaporized and fed back to reactor R-1 and R-2, along with fresh steam makeup. The hydrocarbon phases from both separators can be sent directly to the distillation column, C-1, where only benzene is separated, as head-product, from the rest of aromatic hydrocarbons; toluene, xylene, and C9+ aromatics.

The material balance is shown in Table 4.18 for the flow diagram and it is illustrated by Figure 4.23. In Figure 4.22 is shown the suggested flow scheme for steam dealkylation of pygas. The following parts can be seen:

- Reactors
- Distillation
- Separators
- Gas cyclones

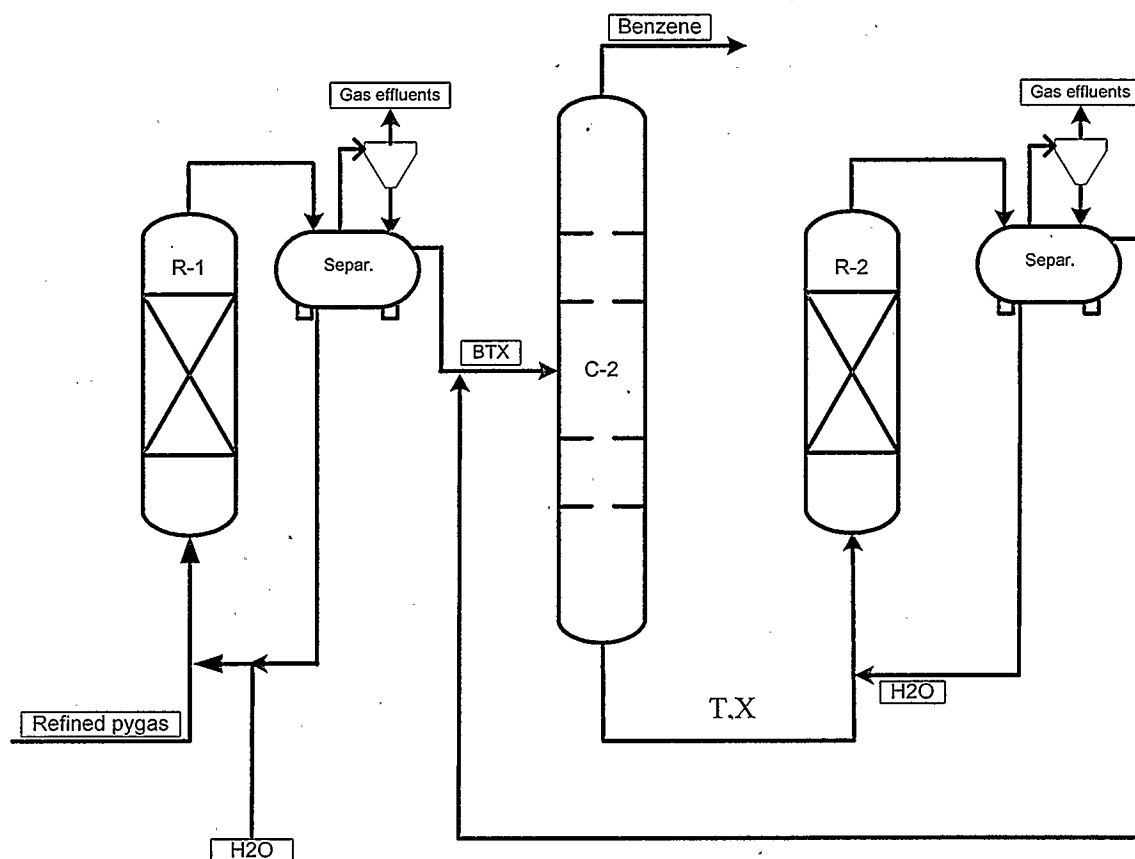


Figure 4.22: Flow scheme of pygas steam dealkylation

Table 4.18: Mass balance calculations

R-1	kg	C-1	kg	R-2	kg
Liq.: Benzene to C-1	22.6	Head	37.1	Liq.: Benzene to C-	14.6
Liq.: C7_C9 to C-1	5.7	Bttm: C7_C9	9.5	Liq.: C7_C9 to C-1	3.7
gas	12.7	gas	-	gas	8.2
Pygas converted	41	Bttm: non	97.2	Pygas converted	26.5
Liq.: non convr. to C-1	59	Bttm: total	106.7	Liq.: non convr.	38.2
Liq.: total to C-1	87.3	Feed: to C-1	143.8	Liq.: total to C-1	56.5

