NOVEL ADDITIVES FOR SIDE CHAIN ALKYLATION OF TOLUENE AND METHANOL TO FORM STYRENE

BY

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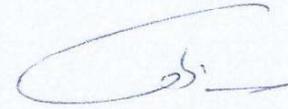
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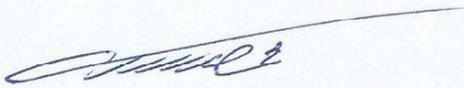
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DEDICATION

This work is dedicated to Almighty Allaah (SWT), the Entirely Merciful, the Especially Merciful.

- To Prophet Muhammad (SAW), the Mercy to the worlds of Mankind and Jinn.
- To my parents, Mr. and Mrs. Akanni Amusa, that showed me the values for knowledge.
- To my wife (Rasheedah Oluwatoyin Amusa-Abdulhameed) and my children (Alhasan, Za'faran and Labeebah) for their understanding when the challenges demanded leaving them at home for months.
- To my elder brothers and sister as well as my siblings in the family of Amusa.
- To my comrades in Agege Area council of Muslim Students' Society of Nigeria in Lagos State.
- To the entire Elegbede family for being there for me when it was difficult defining my focus.
- To the entire Vanguards Academy family for taking care of my family in my absence.

Finally, to everyone striving in acquiring knowledge to contribute to the invitation of man to the path of Al-Islam.

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I cannot but appreciate all those that have supported me during the course of this program in any form.

Conclusively, I give thanks to the Center for Refining and Petrochemicals and the entire staff of the Department of Chemical Engineering at King Fahd University of Petroleum and Minerals. Long live the Federal Republic of Nigeria, Long live the Kingdom of Saudi Arabia.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SCHEMES

LIST OF ABBREVIATIONS

MeOH - Methanol

EB- Ethyl benzene

St- Styrene

TOS- Time on stream

Mol. %- mole percent

GC- Gas Chromatography

BET- Brunauer, Emmett and Teller, surface area and pore size distribution analysis

XRD- X-Ray Diffraction analysis

THESIS ABSTRACT

Name: **ABIODUN ABDULHAMEED AMUSA**

Title of Study: **NOVEL ADITIVES FOR SIDE CHAIN ALKYLATION OF**
                             TOLUENE AND METANOL TO FORM STYRENE

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Styrene is produced from the side chain alkylation of toluene and methanol over zeolite X mechanically mixed with different amounts of zinc oxide and cesium oxide. The added amount of zinc oxide and cesium oxide were varied from 5 to 20 %.

Experimental data were collected from a fixed bed reactor at 410 ^{0}C and atmospheric pressure. The data obtained showed that conversion of toluene varied from 3 to 7 % and that selectivity towards styrene varied from 50 to 80 %. The best conversion and selectivity was obtained for zeolite X mechanically mixed with 10 % zinc oxide and 10 % cesium oxide.

Samples of the synthesized catalysts were characterized using Scanning Electron Microscopy (SEM), Brunauer Emmett and Teller (BET), X-Ray Diffraction (XRD), and Fourier Transform Infrared Spectroscopy (FTIR). The SEM analysis showed that zinc oxide particles are the small particles that are attached to the larger crystallites. The BET showed that there is no observable effect on the normalized surface area. The XRD showed no separate phases of zinc oxide and

cesium oxide. The pyridine adsorption FTIR showed an evidence of basicity. Addition of zinc oxide slightly reduced the strength of Lewis Acid sites of zeolite X while the addition of cesium oxide showed no effect on the Lewis acid sites of zeolite X.

The methanol adsorption FTIR showed a single peak at 1690 cm^{-1}. That suggests the formation of unidentate formate which is responsible for suppressing transfer hydrogenation reaction and consequently has positive impact on both conversion of toluene and styrene selectivity

ملخص الرسالة

الاسم : ابيدون عبد الحميد اموسى

عنوان الدراسة : الاضافات الجديدة لسلسلة المتكيلات من التولين و الميثانول الى الستايرين

الدرجة : الماجستير العلمي

نطاق التخصص : هندسة كيميائية

تاريخ الدرجة العلمية :سبتمبر 2015 م

تم إنتاج مادة الستايرين من خلال مفاعلة الميثانول والتلوين على حفاز ال x زيولايت المعدل ميكانيكياً بإضافة مقادير مختلفة من مادتي أوكسيد السيزيوم وأكسيد الزنك بنسب تراوحت من 5 إلى 20 بالمائة.

أظهرت معلومات التفاعل التي أجريت في مفاعل ثابت تحت ضغط جوي واحد و درجة حرارة 410 درجة مئوية أن معدل تحويل التلوين تراوح ما بين 4 إلى 7 بالمائة، بينما تراوحت نتائج استخلاص الستايرين من 50 إلى 80 بالمائة. وكانت النسبة الأفضل لحفاز الزيولايت المعدل ميكانيكياً بنسبة 10% أوكسيد السيزيوم و 10% أكسيد الزنك.

تم فحص عدة عينات من الحفازات المعدلة ميكانيكياً باستخدام تقنيات الـ SEM، BET، FTIR XRD. أظهرت نتائج SEM ظهور مادة الزنك بجزيئات صغيرة متعلقة بالبلورات الأكبر حجماً، كما أظهرت نتائج BET عدم تأثر مساحة الحفاز بإضافة مادة أوكسيد الزنك. كذلك أظهرت نتائج الـ XRD عدم إنفصال أوكسيد الزنك عن أوكسيد السيزيوم. وكذلك أظهرت نتائج الـ"FTIR" أن إضافة أكسيد الزنك أثر في قاعدية الحفازات مع تأثر صغير لحمضية مواقع لويس. كما أظهرت نتائج هذا الفحص وجود عمود عند درجة 1690 سم$^{-1}$ يشير إلى تقليص دور التفاعل الناقل للهيدروجين مما أدى إلى زيادة نسبة تحويل التلوين وكذلك زيادة نسبة إنتاج الستايرين.

CHAPTER ONE
INTRODUCTION

1.1   Styrene Background Studies

An interesting reaction is observed as a result of toluene and other methylbenzenes' side-chain alkylation using methanol. Toluene alkylation is the production of xylene over acidic catalyst or ethyl benzene and styrene over basic catalyst. Regardless of the choice of catalyst, petrochemical industry cannot but underscore the products of toluene alkylation.

Xylenes are organic hydrocarbons that contain benzene ring with two methyl substituents. Xylenes are clear, known to be colorless, with three aromatic hydrocarbon isomers characterized with sweet-smell obtained from crude oil with the help of a process known as reforming. Para-xylene, ortho-xylene and meta-xylene are the three isomers of xylene. The positions of the two methyl groups on the carbon atoms of the benzene ring is indicated with the para-, ortho-, and meta- prefixes.

1,2-dimethylbenzene 1,3-dimethylbenzene 1,4-dimethylbenzene
(ortho-xylene)   (meta-xylene)   (para-xylene)
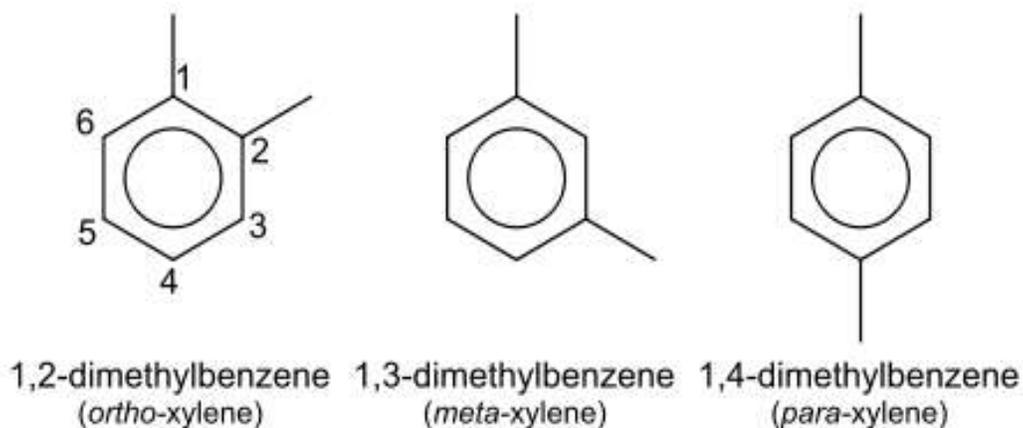
Figure 0-1. Three xylene isomers [1].

A plant family (Hamamelidacreae) has a member named liquidambar tree with a sticky substance. Styrene is also known as styrax balsam, the sticky substance. Naturally occurring styrene is said to be in very minute amounts in some plants and foods such as coffee beans and as well found in coal tar in traces. Natural styrax balsam can be isolated in other to isolate styrene via distillation as it was confirmed in the nineteenth century. The production of styrene by dehydrogenation of ethyl benzene was achieved in the 1930s. The United States witnessed a dramatic increase in the production of styrene and used popularly as a feedstock for synthetic rubber during the 1940s [2].

Styrene, sometimes referred to as ethenylbenzene, vinylbenzene and phenylethene, is a compound (organic) with the chemical formula $C_6H_5CH{=}CH_2$. Styrene is an oily liquid with sweet smell, colorless, evaporates easily, although high concentrations give a less refreshing odor [3].
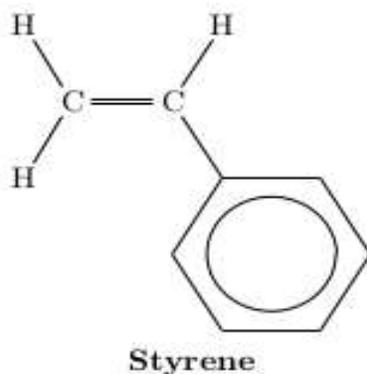
Figure 0-2. Chemical structure of styrene [3]

A laboratory production of styrene is achieved by the decarboxylation of cinnamic acid. This method brought styrene into lamplight. Styrene can be produced from benzene and ethane.

Development of this process was done by Snamprogetti S.p.A. and Dow. A dehydrogenation reactor is fed with ethane along with ethyl benzene using a catalyst suitable of yielding styrene and ethylene simultaneously. The waste gas due to dehydrogenation is cooled and followed by separation while the alkylation unit is used for the recycling of the ethylene stream. The aim of the process is to overcome wasteful recovery of aromatics, heavies and tars high levels of production, and poor separation of hydrogen as well as ethane. This technique is still undergoing developments [4, 5].

Styrene is a very useful monomer in producing polymers or copolymers of different types used in manufacturing toys, fiberglass, medical devices, food containers, and paper coatings. Majority of different polymers considers styrene as an intermediate raw material [6, 7].

It is established that styrene is a building block for production of numerous materials used throughout the whole wide world. Polymerization of styrene materializes due to the presence of the vinyl group. Collection of commercially available polymers containing styrene as main content is given in Figure 1-3 and Table 1-1. Figure 1-4 shows the market allotment for styrene in the manufacturing of polymers of different forms, while typical features and everyday uses of these polymeric materials are displayed in Table 1-1.

Before World War II, no significant record was available about the use of ethyl benzene as a raw material for styrene industry. During the war, the sharp SBR demand enhanced an accelerated technology improvement and capacity expansion. Figure 1-4 depicts the demand and supply of styrene globally. The growth was maintained at about 25 million metric tons in 2011 and 2012. A steady growth was observed from 2012 all through to 2017. At the moment, the market is

expected to grow by an increase of 1million tons/year for 2015 based on global new styrene capacity [9]. Figure 1-5 depicts styrene capacity breakdown by region in 2013.

Table 0-1: Typical features and habitudes of styrene containing polymers [8, 9,10]

(Co-)polymer	Typical features	Habitude
Polystyrene	Rigid, brittle, low strength	Package material (CD, MC), toy
Foamed polystyrene	Lightweight, rigid	Food package, protection,insulation
Acrylonitrile-butadiene-styrene	Rigid, thermal resistance, glossy	Toys, protection, chairs
Acrylonitrile-styrene	Clarity, chemical resistance	Auto lenses, medical devices
Styrene-butadiene rubber	High-performance elastomers	Shoe soles, conveyor belts
Styrene-butadiene latex	Thermal/chemical resistance	Paper coating, carpet adhesive
Styrene-*p*-divinylbenzene	Ion-exchange material	Separation or cleaning

Figure 0-3: Global styrene consumption 2013[11]
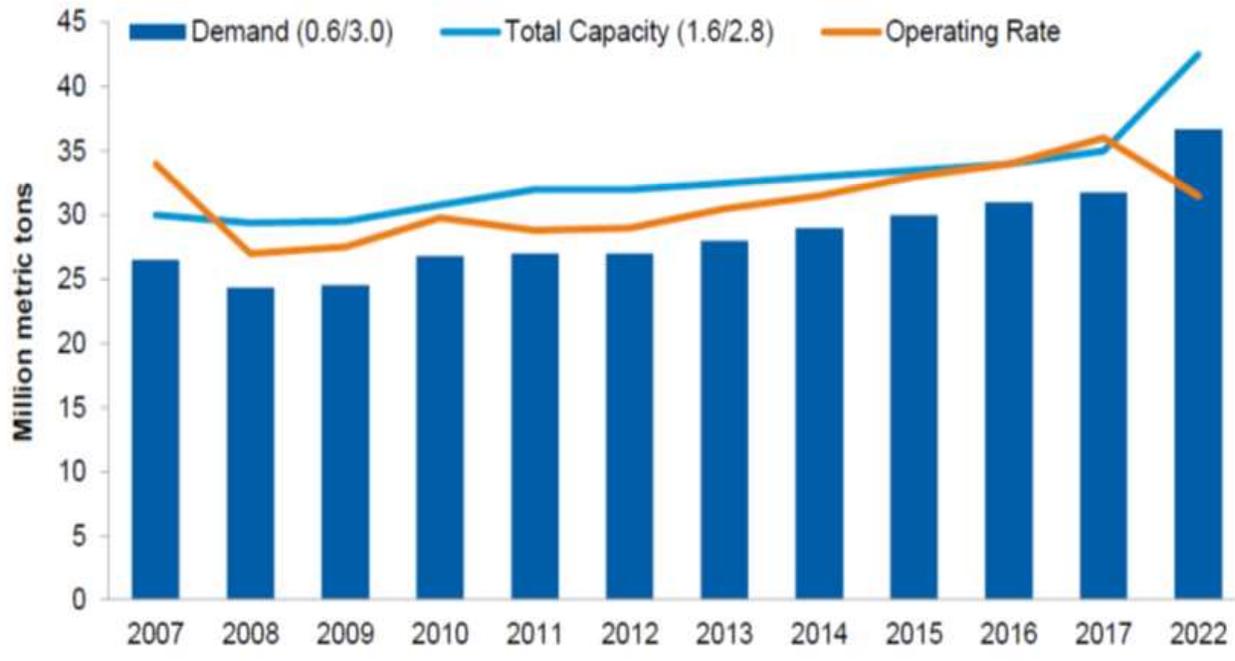
Figure 0-4: Global demand and supply for styrene [12]
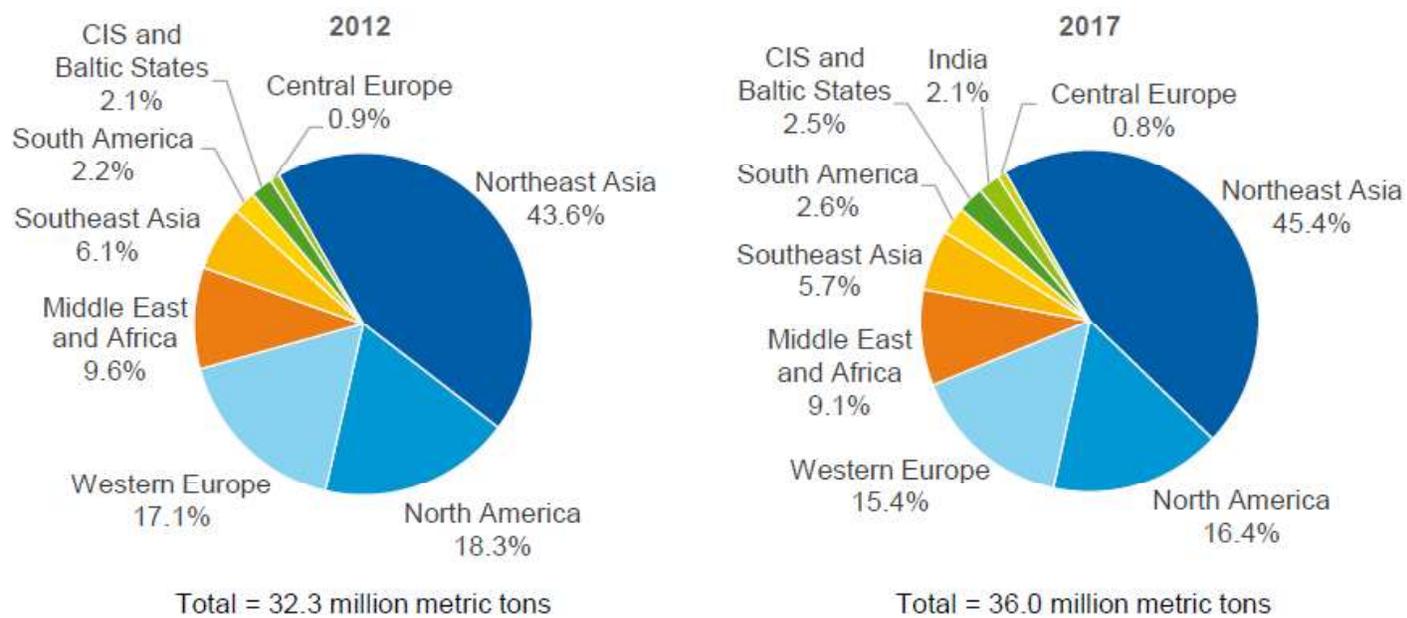
Figure 0-5: Styrene capacity breakdown by region in 2013 [12]

1.2   Commercial Production of Styrene

Several techniques have been explored for styrene monomer production. As an overview, commercial production has had a fair share of the following methods:

a) Ethyl benzene dehydrogenation.

b) Reaction of propylene oxide with ethyl benzene hydro peroxide (obtained from oxidation of ethyl benzene), followed by dehydration of alcohol to styrene.

c) α-phenyl ethanol is obtained from oxidation of ethyl benzene via acetophenone and subsequently followed by dehydration of alcohol to styrene.

d) Ethyl benzene chlorination by side-chain followed by dechlorination.

e) Ethyl benzene chlorination by side-chain, hydrolyzed to alcohol, and subsequently dehydrated.

f) Several petroleum processes can be adopted in pyrolysing petroleum recovery.

Commercially utilized routes to producing styrene are methods (a & b). Union-Carbide Corporation adopted method (c) but dehydrogenation process later replaced it. High cost of raw materials will be needed due to involvement of chlorine in methods (d & e) and has put researchers off and the monomer is contaminated with chlorine. Direct production of styrene from petroleum streams is difficult and costly.

Production of styrene is via two main commercial routes as stated earlier and they are; (1) the Styrene Monomer/Propylene Oxide (SMPO or POSM) process which entails the co-production with propylene oxide, and (2) adiabatic dehydrogenation of ethyl benzene (EB). The intermediate for the two routes is EB, which is obtained over either zeolite catalysts or aluminum chloride due to catalytic alkylation of benzene with ethylene. Installation of EB and styrene with matching capacities is almost always together due to conversion ability of approximately all the EB formed

to styrene. Other processes to produce styrene include Toray's STEX process (styrene extraction via pyrolysis gasoline) as well as EB dehydrogenation by isothermal Lurgi's process [13-15].

1.2.1 Styrene Monomer/Propylene Oxide (SMPO) Process

Halcon in the mid 1970's discovered this process and it was extended by Royal Dutch SHELL [16].This production route is used by Royal Dutch SHELL and it accounts for about 15% of the total global styrene production. Hence, encouraging formation of styrene using different approaches. Propylene-epoxide is used together with EB to produce styrene; auto-oxidation of EB by air is done to yield 90% activity of ethyl benzene hydroperoxide: *1*-phenylethanol and with 5-7% selectivity of acetophenone. Minimization of byproduct is achieved by keeping conversion very low (13%) [17-19]. Hydrogenation of acetophenone to *1*-phenylethanol in the liquid phase was done to improve the yields. Mixture of ZnO and CuO is used as catalyst. Conversion of acetophenone is estimated at approximately 90%, while selectivity to *1*-phenylethanol is 92%.

To produce propylene oxide (PO) concurrently with styrene monomer (SM) via a production route is tedious and expensive when compared with dehydrogenation of EB. SMPO process encompasses reaction with three steps:

a) Formation of ethyl benzene hydro peroxide (EBHP) from EB oxidation.

$$C_6H_5\text{-}CH_2CH_3 + O_2 \implies H_5\text{-}CH_2CH_2O_2H \tag{1-1}$$
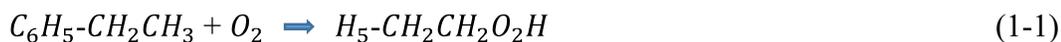
b) Formation of α-phenyl ethanol alongside propylene oxide by epoxidation of (EBHP) with propylene.

$$C_5H_5\text{-}CH_2CH_2O_2H + CH_3 \implies C_5H_5\text{-}CH_2CH_2OH + CH_3CHCH_2O \tag{1-2}$$
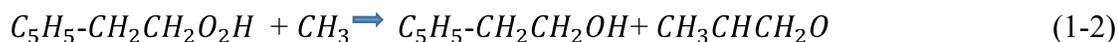
c) Formation of styrene by dehydration of α-phenyl ethanol.