The above table shows calculations results based on 100 kg/h of Pygas. At the considered reaction conditions conversion of water is about 39 %. The benzene selectivity is 71.9 mol. % which amounts to 37 kg/h of benzene. The total gas produced is about 21 kg/h. A total yield to benzene from pygas of 62.3 % is ideally possible.

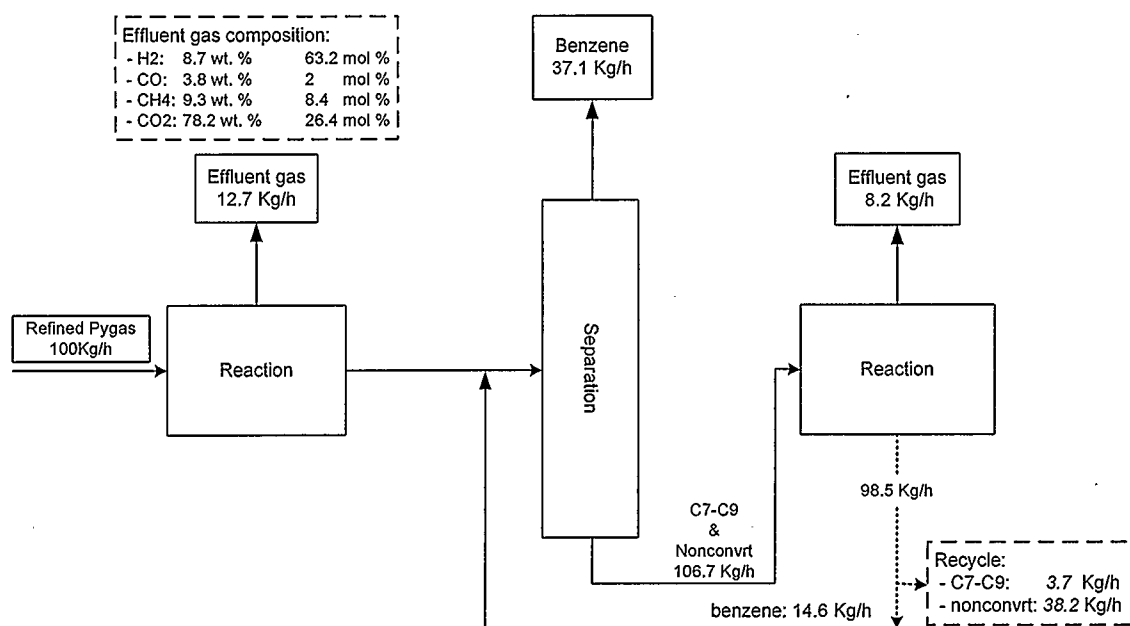


Figure 4.23: Mass balance chart

Understandably there are missing details in this chapter, which need to be specified and studied more carefully in order to achieve conceptual engineering of this process. For instance, the response of the catalyst to more severe reaction conditions and heavier aromatic compounds in the second reactor, its stability in the presence of Pygas, and its regenerability. Furthermore, different distillation columns may be used depending on the required benzene quality. The efficiency of liquid-liquid separators may not be sufficient; therefore, other separation techniques may be added. The final apparatus arrangements may be optimized after a laboratory pilot plant is defined and tested. It is evidently premature to discuss the economic attractiveness of the Pygas SDA. This in addition will greatly depend on many other parameters; like the BTX formation process and composition, technology selected to separate the BTX fraction, sulphur content, catalyst stability and reactivation, etc.