$$C_5H_5\text{-}CH_2CH_2OH \implies C_5H_5\text{-}CH = CH_2 + H_2O \tag{1-3}$$
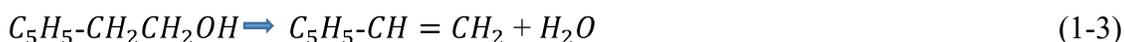
SMPO process in flow diagram is represented in figure 1-6. This process gives fewer by-products and less energy is consumed. The main shortcomings are due to; smaller quantity of propylene-epoxide required for the production of propylene glycol and polyurethanes which will in turn affect the formation of propylene-epoxide and the demand for high-pressure reactors (20-50 bars). SHELL is using cumene hydroperoxide from phenol plants as another source for oxygen [20].
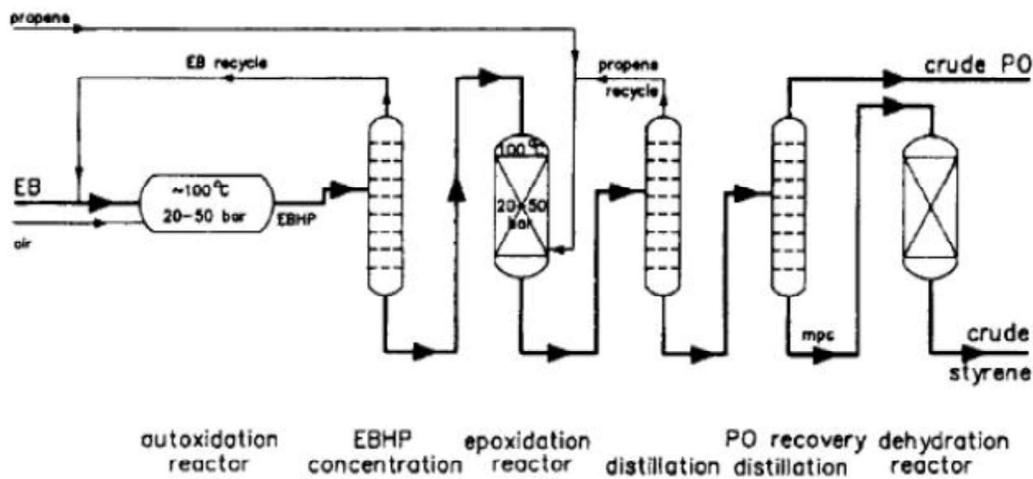
Figure 0-6: SMPO process in flow diagram [18, 19]

1.2.2 Adiabatic Dehydrogenation of Ethyl Benzene

This is the most important route to produce styrene commercially since it accounts for 90% of the total global production. IG Farbe in 1931 discovered and developed this process which was later modified and improved by an American styrene-producing company (ClassicSM^{TM} process) known as ABBLummus/UOP [17]. A SHELL company, Criterion Catalysts Corp., produced iron oxide catalyst (S-105, C-105, etc.) that are potassium-promoted, which was previously used for

the reaction [18, 19]. At the moment, majority of the catalyst retail share with G-64 and G-84 catalyst types is owned by the Süd-Chemie Group. Approximately 1-2 years is the average catalyst lifetime [20].

It has been found that for the ethyl benzene dehydrogenation reaction, an active potassium-ferrite phase ($KFeO_2$) is evidently effective. Although, from literatures, it is accepted that the initial $KFeO_2$ surface one started with is not the active sites on the catalysts [21, 22]. Nowadays, the active phase is taken to be a carbonaceous over-layer with surface containing carbon, oxygen and possibly hydrogen as deposits on the surface [23]. The conversion rate is observed to be high only after its formation. Surface carbonyl and quinone groups might be identified as the active sight [24, 25]. Polymerization of the product styrene gives coke deposits, and these coke deposits will decompose to form graphite-like structures on the catalyst surface by dehydrogenation. Initiation of polymerization of styrene to polystyrene is due to the presence of a Brönsted basic surface [26]. Gasification process of carbon deposits with steam is facilitated by potassium doping. Carbon monoxide (CO) and carbon dioxide (CO_2) are formed from the surface reaction between steam and carbon (C) deposited on that surface in a Sequence of steps. K_2CO_3 is used as catalyst.

a. $C + H_2O \implies CO + H_2$ (1-4)

b. $CO + H_2O \implies CO_2 + H_2$ (1-5)

It is evident that there is a complicated balance between the rate of coke boost (EB dehydrogenation active catalyst) and the rate of coke gasification (needed to avoid deactivation of catalyst). Build-up of coke and deactivation will arise due to an unevenness of this weak balance of rates under the following severe operating conditions; lower steam-to-aromatics (S/O) ratio (less than 7-12 mol/mol^{-1}), huge reaction temperature or the loss of promoter (K_2CO_3) for gasification.
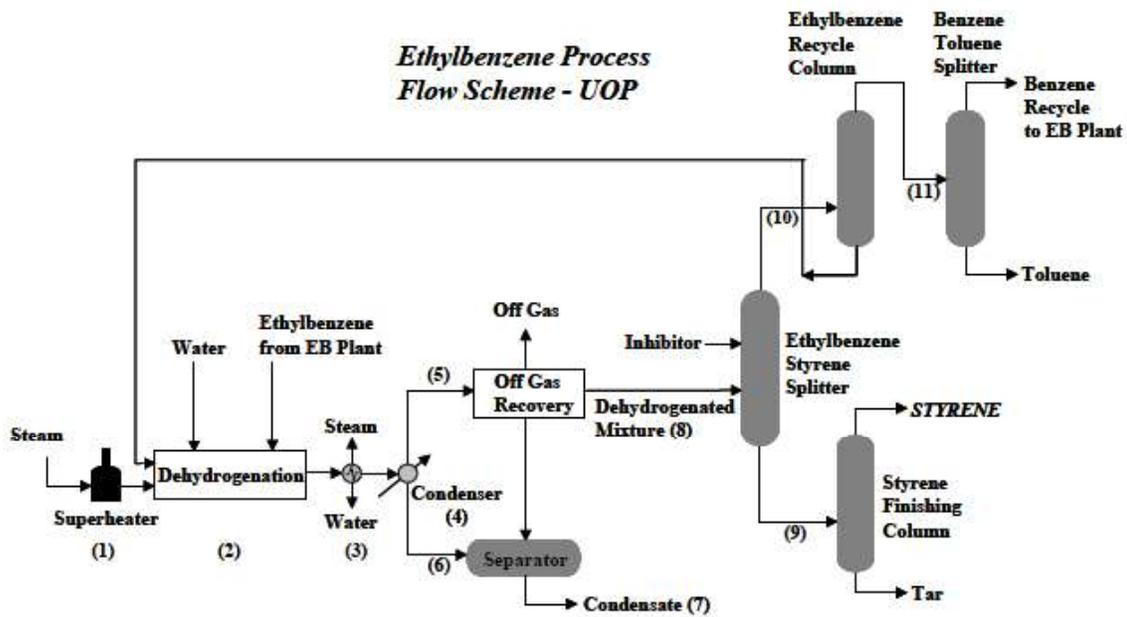
Figure 0-7: Flow diagram for a conventional adiabatic Lummus/UOP dehydrogenation plant for ethyl benzene [27]

Figure 1-7 depicts the flow diagram for a conventional adiabatic Lummus/UOP dehydrogenation plant for ethyl benzene and has the ensuing process steps and units:

A superheater (1) is used in other to excite the temperature of the reaction to an approximately 913K so as to generate steam at approximately 993K temperature from the system. A dehydrogenation unit (2) consisting of two radial flow reactors which are adiabatic in nature attached to a fixed bed. Reheating of the outlet stream is ensured before the second reactor is passed over since the process temperature drops due to adiabatic nature of the reaction. Fresh feed EB is mixed with the outlet from distillation system which is recycled EB, then vaporized and the steam is diluted as a result. Optimum yield with an accompanying minimum utility cost must be the choice of steam/ethyl benzene. Variation is often expected in the ethyl benzene conversion to be about 35% in the first reactor and 65% overall.

Safe lowest pressure of about 0.5-0.8 atm vacuum is needed, because low pressure is favorable for the reaction for efficient running of the reactor. Energy consumption is minimized by ensuring that heat recovery system which is efficient is used to receive the reactor effluent (3). Condensation (4) takes place, followed by separation into vent (off) gas (5) and a steam condensate (6). Compression, processing through the off gas recovery section of hydrogen and carbon dioxide, main components of vent (5),was ensured so as to obtain aromatics which are used as steam superheater fuel or as a chemical hydrogen feed stream. Steam- stripping, treatment and reuse take place in the steam condensate (6). Separation of hydrogen and water phases from each other takes place in the separator (7), in which the condenser (4) sends the condensates to it while gas recovery section (5) sends vent gas. Fractionation (8) of the dehydrogenated mixture gives styrene monomer product (9) and recycle EB (10), along-side by products (11) which are benzene, toluene and α-

methylstyrene. Thermal degradation of EB to benzene and catalytic degradation of styrene to toluene is due to competing reactions [28]. Addition of inhibitors, mostly free radical scavengers, prevents polymerization of styrene in the process equipment.

Styrene monomer purity of about 99.85 wt%, styrene-selectivity of over 97 mol% and typical conversions of EB up to 69% are obtained. This seems satisfying while the route has the following setbacks;

1. The ethyl benzene in dehydrogenation reaction is thermodynamically.

2. Catalyst deactivation

3. Operation of the reactor under vacuum

5. Costly inter-stage reheater

6. The superheated steam required for the reaction.

To overturn part of these shortcomings, a new process based on the Classic SM^{TM} process known as SMART Classic SM^{TM} was developed by ABBLummus/UOP [15, 28]. This process results in more than 80% EB conversion, very high purity of more than 99.85 wt% styrene monomer produced, with removal of the expensive inter-stage reheater and cutback of the superheated steam requirement.

1.3   Free Radical and Thermal Polymerization of Styrene

During storage, transportation and partly all along processing, thermal and free radical polymerization are the main challenges facing styrene production. Processing of styrene leads to distillation tower and other equipment being used to be fouled which means such styrene must be further treated before being appropriate for use. As such, substances that will inhibit the activity

14

of polymerization should be introduced into the feed containing crude styrene so as to minimize polymerization.

Inhibitors for styrene polymerization can be prorated into two:

a) Polymerization can be inhibited completely by some substances for as long as they are present in the styrene stream, these compounds are known as 'true inhibitors'. Free radicals scavengers are most frequently inhibitors with a *1*-piperidinuloxy or catechol structure. Example, using *para*-tertiary-butylcatechol, abbreviated as *p*-TBC, at a *p*-TBC level of $12\ mgKg^{-1}$ will ensure 6 months for monomer lifetime at ambient temperature which is equivalent to 3 months at 303 K [29]. Effectiveness of inhibitors will be established only in the presence of small amount of oxygen.

b) Retarders are the second groups of inhibitors for polymerization of styrene. Retarders only impede the rate of polymer growth but do not stop polymerization [29, 30]. Dinitrophenols are one of the commonly used retarders despite being extremely toxic. Nitroxides (very toxic) are one of the generally preferred inhibitors.

1.4   The Production of Ethyl Benzene; Offset Material of Styrene

Production and storage of styrene is known to have some setbacks, just as justified above. Production of its reactant on site (ethyl benzene) is not exempted from some major threats to the environment. Monsanto-process, i.e., benzene and ethylene Friedel-Craft alkylation using homogeneous $AlCl_3$-HCL is used to produce ethyl benzene commercially [14]. Benzene which is a reagent is carcinogenic (harmful to human health). As such, it must be carefully handled and stored. On the same reason, $AlCl_3$ is not exempted due to its corrosive nature as well as using

chlorinated compounds to poison the alkyl aromatic products. Removal of the product from the catalyst is by washing and it requires being careful. More so, $AlCl_3$ catalyst used for the benzene alkylation gives di- and tri- alkylated products with high yields which must be recycled because benzene is less reactive as compared to the desired product, ethyl benzene.

This time around, a zeolitic catalytic in liquid phase via ABBLummus/UOP produces ethyl benzene, an example is to use H-ZSM5 (Liquid Phase EB^{TM} process) instead of the aged $AlCl_3$-HCL process [15]. SHELL produces on site ethyl benzene using alkylation of benzene in vapor phase with ethylene over H-ZSM5 while employing Mobil-Badger technology different than liquid phase production by ABBLummus/UOP. A very low chance of forming di- and tri- ethyl benzene from these new technologies is established.

1.5   Novel Routes to Styrene

The toluene side chain alkylation is a plausible surrogate technology to yield styrene. Considering industrial importance of ethyl benzene and styrene, an interesting reaction is that of direct side chain alkylation of toluene using basic zeolite [18]. Zeolites possessing some basicity is needed to catalyze styrene formation from side chain alkylation of toluene, further hydrogenation gives ethyl benzene whereas ring alkylation is only possible with acid sites. $420\,^0C$ Gas phase and pressure of about 4-7 bar using zeolites X catalyst must be ensured for alkylation of toluene to produce styrene monomer.

Styrene and ethyl benzene production occur in two parallel reactions. Preheating of the raw materials, liquid toluene and liquid methanol, at $420\,^0C$ is ensured before entering the reactor. Selectivity to styrene dominates the choice of catalyst to be used. Lessened raw material cost when

correlated with conventional process has been a very good reason for the attraction of researchers towards this route [19].

To obtain α-phenyl ethanol by oxidative conversion of ethyl benzene through acetophenone followed by alcohol dehydration, ethyl benzene chlorination by side chain and extraction of styrene from pyrolysis gasoline (Toray's STEX process) are other processes for styrene production [20].

1.6   Feed-Stock Cost Analysis

Considering overall equation of reaction;

$$C_6H_5CH_3 + CH_3\ OH \implies C_6H_5CH=CH2 + H_2O + H_2 \tag{1-6}$$
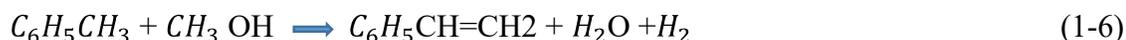
Toluene (0.885 ton) + Methanol (0.3076 ton) $\implies$ Styrene (1 Ton)

Based on reports in June 2014 [31], the market price of methanol, toluene and styrene was found in the US dollars per ton to be between 1000-1150, 200-400 and 1400-1700 respectively.

As such, at most \$1140.79 per ton is required as cost of feed stock for toluene side chain alkylation to produce styrene.

1.7   Motivation

Continuous pursuit to achieving process advancement has led to researching for and developing new catalysts, reactor design and different process routes. In recent times, catalysts modification and process development have received quite an increase in number of patent works. Such that, developing catalytic process which is energy-saving has enhanced the cost of unit raw materials being reduced and an improvement in production capability. Saudi Arabia being one of

the largest methanol producing countries as shown in Figure 1-8 below will make styrene production from side chain alkylation of toluene and methanol more realistic. A process integration can be made between the leading petroleum and petrochemical company in the country, thus making the process cheaper and achievable. The process is economically effective and less energy intensive.
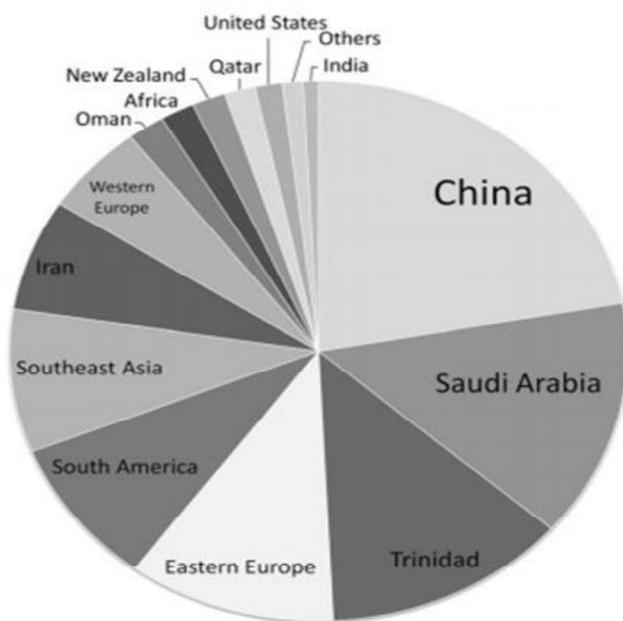
Figure 1-8: Global Methanol Production [31]

1.8 Thesis Objectives

There are two sides to these objectives;

i.   To produce styrene from side chain alkylation of toluene and methanol (feed ration of 1:1), and

ii.   To study the promoting effects of zinc oxide additive on Cs-X and Cs_2O /Cs-X.

1.8.1 Methodology

i.   To synthesis of zeolites X catalyst (Cs-X) via ion exchanged method.

ii.   To study the effect of Cs_2O loading on catalytic activity of Cs-X.

iii.   To investigate the effect of different additives over Cs-X on side chain alkylation of toluene is carried out.

iv.   To investigate the effect of Zinc oxide (ZnO) on the activity of Cs-X.

v.   To compare the catalytic activities of Cs-X, Cs_2O /Cs-X and ZnO/Cs_2O/Cs-X.

vi.   To investigate the effect of ZnO loading on the catalytic activities of Cs-X, and Cs_2O/Cs-X.

vii.   To determining the physico-chemical properties of synthesized catalysts via characterization techniques.

1.8.2 Testing Catalysts Performance

Determination of the activity and selectivity of the prepared catalysts' for toluene alkylation will be carried out. 250 mins time on stream and $410\,^0C$ established optimum temperature will be ensured for the catalytic test in a fixed bed reactor.

1.9 Overview of Thesis Written Description

- **Chapter 2** covers review of literature for side chain alkylation of toluene and methanol using base zeolite catalysts. Composition of catalysts and its deactivation are given as well as the reaction mechanism. A review of reaction kinetics is studied as well.

- **Chapter 3** describes the experimental set-up in view of the equipment used and the adopted procedures. Catalyst synthesis, characterization and evaluation are also explained in this chapter.

- **Chapter 4** expounds on the experimental results using zinc oxide as an additive on basic zeolite catalysts for the reaction. Also gives the catalytic activity as well as product selectivity to promoting effects of ZnO and Cs_2O additives.

- **Chapter 5** presents conclusions and recommendations of this study.

CHAPTER TWO
LITERATURE REVIEW

2.1   Background

Alkylation entails the transmission of an alkyl group from one molecule to another. Alkyl group being transferred can be in the form of an alkyl carbocation (ion with a carbon atom which is positively charged), a free radical (atom, molecule, or ion with an unpaired electrons), a carbanion (an anion with carbon containing an unshared pair of electrons and thus possess negative charge) or a carbene (molecule with a neural carbon atom having a valence of two and two unshared valence electrons) or their equivalents. Alkylation as used in oil refining framework is the alkylation of isobutane with olefins. An excellent blending stock for gasoline of synthetic C_7 - C_8 alkylate will be obtained as an upgrade of petroleum. On medical platforms, the damage of DNA of cancer cells in chemotherapy is achieved by alkylation of DNA [32].
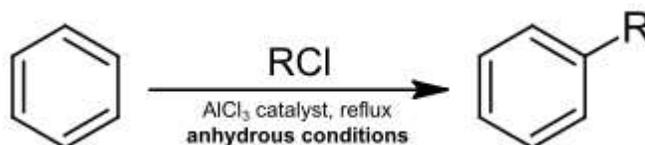
Figure 2-1: Typical illustration of alkylation [32]
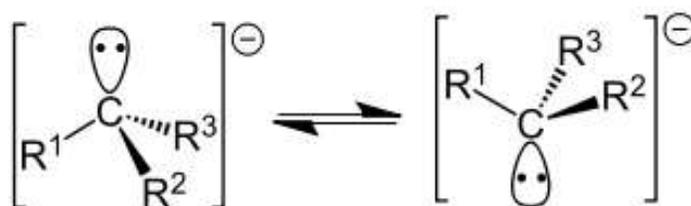
Figure 2-2: Structure of Carbanion [32]

H
\
C:
/
H
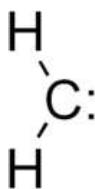
Figure 2-3: Structure of Methylene, the simplest carbene [32]

An important and interesting reaction is observed during toluene side chain alkylation with methanol based on diversity in the catalysts choice. The reaction will progress either via acid or base catalyst. Using acid catalyst, ring alkylation occurs yielding the mixture of xylenes (main product), benzene and trimethyl benzene. Toluene disproportionation gives rise to the formation of benzene whereas further alkylation of toluene yields trimethyl benzene [33].

At high temperatures using zeolite with strong acidity, formation of benzene and xylenes via toluene disproportionation is observed. It must be noted that water and gaseous hydrocarbons are formed because reactivity of methanol is more than that of toluene using acid catalysts [33].

Considering alkylation of toluene using base catalyst, alkylation occurs at the side of the ring forming styrene and ethylbenzene. Side chain alkylation of Toluene and methanol using moderately basic zeolites X with low Si/Al ratio gives styrene (with high selectivity) and ethylbenzene as reported and depicted by Scheme 2-1. Side chain alkylation is known to possess a novel route to styrene, thus, receiving a lot of attentions. Formation of formaldehyde from methanol dehydrogenation is endothermic in nature while the reaction of toluene and formaldehyde is exothermic. Well balanced rates will ensure a process that is thermodynamically close to zero.
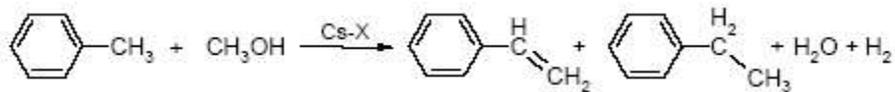
Scheme 2-1: Toluene side chain alkylation reaction scheme using basic catalyst.

A minute electrostatic potential such as Cs^+ and Rb^+ at the ion exchange site will give high styrene selectivity at 425 ^{0}C. Dehydration of methanol due to the formation of formaldehyde as intermediate enhances the high styrene selectivity. The presence of a very strong basic site possessing pores with weak Lewis acidic centers containing framework oxygen in the zeolite aids methanol dehydrogenation [34].

The styrene selectivity and alkylation activity can be increased by using formaldehyde as alkylating species [35]. Not quite long, the use of dimethoxy carbonate as an alternative alkylating agent other than methanol or formaldehyde was established to yield high selectivity to styrene for side chain alkylation of toluene and methanol. On the other hand, isobutyl benzene is formed using isopropanol as the toluene alkylating agent [36].