Without doubts, Pygas SDA, as an alternative for benzene production, has to overcome several challenges in order to be competitive with the very well established toluene hydrodealkylation technology. For comparison purposes the conversions of toluene hydrodealkylation process normally reach 90 % and selectivity to benzene is often around 95 %. Meanwhile for toluene steam dealkylation (synonymous of Pygas SDA) the highest conversion reaches 60 % with about 60 % benzene selectivity and the maximum selectivity to benzene was 80 % at 40 % toluene conversion.

At this stage, the advantages of SDA process over HDA are the mild reaction conditions and the use of water instead of hydrogen. The steam dealkylation process actually produces hydrogen, while HDA consumes it.

Most of the research on this topic was conducted in the beginning of the 80's, and then some in the 90's. It is evident that there is a lack of studies in recent years. From the results presented, the need of further research and development on the topic is justified. A detailed research program may help to generate a more effective catalyst to enhance the benzene production via SDA. This would be the case particularly, if the demand for hydrogen increases, the current HDA technology becomes expensive and is unable to satisfy the market demand for benzene.

Chapter Five: Conclusions and Recommendations

5.1 Conclusions

The following conclusions and recommendations stem from the results and discussions just presented:

1. In the presence of alumino-rhodium catalysts at temperatures of 400-440 °C, toluene is dealkylated by interaction with water to form mainly benzene and gaseous by-products that contain hydrogen, methane, carbon monoxide and carbon dioxide.
2. Catalyst formulations containing alkali-earth alkali with reduced Rh content were developed. Experimental results, when using pure components such as toluene, are indicative that this catalyst has higher selectivity and productivity per metal atom towards benzene than the catalyst with higher Rh content. Considering that Rh is an expensive metal, this reduced proportion adds an economical value to the catalyst.
3. The introduction of the alkali-earth alkali to the alumina-support has definitely delayed the catalyst deactivation. Experimental results of the toluene-naphthalene mixture on the alkali-earth alkali catalyst show that significantly low deactivation rate and conversion was maintained during extended reactivity runs.
4. Composition of the gas products, when benzene reacts with water at similar reaction conditions of toluene SDA, suggest that the freshly formed benzene undergoes further decomposition and therefore it may be an important source of aromatic ring degradation.
5. Research presented in this thesis has shown that important advances in the catalyst design can still be achieved, which might make the steam dealkylation of abundant alkylaromatic-streams an attractive process for petrochemical applications in an environment of constrained hydrogen availability.

5.2 Recommendations

1. It is recommended that the activity and selectivity performance of alkali-earth alkali-rhodium catalysts, in terms of sulphur resistance by using toluene-thiophene mixture as reactants be evaluated.
2. Since heavy feedstocks (shale oils, Vacuum Gas Oils, or, others) are rich in aromatics, it makes sense to explore the possibility of developing two different catalytic systems. One designed for steam dealkylation of monocyclic alkyl aromatics and the other to be engaged in the steam conversion of condensed aromatic rings to produce benzene and hydrogen.
3. Further investigation of the role inert gas addition on conversion, and selectivity is needed.
4. An improvement in the catalyst performance could be reached by combining several transition metals with K-Ca binary oxide, as well as by using other alkali-earth alkali metal oxide combinations that may be even more active than the K or Ca.