Network for the reaction over acid and base catalysts for side chain alkylation of toluene and methanol is represented using Scheme 2-2.
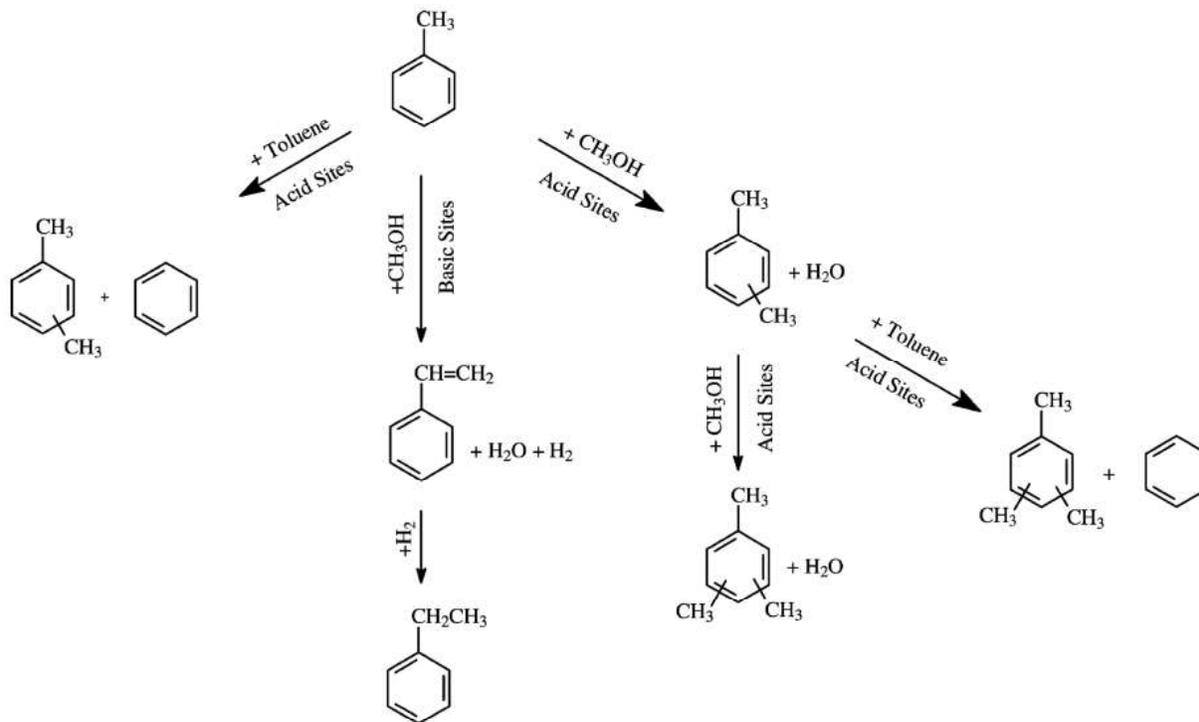
Scheme 2-2: Reaction network over acid and/ or base catalyst for side chain alkylation of toluene and methanol.

2.2   Overview of styrene industry, technology and economic considerations

Publications and patents traced to Scopus and SciFinder Scholar data bases are the sources of this review on styrene monomer (SM) formation from alkylation of toluene and methanol. When compared with conventional SM process, interests (scientific and industrial) in SM or ethyl benzene (EB) formation from side chain alkylation of toluene and methanol using alkali-exchanged zeolites is multiplying due to availability of environmentally friendly reaction and lower raw-material-cost process. Styrene monomer is a valuable commodity liquid chemical usually produced in large-volume used for producing polystyrene plastics, protective coatings, polyesters, and resins. SM is most commonly used in the production of valuable styrene

homopolymers and copolymers, which can either be solid polystyrene (SPS) or expandable polystyrene (EPS) [37].

2.2.1 Conventional SM Process

Alkylation of benzene and ethylene preceded by a dehydrogenation (EB/SM method) is the conventional process to produce styrene monomer. The raw materials benzene and ethylene made up most of the commercially produced SM today. Ethylbenzene (EB) is produced from alkylation of benzene and the conversion of EB to SM is through conventional dehydrogenation SM process. Approximately 70% of the globally produced SM comes from this "on-purpose" method. Nonetheless, during production of propylene oxide, styrene is a co-product (POSM method).

Benzene, a liquid which is cheap and easy to transport, comprises about 73% of the styrene molecule by mass. So, it is an important component of styrene. More than 50% of the world commercial production of benzene is consumed by manufacturer of styrene from EB. On the basis of comparison, 27% of styrene molecule by weight is ethylene. However, ethylene is a gas with the challenge of transportation and this compels SM plants to be typically located close to ethylene crackers.

Importance must be given to the integration between EB and SM plants since SM plant consumes large amount of steam while the EB plant is exothermic in nature. The most economical route to produce SM for about 60 years has been the dehydrogenation of EB. Every current SM technology available are based on accepted two-step chemistry and they are:

1. Alkylation of benzene and ethylene using solid acid catalyst to produce EB.

2. Dehydrogenation of EB at a temperature above 870 K using an iron oxide catalyst to produce styrene in the presence of steam.

Toluene and benzene are the main by-products of the dehydrogenation reaction which led to loss in yield because both are products of high values. Recycling of benzene takes place many times in the recycling-unit to give EB whereas either toluene is returned to an aromatics unit or sold to refiners. From above cases, toluene is produced from both EB and styrene while the styrene route accounts for the greater portion. Thermodynamically, it is a limited reaction and strongly endothermic. Large amount of energy is needed due to the high endothermic heat of reaction.

2.2.2 Alternative styrene route

The side chain alkylation of toluene and methanol using basic zeolites makes up the alternative route to SM. Compared to the conventional process, this process has numerous economic, energy and environmental benefits. Toluene alkylation is an age long process since Sidorenko et al. (1967) who reported that in comparison to other alkali ion-exchanged zeolite X and Y, Rb-X and Cs-X catalysts were efficient. The following reaction depicts the alternative route which produces styrene, hydrogen, and water.
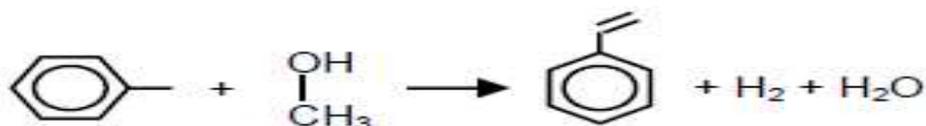
Scheme 2-3: Alternative route to styrene.

This single-step reaction is operated at 675 K and atmospheric pressure compared to the conventional benzene-ethylene alkylation process. Metallurgical requirements and capital costs have reduced greatly due to the reduction in the reaction temperature by over 473 K. However, commercialization of this technology has been avoided because of the high rates of methanol decomposition and low yields of SM.

2.2.3   Exelus Process

Replacement of ethylene and benzene as raw materials in the traditional routes with toluene and methanol was developed by Exelus (an alternative SM process, ExSyM) in the United States of America. Feed ratio of 9:4 for toluene:methanol is operated at 675-700K and 1 atm in a bench-scale operation [14, 15]. The process flow diagram of ExSyM is represented with Figure 2-4 which in summary relied on an improved catalyst technology which can avoid the need for a separate dehydrogenation step thereby leading to high yields and high conversions single-step process.

Exelus claims that its SM-yield far exceeds the results achieved in previous patents assigned to Monsanto [38], Exxon [39], and Shell [40]. The technology has minimized methanol decomposition and styrene hydrogenation to reduce raw material costs and energy consumption. The operation of the process is at significantly lower temperatures when compared to the conventional route, resulting in the overall process being more energy efficient.
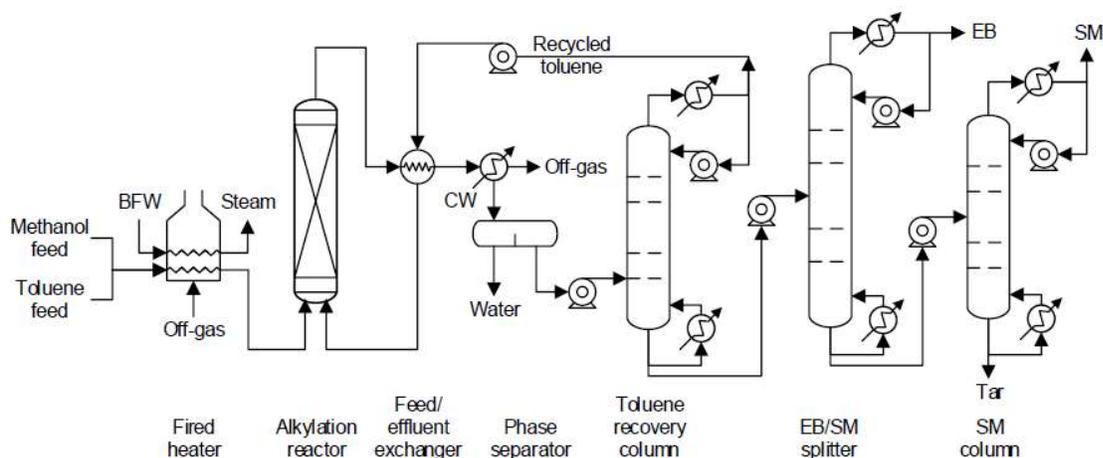
Figure 2-4: Flow diagram by ExSyM for SM from toluene and methanol [12]

Despite that bench-scale level has only been used to demonstrate this technology, if the pilot tests demonstrated high selectivity as claimed, the production cost and cost of feedstock could be improved significantly over conventional styrene processes. Bench-scale reactors have been used for testing this process. No sign of deactivation was shown by the catalyst and long-term stability tests continue. Piloting is expected to continue. Also note that the company Exelus has not filed any patents at this time.

2.2.4   Benefits of SM Alternative process

The alternative SM process boasts economic, energetic and environmental advantages over the conventional dehydrogenation process. As discussed earlier, the conventional production of SM consumes about ten times the energy of similar chemicals and serving as a major contributor to GHG emissions. Table 2-1 presents economic and process benefits of side-chain alkylation process vs. conventional styrene monomer production [14].

The greatest economic driver of this technology is a 20% reduction in feedstock costs. The choice of feedstock has a significant impact on the production economics. The production cost is elevated by the high-priced feedstock and the severity and endothermic nature of the second dehydrogenation step. The two feedstock for the alternative side-alkylation route to SM are toluene (basic aromatic chemical derived from naphtha) and methanol (C1 basic chemical derived from natural gas). It also offers lower capital costs than conventional plants by eliminating the need to generate 900 °C steam used to provide the heat of reaction.

Table 2-1: Economic and process benefits of side-chain alkylation process versus conventional styrene monomer production [14].

Impact	Conventional SM Production	Side-Chain Alkylation Process

Economics	• High cost of raw materials: benzene and ethylene have eroded profitability
	• Investment cost to build a 250,000 metric ton/year plant: $125 million
	• Feedstock Prices
	  • Benzene: $1000-1500/ton
	  • Ethylene: $1100-1500/ton
		• Reduced feedstock (toluene and methanol) costs of result in operating cost savings of $250/ton of SM
		• Investment cost to build a 250,000 metric ton/year plant: $63 million (ExSyM retrofit: $10-15 million)
		• Feedstock Prices
		  • Toluene: $1000-1150/ton
		  • Methanol: $200-400/ton

Energy	• Large utility requirements to supply the endothermic reaction ($\Delta H = 120$ kJ/mol) • Second-step dehydrogenation required • Operation temperature > 870 K; steam ~ 1170 K	• Eliminated of energy-intensive dehydrogenation step • Reaction temperatures ranges between 675-700 K • It is 50% less endothermic • It saves up to 40% of the Energy
Environment	• Significant GHG emissions result from the need to use large amounts of steam and benzene is a well-known carcinogen	• Lower GHG emissions by 40% • carbon emissions is reduced due to recovery and reuse possibility of up to 50% of H_2 byproduct

Impact	Conventional SM Production	Side-Chain Alkylation Process
	• Large contributor to GHG emissions such as CH_4 and CO_2	• Less toxic feed replaces carcinogenic benzene feed with toluene

2.2.5   Future of alternative process for SM in Saudi Arabia

In Saudi Arabia, SM is currently produced at three plants in Jubail using the conventional ethylene-benzene alkylation process. Almost all the production is converted further to various grades of polystyrene. The current total capacity of the SM plants is 1.9 million tons per year as shown in Table 2-2. SM is produced by two 50:50 joint-venture companies: (1) Sadaf, a joint venture between Saudi Basic Industries Corporation (SABIC) and Shell in Jubail; and (2) ChevronPhillips Chemicals-Saudi Industrial Investment Group-SIIG in Jubail.