References

1. Alibeyli, R., et al., *Development of a polyfunctional catalyst for benzene production from pyrolysis gasoline*. Applied Catalysis A: General, 2003. **238**(2): p. 279.
2. Maslyanskii, G.N., Rabinovich, G. L., *Demethylation of toluene by conversion with steam*. Petroleum Chemistry U.S.S.R., 1962. **1**(1): p. 104-109.
3. Duprez, D., *Selective steam reforming of aromatic compounds on metal catalysts*. Applied Catalysis A: General, 1992. **82**(2): p. 111-157.
4. Weitkamp, J.R., A.Traa, Y., *Novel zeolite catalysis to create value from surplus aromatics: preparation of C₂+*n*-alkanes, a high-quality synthetic steamcracker feedstock*. Applied Catalysis A: General, 2001. **222**(1-2): p. 277.
5. Web site, *Chem. World*.
www.rsc.org.ezproxy.lib.ucalgary.ca/chemistryworld/Issues/2005/November/landscape.asp, Accessed 2007.
6. World., C., www.rsc.org/chemistryworld/Issues/2005/November/landscape.asp, 2007.
7. Bus. Communications Comp., I., <http://www.bccresearch.com>, 2007.
8. Scherzer, J. and A. Gruia, *Hydrocracking science and technology*. Chemical industries; v. 66. 1996, New York: Macel Dekker.
9. Uhde-GmbH, *Aromatics*.
http://www.uhde.biz/cgi-bin/byteserver.pl/archive/upload/uhde_brochures_pdf_en_16.00.pdf.
10. Fishbein, L., *An overview of environmental and toxicological aspects of aromatic hydrocarbons. I. Benzene*. The Science of The Total Environment, 1984. **40**(1): p. 189.
11. Tsai, T.C., S.B. Liu, and I. Wang, *Disproportionation and transalkylation of alkylbenzenes over zeolite catalysts*. Applied Catalysis A: General, 1999. **181**(2): p. 355.

12. Serra, J.M., E. Guillon, and A. Corma, *A rational design of alkyl-aromatics dealkylation-transalkylation catalysts using C8 and C9 alkyl-aromatics as reactants*. Journal of Catalysis, 2004. **227**(2): p. 459.
13. Rabinovich, G.L., G. N. Maslyanskii, *A new process for Toluene Dealkylation*. Translation from: Khimiya i Tekhnolgiya Topliv i Masel, 1973. **2**: p. 1-2.
14. Wikipedia, <http://en.wikipedia.org/wiki/Benzene>. 2007.
15. Duprez, D., P. Pereira, Miloudi, A, and R. Maurel, *Steam Dealkylation of Aromatic-Hydrocarbons.2. Role of the Support and Kinetic Pathway of Oxygenated Species in Toluene Steam Dealkylation over Group-Viii Metal-Catalysts*. Journal of Catalysis, 1982. **75**(1): p. 151-163.
16. Grenoble, D.C., M.M. Estadt, and D.F. Ollis, *The chemistry and catalysis of the water gas shift reaction: 1. The kinetics over supported metal catalysts*. Journal of Catalysis, 1981. **67**(1): p. 90-102.
17. Grenoble, D.C., *The chemistry and catalysis of the water/toluene reaction: 2. The role of support and kinetic analysis*. Journal of Catalysis, 1978. **51**(2): p. 212-220.
18. Beltrame, P., Casalone, G, Forni, L.Ferino, I.,Marongiu, B and S. Torrazza, *Kinetics and Products Inhibition Effects in Toluene Steam Dealkylation over Rh/Cr₂O₃/Gamma-Al₂O₃*. Industrial & Engineering Chemistry Process Design and Development, 1984. **23**(1): p. 176-179.
19. Pereira, P., *Etude de la Dealkylation Catalytique du Toluene par Vapeur d'Eau*. 1979, L'Unersite De Potiers.
20. Rabinovich, G.L., Maslyanskii, G. N, Vorob'ev, V. S, Biryukova, L. M, Ioffe, I. I., *Demethylation of toluene by reaction with steam under pressure*. Petroleum Chemistry U.S.S.R., 1973. **13**(3): p. 155 -160.
21. Treiger L. M, Rabinovich G. L, and Maslyanskii G. N, *Toluene conversion by interaction with steam on rhodium catalyst*. Neftechimiya, 1972. **12** (1): p. 1-5.
22. Maslyanskii, G.N., Rabinovich, G. L., Neftechimiya, 1962. **2**: p. 709.
23. Rostrup-Nielsen, J.R., *Activity of nickel catalysts for steam reforming of hydrocarbons*. Journal of Catalysis, 1973. **31**(2): p. 173.
24. Rabinovich, G.L., Mozhaiko, V. N., Neftekhimiya, 1975. **15**: p. 373.

25. Duprez, D., A. Miloudi, and P. Pereira, *Steam dealkylation of aromatic hydrocarbons: II. Role of the support and kinetic pathway of oxygenated species in toluene steam dealkylation over group VIII metal catalysts*. Journal of Catalysis, 1982. **75**(1): p. 151-163.
26. McNaught, W.G., C. Kemball, and H.F. Leach, *Some catalytic exchange reactions with deuterium oxide on evaporated metal films*. Journal of Catalysis, 1974. **34**(1): p. 98.
27. Ferino, I., B. Marongiu, and S. Torrazza, Forni, L, *Toluene Steam Dealkylation over Rh-Al₂O₃ - Effect of the Support*. Reaction Kinetics and Catalysis Letters, 1980. **15**(1): p. 95-101.
28. Balandin, A.A., Masljansky G.N, Slovochtova T.A, Rabinovich G.L, *Catalytic dealkylation of alkyl aromatic hydrocarbons by means of steam*. 7th World Petrol. Congr., Mexico, 1968. **8**: p. 121.
29. Maslyanskii, G.N., G.L. Rabinovich, and N.K. Avtonomova, *Catalytic dealkylation of trimethylbenzenes*. Petroleum Chemistry U.S.S.R., 1966. **5**(2): p. 112 -119.
30. Maslyanskii, G.N., Rabinovich, G. L.,Brisker, K. L.,Avtonomova, N. Kh, *Catalytic dealkylation of isopropylbenzene and tert.-butylbenzene*. Petroleum Chemistry U.S.S.R., 1966. **6**(3): p. 178 -183.
31. Duprez, D., Miloudi, A., Delahay, G.,Maurel, R., *Selective steam reforming of aromatic hydrocarbons: V. Steam conversion and hydroconversion of selected monoalkyl- and dialkylbenzenes on Pt and Ni catalysts*. Journal of Catalysis, 1986. **101**(1): p. 56.
32. Duprez, D., Miloudi, A., Delahay, G.,Maurel, R., *Selective steam reforming of aromatic hydrocarbons: IV. Steam conversion and hydroconversion of selected monoalkyl- and dialkyl-benzenes on Rh catalysts*. Journal of Catalysis, 1984. **90**(2): p. 292-304.
33. Kim, C.J., *Noble metal-catalyzed water-hydrocarbon reaction paths*. Journal of Catalysis, 1978. **52**(1): p. 169-175.

34. Yamamoto Mitsuyoshi, Y.R., Maekawa Yosuke and K. Takeshi, *Selective steam reforming of alkylated hydrocarbons and coal liquids over NiO/Fe₂O₃ catalysts*. Applied Catalysis, 1990. **64**: p. 55.
35. Chen, I. and D.W. Shiue, *Resistivity to sulfur poisoning of nickel-alumina catalysts*. Ind. Eng. Chem. Res., 1988. **27**(8): p. 1391-1396.
36. Praliaud, H., Dalmon, J. A., Mirodatos, C, Martin, G. A., *Influence of potassium salt addition on the catalytic properties of silica-supported nickel*. Journal of Catalysis, 1986. **97**(2): p. 344.
37. Chen, I. and F.L. Chen, *Effect of alkali and alkaline-earth metals on the resistivity to coke formation and sintering of nickel-alumina catalysts*. Ind. Eng. Chem. Res., 1990. **29**(4): p. 534-539.
38. Ertl, G., M. Weiss, and S.B. Lee, *The role of potassium in the catalytic synthesis of ammonia*. Chemical Physics Letters, 1979. **60**(3): p. 391.
39. Lang, N.D., S. Holloway, and J.K. Norskov, *Electrostatic adsorbate-adsorbate interactions: The poisoning and promotion of the molecular adsorption reaction*. Surface Science, 1985. **150**(1): p. 24.
40. Blackmond Donna G, W.J.A., Kesraoui Sabeha and D.S. Blazewick, *The effects of Cs promotion on Rh/Al₂O₃ catalysts*. Journal of Catalysis, 1986. **101**(2): p. 496.
41. Chai, G.Y., Falconer, John L., *Alkali promoters on supported nickel: Effect of support, preparation, and alkali concentration*. Journal of Catalysis, 1985. **93**(1): p. 152.
42. Crossley, A. and D.A. King, *Infrared spectra for co isotopes chemisorbed on Pt "111": Evidence for strong adsorbate coupling interactions*. Surface Science, 1977. **68**: p. 528.
43. Hammaker, R.M., S.A. Francis, and R.P. Eischens, *Infrared study of intermolecular interactions for carbon monoxide chemisorbed on platinum*. Spectrochimica Acta, 1965. **21**(7): p. 1295.
44. Stoop, F., F.J.C.M. Toolenaar, and V. Ponec, *Geometric and ligand effects in the infrared spectra of adsorbed carbon monoxide*. Journal of Catalysis, 1982. **73**(1): p. 50.