Table 2-2: Production capacity of SM in Saudi Arabia.

Company and Location	Capacity, ton/yr	Start-up Date
SABIC- Shell: Sadaf, Jubail		
Plant-1	560,000	1986
Plant-2	500,000	2010
Plant-3*	720,000	2016*
Jubail ChevronPhillips, JCP, Jubail	750,000	2008
Methanol Chemicals Chemanol, Jubail	230,000	2009

* Planned

The key driver for SM alternative technology on the supply side is the availability of methanol in the Kingdom and its attractive cost of production that results from discounted natural gas prices available to local producers. Currently, Saudi methanol production capacity stands at 6.2 million

tons. SABIC has a production capacity of 5.7 million tons (83% of total methanol capacity: Ar-Razi-4.7 million and Ibn Sina-1.0 million). Moreover, Sipchem has 1.0 million tons SM capacity and Chemanol produces 0.23 million tons of SM (captive production).

Methanol is either exported or used at SABIC plants for the production of MTBE. Other uses are in the production of acetic acid and formaldehyde. The driver on the demand side is naturally the high demand and projected growth rate of demand for SM within the Kingdom and beyond. Regarding the other feedstock, toluene is either kept in gasoline to raise octane, or converted to benzene for styrene production (Sabic Sadaf), or exported with naphtha.

2.3   Catalytic Systems under review

2.3.1 Types of Catalysts

Table 2-3 presents major catalytic systems and organizations (academic and industrial) having publications related to side-chain alkylation technology [41]. Since then, various zeolite-based catalytic systems were investigated to enhance the selectivity to SM. However, until now and despite many efforts, catalysts producing high conversion and selectivity via side chain alkylation has not been reported and a generally accepted mechanism of the reaction is not available [42].

The reaction is favored over solid basic catalysts such as modified Faujasite zeolites (Cs-X and Rb-X, and Cs-Y). Other basic catalysts include various zeolites (ZSM-5, IM-5, L, Beta), silicalite/MgO and hydrotalcite have also been investigated [43-44].

Table 2-3: Various catalytic systems reported for the side-chain alkylation of toluene and methanol to SM/EB.

Catalytic System/Feature	Organization	References
Alkali metal exchanged zeolites ZSM-5, X and Y (basic sites)	Academy of Sci., Czech Republic	Žilková et al. (2005)
Mg/Al layered double hydroxide	Anna University, India	Manivannan et al. (2008)
KRbCs-X zeolite (effect of reaction conditions)	East China University of Science & Technology	Jiang et al. (2013)
Nano-size Y-zeolite; BCsX using various C1 alkylating agents such as CH4; syngas; formalin	Fina Technology (Total Petrochemicals), USA	Butler (2012); Chinta et al. (2012); Pelati et al. (2011) Thorman (2011)
MgY; Cs-Na-Y zeolite (effect of Cs)	INCAPE, Argentina	Borgna et al. (2004); Borgna et al. (2005)
Cs-X zeolite (FTIR and TPD studies)	Indian Institute of Science, Bangalore, India	Sivasankar et al. (2010)
MgO mesoporous silicalite-1	Inha University, S. Korea	Jiang et al. (2010)
K-exchanged X zeolites	Institute of Coal Chemistry, China	Song et al. (2012)
X, Y, Beta, ZSM-5 and L) with alkali and alkali-earth	Instituto de Tecnologia Quimica (ITQ), Spain	Serra et al. (2003)
Cs-IM-5 zeolites (high conversion)	Jilin University, China	Shi et al. (2012)
KX NaY with alkali carbonates	Nanjing University, China	Lin et al. (2012)
Na, Cs, Mg, Zn-X zeolite	Nation. Acad. Sci. Ukraine	Dolgikh et al. (2006)
Aluminum/various amines using triblock copolymer Pluronic/ resol	Taiyuan University of Technology, China	Wang et al. (2011)

Catalytic System/Feature	Organization	References
Na-K; Cs-X zeolite	Universidad Complutense de Madrid, Spain	Romero et al. (2003)
Modified Y-zeolite (mechanism)	Shihezi University, China	Wang et al. (2014)

2.3.2   Reaction Conditions

Feed composition, temperature and space velocity greatly influence the catalytic performance of various zeolites for toluene alkylation. In addition to methanol, various C1 sources were used as alkylating agents such formaldehyde, methane and syngas [45, 46]. Typically, the reaction is carried out at the following conditions [47]:

- Gas phase reaction at atmospheric pressure;

- Temperature range of 380–500 °C and WHSV of 1–10 h-1

- Toluene/methanol molar ratio from 0.1 to 5, often with inert dilution to assist vaporizing the liquid feed (i.e. He/mixture ca. 5/1);

- In other cases H_2 is co - fed to improve activity, selectivity and stability.

2.3.3   X-Zeolite

Attempts were made to enhance catalytic activity and selectivity to SM by modification of Cs-X with various compounds. Modification with B component have been reported to yield positive results in several studies such as by Wieland et al. [48], Unland et al. [49] and Liu et al. [50]. Various metal components such as Ca, Mn, Ni, Cu, Zn, Ag, Ce, Cr, and Fe were also reported to have promoting effect. The main drawbacks of these catalytic systems have been poor efficiency of methanol utilization and low yield of SM/EB. Cu and Ag were reported to be effective metal

components [51]. Besides the metal components, promoting effects of addition of B and P on the activity were reported in literature [48] and patents [39, 50, 52].

The impregnation of Cs-X with Cs increased the basic properties of Cs-X [53-57]. All of them reported that the toluene conversion and selectivity to EB were increased by addition of Cs_2O to Cs-X. However, they examined only a limited number of catalysts; no systematic study has been reported to elucidate optimum loading of Cs_2O.

Barthomeuf et al. [52] reported impregnation of sodium metal with Cs-X to be very good and highly selective catalysts for toluene alkylation. Table 2-4 compares the results with zeolites impregnated with Cs_2O clusters or boron.

Table 2-4: Alkali metal impregnated X zeolite in the side-chain alkylation of toluene, compared to modified X zeolite at 700 K [52].

Catalyst System	CsXOH [1]	CsX-Na [2]		CsXB [3]		CsXB-Na [4]	
Time-on-stream, h	6	6	15	6	15	6	15
Methanol conversion, %	15	45	40	15	12	8.5	5.5
SM yield, %	0.7	4.3	4.0	5.0	3.1	3.5	2.7
EB yield, %	0.25	4.1	3.8	0.35	0.1	1.1	0.65
Total selectivity, % [5]	6.3	18.6	19.5	36.0	27.0	54.0	60.0

1. CsXOH: unwashed Cs-X exchanged with CsOH, probably containing CsO-clusters.

2. CsX-Na : CsXOH sample is mechanically mixed with sodium-azide and heated.

3. CsXB: CsXOH impregnated with boric acid.

4. CsXB-Na: CsXB impregnated with sodium metal using sodium vapor deposition.

5. with respect to methanol conversion.

Also active as alkylation catalysts were Cs-exchanged zeolites L and Beta but similar aromatic yields require higher temperatures. The results implied that methanol decomposition was not affected by variations in particle size of Y zeolite and much higher amounts of CO_2 were adsorbed by alkali-exchanged X and Y zeolites Cs-L and Cs-Beta zeolites [48].

Toluene alkylation was not favored by mesoporous alumina modified with cesium and boron which yields carbon monoxide from methanol decomposition. Cs-L was also found in side chain alkylation of toluene to be a unique catalyst. Similar yield was obtained over Cs-L at 760 K and over boron-promoted Cs-Y at 680 K, but substantial amount of CO was not produced by Cs-L catalyst.

Ring alkylation is preferentially favored for reaction over Li+ and Na+ cation exchanged X zeolites and over alkali cation exchanged ZSM5 (MFI) zeolites, whereas intermediate selectivity was shown by K+ cation exchanged X zeolites [44]. Though selectivities obtained were high, report gave only low toluene conversions and SM yields.
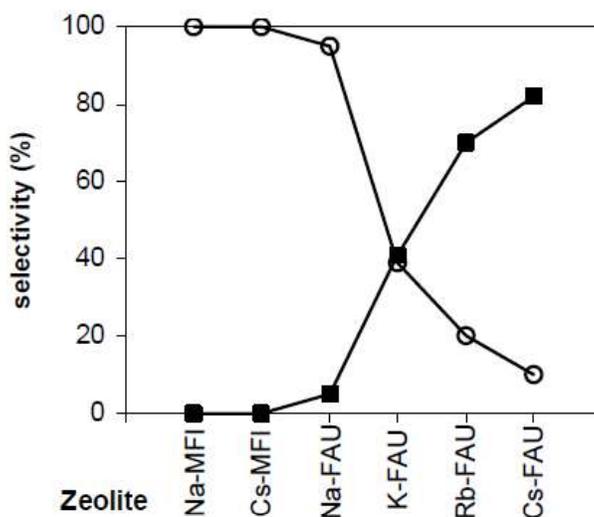
Figure 2-5: Alkylation selectivity of toluene over alkali exchanged ZSM-5 (MFI) and X (FAU) zeolites, yielding xylene (O) or styrene (■) [44].

Serra et al. [47] compared the performance of different zeolites such as NaX, KL, NaZSM-5, NaBeta, and NaY. The fact that NaX zeolite gave the best results confirmed that the low SiO_2/Al_2O_3 ratio and the corresponding high basicity of the alkali exchanged samples (i.e. Li, K and Mg) are adequate to catalyze the first reaction step, i.e. the dehydrogenation of methanol to formaldehyde. It was concluded the following reactions are believed to occur in the catalytic test: toluene disproportionation, alkylation of toluene to xylenes, alkylation of toluene to EB, alkylation of toluene to SM, alkylation of xylenes to trimethylbenzenes (TMBs), disproportion of xylenes and oligomerization of methanol.

Davis [43] showed that the reaction over alkali metal exchanged X-zeolite, particularly, K-X, Rb-X, Cs-X and Rb-X yielded a mixture of SM and EB at 680-730 K. The catalyst consists of basic and acid sites in a microporous structure provided by zeolite and microporous materials. Basic sites were provided by framework oxygen and/or occluded Cs_2O. Acid sites were provided by the Cs cation and, possibly, additives such as boric and phosphoric acids.
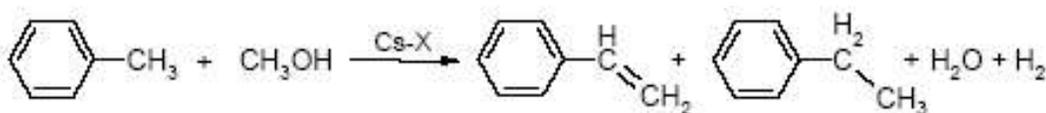
Scheme 2-4: Reaction over alkali metal exchanged X-Zeolite

Formic acid intermediate decomposition was also suppressed by the incorporation of Li^+ ions. There exists a directly proportionality between dehydrogenation ability of methanol and the selectivity for side chain alkylation of toluene to the basicity of alkali metal cation exchanged zeolites and the acid-base sites proximity and the Si/Al ratio is related to zeolite basicity and the topology of zeolite.

Beltrame et al. [59] concluded that CsNaX zeolites were good catalysts since they promoted attack on the side chain with very high selectivity. The distribution of product was in favor of EB at high values of the time factor.

Effect on selectivity and activity for the alkylation of toluene using boron impregnation was increased compared to Cs-X zeolites impregnated with Cs_2O, because it increases the methanol dehydrogenation abilities [60]. This may be as a result of the joint interaction of the Cs^+ exchanged zeolite and Fe-Mo oxide with toluene. Putting this dual catalyst to use, SM/EB ratio was increased by a factor of 4.5.

Xu et al. [61] found that high catalyst activity was obtained on KX zeolites modified simultaneously with B and K compounds The results suggested that different stoichiometric borate compounds ($K_2B_4O_7$(x H2O) and KBO_2(x H2O)) are formed between H_3BO_3 and KOH under impregnation condition, which can act as basic active sites of medium strength for the effective dehydrogenation of methanol.

Romero et al. [62] enhanced the basic properties of X zeolite during synthesis, without further treatment. The control of the washing stage enabled retention of the optimum amount of alkaline hydroxides, which increased the basic catalytic activity of X zeolite in the alkylation of toluene. The alkaline hydroxides neither affected the FAU framework nor the Si/Al molar ratio of the X zeolite. Sivsankar et al. [64] used FTIR and TPD to confirm that methanol decomposes to formaldehyde and formates over Li-X and Cs-X. Based on the results, it was possible to postulate the possible reasons as to why the direction of the alkylation of toluene was different on Li-X and Cs-X. In the case of Li-X, toluene reacts directly with methanol bound to the Li ion which is

available under reaction conditions. In the case of Cs-X, the adsorbed methanol was not retained but decomposed to give formaldehyde.

Lin et al. [66] studied the formation and function of formate over KX promoted with alkali carbonates using infrared spectra of methanol adsorbed on the catalysts. Modification of the surface acid/base property of the catalysts was done by these formate species, which in turn generated more active sites that are very effective.

2.4   Preparation of Catalysts

Styrene production can be improved using base catalyst for toluene side chain alkylation of methanol by specially developing reactor design and catalyst with high selectivity. Handful of consecutive reactions present is responsible for the regular adjustment between the desired product's conversion and selectivity. Hence, development of catalyst for toluene side chain alkylation with methanol is faced with the following challenges among others:

    i.   How to developing catalysts which stable for active species

    ii.   How to developing catalysts which has large surface area

    iii.   How to play down formation of coke as well as deactivation of catalyst

    iv.   How to ensure that nonessential and displeasing products and reactions are minimized

    v.   How to achieve high activity and selectivity towards increase in styrene.

For our study on the side chain alkylation of toluene with methanol, modification of Cs-X catalyst was done different additives such as ZnO , Cs_2O, ZnO/Cs_2O, SiO_2-ZnO Si/Zn = 1

(calcinated at 450 ℃ and 550 ℃), SiO_2-SnO_2 Si/Sn = 1 (calcinated at 550 ℃), ZnO-SnO_2 Zn/Sn = 1 (calcinated at 550 ℃), Sn/SiO_2-ZnO 10 wt% and Zn/SiO_2-MgO Si/Mg = 1 (calcinated at 450 ℃), and reaction condition was optimized to boost both selectivity to styrene and conversion of toluene.

2.5   Deactivation of Catalysts

Deactivation of catalyst entails the loss in catalyst activity during a reaction. As for alkylation of toluene with methanol using base zeolite catalysts, deactivation of catalyst is characterized by coke deposition on the catalyst resulting in poisoning of catalyst active site.

Coke formation is enhanced by acid sites of zeolite, condensation of potential coke precursors, olefins and aromatics, is promoted due to its severity on acid sites which is strong [68]. Polynuclear aromatics formation is due to presence of large pores in on the catalyst [69].

The effect of H_2 and N_2 as carrier gases during toluene alkylation on the catalyst deactivation was reported by Ramakrishna et al [70]. Using both gases independently, Study carried out on Cs-X observing the time on stream based on toluene/methanol feed ratio of 1:1, constant contact time (40 g of catalyst/mol-h), and temperature of 410 ℃. N_2 atmosphere was more favorable for catalyst deactivation than H_2 atmosphere. On the assumption that gaseous atmosphere differs in nature or difference in the distribution of coke is used to account for this behavior.

Deposition of coke on the catalyst outer surface is responsible for the rapid deactivation of the catalyst based on mass spectrum studied by Minachev et al [71]. Consequently, they noticed

that nitrogen atmosphere is made up of coke deposition with compounds having higher molecular weight when compared with the hydrogen atmosphere aided coke deposited.

Coking intermediates were discovered to be carbonium ion [72]. Coke formation was believed to be minimized if a zeolite with very strong acid sites can activate molecular hydrogen so as to enhance adsorbed carbonium ion species to have reduction in concentration on the surface of the catalyst [73].

2.6   Mechanism of Reaction for toluene side chain alkylation

Several research groups have undergone mechanistic study which led to various different reaction mechanisms that explain the selectivity in the course of side chain alkylation of toluene with methanol. Itoh et al. [58] is the basis for most of the proposed reaction mechanisms, with an aldol-type condensation depicted by Scheme 5. A highly activated methyl group was claimed to be formed due to the interaction between the oxygen framework of zeolite and an extra Lewis cation framework, generally referred to as a basic and an acid sites, although interaction only exists between formaldehyde and a site of Lewis acid. Reactivity of the side chain increased in such a way that it becomes negatively polarized due to the toluene interaction with the basic framework oxygen, however, the toluene molecule becomes stabilized as a result of interaction with an acid site which is concurrent [73]. Benzene ring alkylation is highly activated as a result of toluene adsorption only on an acid site. Molecular modeling showed concerted zeolitic acid-base interaction with methanol during side-chain alkylation as well as the poisoning of Cs-X (in situ) for an acid or base alkylation of toluene [74]. A sharp deactivation of the catalyst is observed due to co-feeding of toluene and methanol reacting mixture and pyridine (2, 3-dimethyl pyridine or

butyl amine). Acute catalyst deactivation is also noticed after submission of acetic acid submission to the feed.
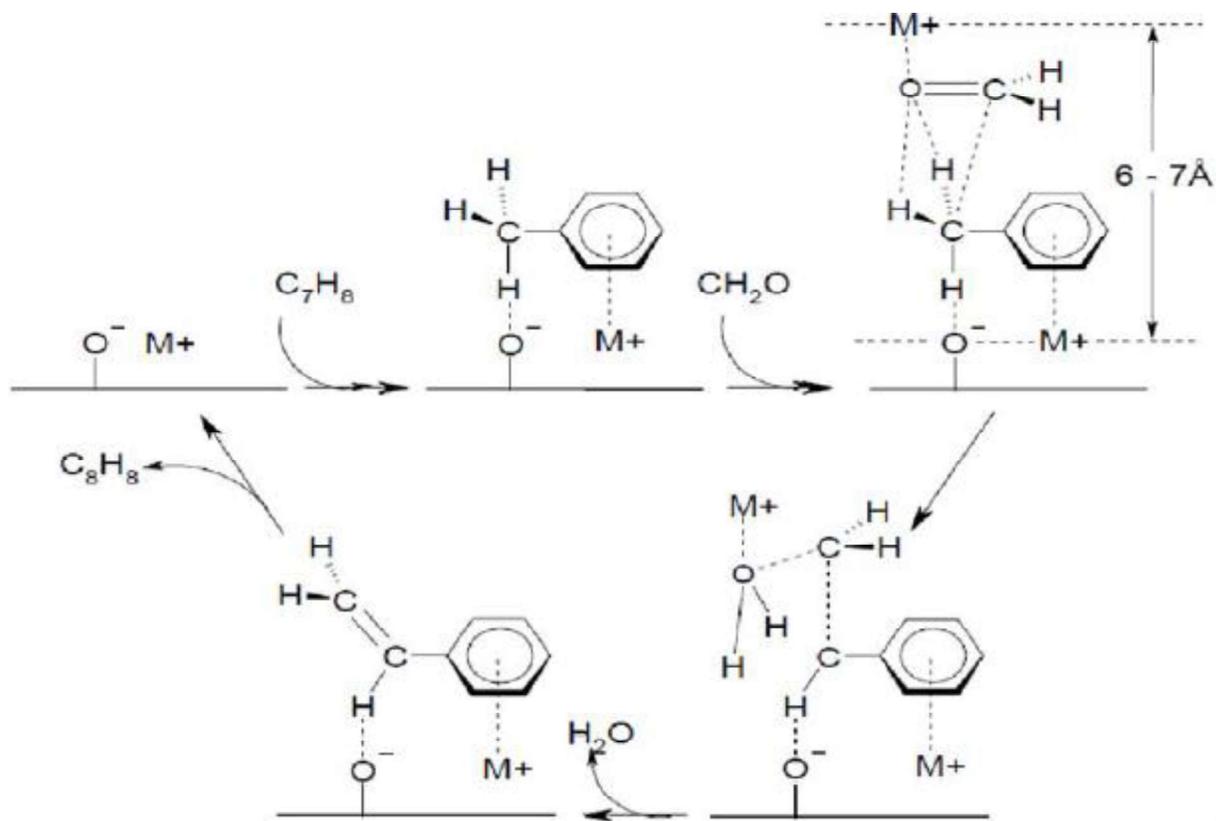
Scheme 2-5: Mechanism for toluene side chain alkylation.

Several proposals are available for the modifications of the reaction mechanism for the side chain alkylation. King and Garces [75] proposed unidentate formate from oxidation of formaldehyde rather than having intermediate alkylating agent to be formaldehyde. Abstraction of proton from toluene to form phenylcarbanion subsequently alkylated by formaldehyde was

proposed by Lacroix et al. [51] and Garces et al. [76]. A mechanism for the reduction-oxidation involving formation of alkali metal vapors in situ during alkylation was acclaimed by Garces et al. [76]. Reduced alkali metal oxides obtained from metal carbonates decomposition during inside zeolite pores activation formed alkali metal vapors.

Nonetheless, the likelihood of this is questionable based on alkali oxide and hydroxide clusters stabilities considerations. Cs^+ cations present in the zeolite pores was proposed to be responsible for styrene and ethylbenzene having high selectivity, whereas the transition states formed led to ring alkylation products being sterically affected. Mobility of toluene Inhibited in the Cs-X pores depicted using NMR experiments.

A lot of debate is still ongoing on the methanol activation and the mechanism for dehydrogenation from basic zeolites to form formaldehyde and the reaction involving methanol in the alkylation of toluene towards styrene. Although, it becomes apparent from the previous discussions that for the formation of styrene and ethylbenzene, balance should exist between activation and dehydrogenation of methanol, activation of toluene and zeolite structure.