45. McClory, M.M. and R.D. Gonzalez, *The role of alkali metals as promoters in the methanation and Fischer-Tropsch reaction: An in situ study*. Journal of Catalysis, 1984. **89**(2): p. 392.
46. Rabinovich, G.L., Mozhaiko, V. N, Curtit, F., *Dealkylation of alkylbenzene fractions by steam conversion*. Translation from: Khimiya i Tekhnolgiya Topliv i Masel, 1988. **7**: p. 11-15.
47. Pereira P, *unpublished technical report*. 2006.
48. ChemBET 3000, *operation manual*. 2003. Quantachrome Instrument.
49. Smith, J.M., *Chemical Engineering Kinetics*. 3rd ed. 1973: McGraw Hill. 331.
50. Duprez, D., *Review: Catalytic converters for reducing pollution caused by traffic*. Journal De Chimie Physique Et De Physico-Chimie Biologique, 1995. **92**(11-12): p. 1952-1983.
51. Duprez, D., *Study of surface reaction mechanisms by O-16/O-18 and H/D isotopic exchange*. Catalysis Today, 2006. **112**(1-4): p. 17-22.
52. Pereira, P., Eldood, A, Peluso, E, Sosa, C., Lopez, F., *Unpublished technical report*. 2005.
53. Wells, G.M., *Handbook of Petrochemicals and processes*. 1991.
54. Waddams, A.L., *Chemicals from Petroleum*. 4th ed. 1980.
55. Othmer, K., *Encyclopedia of Chemical Technology*. Vol. 4. 1996: John Wiley and Sons.

Chapter Six: Appendixes

6.1 Appendix A

Table 6.1: Results of different catalysts at 440°C and 2bar

Catalyst	Rh-X		Rh-2		Rh-3		Rh-4	
	Average	STD Dev.	Average	STD Dev.	Average	STD Dev.	Average	STD Dev.
WHSV, h ⁻¹	1.0	0.03	1.0	0.09	0.9	0.04	0.9	0.03
H ₂ O:HC	7.5	0.37	7.8	0.35	6.5	0.42	8.0	0.36
Tol.Conv., %	42.5	0.510	60.2	0.85	64.0	0.83	40.9	0.97
Selectivity								
Benzene	0.7	0.01	0.7	0.05	0.7	0.02	0.8	0.01
Xylene	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
Ethylbenzene	0.0	0.00	0.0	0.01	0.0	0.00	0.0	0.00
Naphtalene	0.0	0.00	0.0	0.00	0.0	0.00	0.0	0.00
H ₂	3.9	0.15	3.5	0.10	4.0	0.48	3.8	0.11
CO	0.1	0.00	0.1	0.01	0.2	0.05	0.1	0.01
CH ₄	0.5	0.08	0.8	0.08	0.6	0.09	0.5	0.00
CO ₂	1.9	0.02	1.8	0.04	1.8	0.18	1.6	0.04

6.2 APPENDIX B

6.2.1 Calculations

Space velocity:

$$\text{WHSV (h}^{-1}\text{)} = \frac{\text{HC mass flow (g/h)}}{\text{Cat. mass (g)}}$$

$$\text{WHSV} = \frac{0.026 \text{ (g/h)}}{1.572 \text{ (g)}} = 1 \text{ h}^{-1}$$

6.2.1.1 Mass Balance

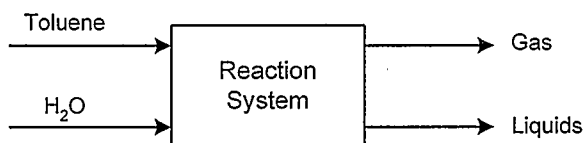


Figure 6.1: Block diagram of the experimental system

Figure 6.1 shows a simplified diagram for the inlet and outlet streams. The inlet streams to the system are the toluene and steam, which enters the reactor as mixture. The outlet includes a gas stream which contains H₂, CH₄, CO, CO₂ and liquid stream which contains the produced benzene, un-reacted toluene and the condensed steam. The gases and the liquids are quantified by a GC-TCD and a GC-MS respectively and the results are presented in mol. % and wt. %.

In the following, examples of mass balance calculations and other calculations, such as selectivity and toluene conversion, are presented for experiment data in Table 6.3 at 400 °C.

6.2.1.2 Gases

Molar Flow, mol per min, of gas effluents, F_{Gm} :

$$F_{Gm} = \frac{P * F_G}{R * T * 1000}$$

$$F_{Gm} = \frac{0.92 * 17}{0.0821 * 296 * 1000} = 0.00064 \text{ mol/min}$$

Moles of gas species:

$$N_G = X_G * F_G * \tau$$

For hydrogen is as follows:

$$N_{H_2} = X_{H_2} * F_{H_2} * \tau = 0.62 * 0.00064 * 710 = 0.283 \text{ mol}$$

Gas Selectivity:

$$S_G = \frac{N_G}{N_T}$$

Gas selectivity is calculated for hydrogen as follows:

$$S_{H_2} = \frac{N_{H_2}}{N_T} = \frac{0.283}{0.084} = 3.37$$

The selectivity to different compounds SDA reactions is presented in below:

Table 6.2: Selectivity of different compounds

Compound	Selectivity (mol.%)	Standard deviation
Benzene	0.80	0.003
Xylene	0.01	0.001
Ethylbenzene	0.00	0.000
Naphtalene	0.00	0.000
H ₂	3.94	0.250
CO	0.11	0.033
CH ₄	0.53	0.038
CO ₂	1.68	0.004

6.2.1.3 Liquids:

Mass of Benzene in liquid collected:

$$B_e = X_B * A_e$$

$$B_e = X_B * A_e = 0.3283 * 16.132 = 5.30\text{g}$$

Moles of Benzene:

$$N_B = \frac{B_e}{MW_B}$$

$$N_B = \frac{5.30}{78} = 0.068\text{mol}$$

Selectivity of Benzene: see Table 6.2 for selectivity values of different compounds.

$$S_B = \frac{N_B}{N_T}$$

$$S_B = \frac{0.068}{0.084} = 0.81$$

Amount of toluene converted (N_T) is found as follows:

$$N_T = T_i - T_e$$

Toluene conversion (T_{conv}) is calculated as follows:

$$T_{\text{conv.}} = \frac{N_T}{T_i} * 100$$

$$T_{\text{conv.}} = \frac{7.713}{18.422} * 100 = 42 \%$$

6.2.1.4 Global mass balance

The global mass balance closure is determined by:

$$\text{Global mass balance} = \frac{m_e}{m_i} \times 100 = \frac{43.945g}{46.016g} = 95.5\%$$

6.2.2 Mass balance correction

The mass balance of all experiments was closed with about 95 % to 100 %. In cases where the mass balance was not closed by 100 %, the closure then was achieved by correction of the uncompleted mass balance. The results reported in this thesis work are from the corrected mass balance. Followed are the examples of calculations:

6.2.2.1 Oxygen balance:

$$O_{\text{bal}} = \frac{N_{CO} * 16 + N_{CO2} * 32 - N_{CH4} * \frac{16}{18}}{(W_i - W_e) * \frac{16}{18}} * 100$$

$$O_{\text{bal}} = \frac{0.004 * 16 + 0.133 * 32 - 0.037 * \frac{16}{18}}{(27.596 - 22.776) * \frac{16}{18}} * 100 = \frac{4.287}{4.287} = 100\%$$

6.2.2.2 Difference in oxygen balance

Presents the lost oxygen during the reaction and is found from the following:

$$O_{dif} = \left((W_i - W_e) * \frac{16}{18} + N_{CH_4} * \frac{16}{18} \right) - (N_{CO} * 16 + N_{CO_2} * 32)$$

The corrected mass balance (A_{corr}) is determined from the lost amount in mass and oxygen during the reaction:

$$A_{corr} = A_{e_0} + (m_i - m_e) - O_{Dif}$$

$$A_{corr} = 14.15 + (46.016 - 43.945) + 0.089 = 16.13g$$

Table 6.3: Data used for mass balance calculations

Parameter	Value
Catalyst mass, g	1.572
Gas flow, cc/min	17
Pressure, atm	0.92
Temperature, K	296
Balance time, min	710
Hydrogen mol. fraction	0.62
Total molar gas Flow, mol/min	0.00064
Toluene feed, cc/min	21.3
Water feed, cc/min	27.7
Total amount of toluene In (Ti), g	18.422
Toluene mass flow, g/h	0.026
Total amount of toluene converted (N_T), g	7.713
Converted moles of Toluene	0.084
Benzene fraction, X_B	0.3283
Hydrocarbon collected in reservoir (Ae), g	16.13
Hydrocarbon collected in reservoir before correction (Ae0), g	14.150
Total products mass Out (me), g	43.945
Total feed mass In (mi), g	46.016

Table 6.4: Physical properties

Parameter	Value
Toluene Density, g/cm^3	0.8668
MWT, g/mol	92
MWB, g/mol	78
MWH ₂ O, g/mol	18

6.2.2.3 Reaction rate

The reaction rate is defined as the moles reacted per catalyst metal content per hour. It was calculated for different catalysts from:

$$\text{reaction rate} = \frac{\text{converted toluene moles}}{\% \text{ Rh of catalyst} * \text{hour}}$$

For Rh-3 and the following data: Moles of toluene converted: 0.0165 mol.; Catalyst mass: 1.906g; Metal content: 0.3 wt. % Rh; Time: 1.83h, we can obtain the reaction rate for toluene as:

$$\text{reaction rate} = \frac{0.0165 \text{ moles of toluene converted}}{0.6\% * 1.608\text{g} * 1.83\text{h}} = 0.93$$

6.2.2.4 Activation energy:

The activation energy using the Arrhenius equation:

$$\ln k = -\frac{E_a}{RT} + \ln A$$

The above equation can be expressed the familiar form $y = -mx + b$. then a plot of $\ln k$ versus $1/T$ produces a straight line with a slope m .

where:

$$x = 1/T$$

$$y = \ln k$$

$$m = -E_a/R$$

$$b = \ln A$$

k is expressed as mmol of toluene converted per mass of catalyst per hours

Calculation example:

Toluene converted = 0.1417mol

Mass of catalyst = 1.609g

Mass balance time = 2hr

$$k = \frac{0.01417 * 1000}{2 * 1.609} = 4.4$$

$$\ln 4.4 = 1.5$$

The activation energy E_a can be determined from the slope m of this line:

$E_a = -m * R$. The reported activation energy value was determined from runs completed at different reaction temperatures. The temperature intervals used was 10°C.