CHAPTER THREE
EXPERIMENTAL SECTION

3.1   Set-up of the Experiment

A packed bed reactor was used for the experimental runs. The side chain alkylation of toluene and methanol using zeolite X catalysts with zinc oxide as an additive were carried out with 400 mg of the catalyst sample packed inside a packed bed reactor. 0.1 MPa of flowing nitrogen at $450^0 C$ was passed through the reactor for 2 h to pre-reduce (agitate) the catalyst. Thereafter, the reactor temperature was reduced from $450\ ^0C\ to\ 410\ ^0C$ (experiment temperature). 0.12 ml/min reactant feed flow rate and 40 ml/min N_2 flowing rate was maintained. Autoclave Engineers with high pressure feeding pump (Series III Digital HPLC Pump), and smart mass flow controller (Model # 5850S/BC, Brooks) were also used. Online gas chromatograph (Agilent Technologies, Model # 6890N) was used the products analysis. Comparison analysis was used for identifying products with respect to some samples known to be authentic. Figure 3-1 depicts the reaction set up diagram schematically.

3.2   Gas Chromatography (GC)

The products of the reaction were quantitatively analyzed online using an Agilent GC. The GC was equipped with Flame Ionization Detector FID (Agilent Chromatograph Model 6890N) and HP-INNOWAX capillary column (Polyethylene glycol (PEG)) (length 60 m x internal diameter 0.32 mm x film thickness 0.50 μm). The carrier gas is Helium, while the FID detector were air and hydrogen gases. The GC temperature program used for the initial cryogenic operation was facilitated with the aid of liquid nitrogen. The GC oven cools to -30 °C using liquid nitrogen.

Internal oven temperature controller of the GC with the aid of a solenoid valve was used to administer the flow of liquid nitrogen. The GC detector signal was integrated and strip chart recording was done due to the presence of the integrator. HPIL instrument network cabling system was the link between the integrator and the GC. Figure 3-1 represents the gas chromatography diagram in schematic form.
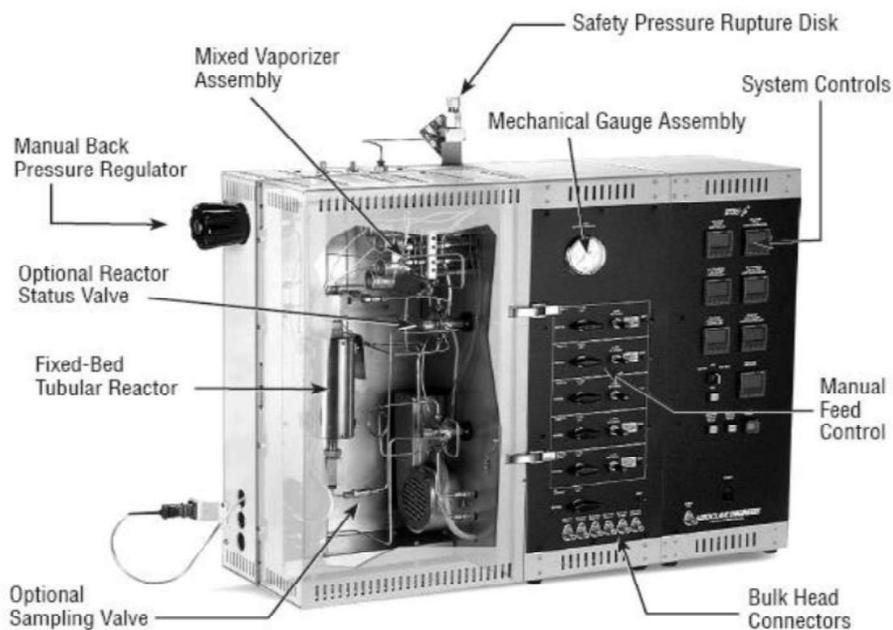
Figure 3-1: Reaction systems for a fixed bed reactor in pictorial form
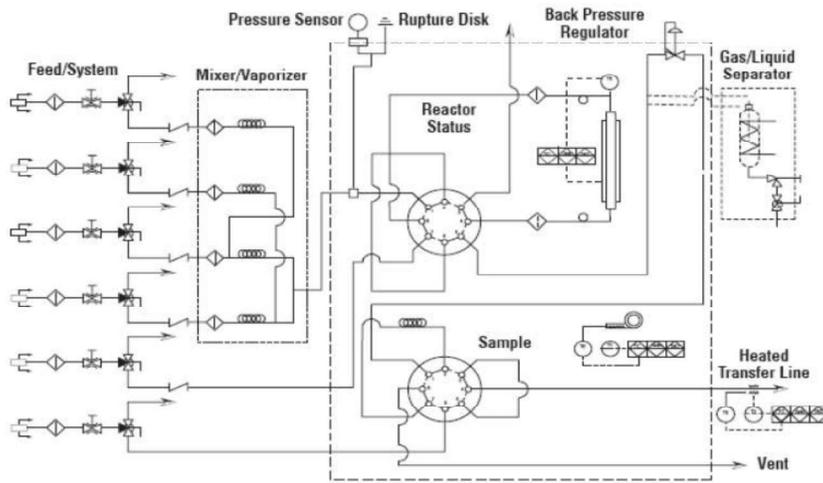
Figure 3-2: Reaction systems for a fixed bed reactor in schematic diagram form
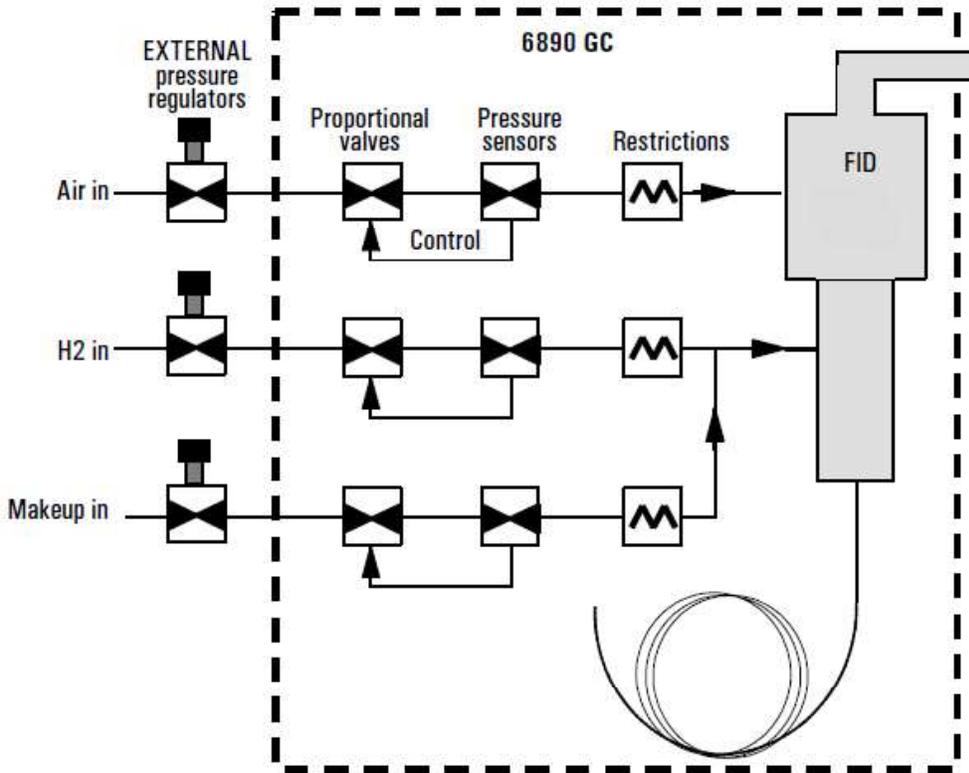
Figure 3-3: Gas chromatography in schematic diagram form.

45

3.3 Experimental Procedure

3.3.1 Materials

Tosah Corporation Company, Junsei Chemicals and Kanto Chemicals Corporation supplied the zinc source (zinc carbonate), NaX, and CsOH respectively. Zinc oxide was synthesized, while Sigma-Aldrich Company supplied methanol (99.9% purity) and toluene (99% purity).

3.3.2 Preparation of catalysts

The ion-exchange of Cs^+ from NaX (Junsei Chemicals, Japan) formed the base catalyst Cs-X. According to Engelhardt et al, a source of Cs^+ used was Cesium hydroxide. NaX (15 g, Si/Al=1.24) was immersed into an aqueous solution of CsOH (75 ml, 0.5 M), stirred for 5 min and keep for ca. 8h. Buchner funnel was used to filter the slurry. The immersion of the filtered cake was done in an aqueous solution of CsOH, stirred and keep for Ca. 8 h. Repetition of the immersion and filtration procedures was done four times were. Filtration of the resulting slurry was ensured. Immersion of the resulting cake in 100 ml water and later filtered was done to minimize Cs^+ ion-exchange with H^+ during washing with water. Oven at 353 K was used to dry the filtered cake and calcined at 753 K for 3 h in air.

Wetness impregnation of Cs-X with CsOH aq. solution was used to prepare Cs-X containing Cs in excess of ion exchange capacity (Cs_2O/Cs-X). The loading of Cs_2O was adjusted by the concentration of CsOH aq. solution. After impregnation, catalysts drying at 353 K and calcined at 773 K for 3 h in air was done. The catalysts were designated as Cs_2O (D)/Cs-X, where D referred to the weight % of Cs_2O in the catalyst.

A mixture of Cs-X and ZnO was grinded in a dry state with mortar for 30 min giving rise to the Cs-X modified with ZnO. Slow ramp rate of 2 K/min at 773 K for 3 h was used for the calcination of the ground mixture.

3.3.2.1 Synthesis of ZnO

To make 20 g of ZnO, 73.09 g of $Zn(NO_3)_2$ is required. Prepare 1M aqueous solution containing 73.09 g of $Zn(NO_3)_2$: Solution A is 246 ml. Into a solution A, NH_4OH is added drop wise with stirring until pH of the solution becomes 8.0. $Zn(OH)_2$ is precipitated: Slurry B. Stand the slurry B overnight. Filter the slurry B, and wash with deionized water. Dry the filtered cake at $100\ ^0C$, and calcine at $450\ ^0C$ for 3 h.

3.3.2.2 Synthesis of 10 wt% Sn/SiO₂-ZnO (Si/Zn = 1)

10 wt% Sn/SiO₂-ZnO (Si/Zn = 1) was prepared by dissolving 12.933 g of Zn(NO₃)₂.6H₂O and 2.073 g of SnCl₄.5H₂O into 10 ml of 0.1 M HNO₃ in a 50 mL beaker. Into the solution, 2.0 g of urea is added and the solution is stirred till urea becomes dissolved. 10 mL of TEOS is added with whole pipette (one-mark pipette), and stirred till the solution becomes homogeneous. The solution is transferred to autoclave (100 ml) and heated at 373 K for 48 h. Spherical solid formed in the autoclave is recovered by filtration. After crushing with glass rod, it is dried for 2 days. Then crushed with a mortar, dried at 443 K for 1 h, and finally calcined at 823 K for 2 h.

3.3.2.3 Synthesis of SiO₂-ZnO (Si/Zn = 1)

Preparation of SiO₂-ZnO (Si/Zn = 1) was done via dissolution of 12.933 g of Zn(NO₃)₂ 6H₂O into 10 ml of 0.1 M HNO₃ in a 50 mL beaker. 2.0 g of urea is added to the solution and the solution is stirred till urea becomes dissolved. 10 mL of TEOS is added with whole pipette (one-

mark pipette), and stirred till the solution become homogeneous. The solution is transferred to autoclave (100 ml) and heated at 373 K for 48 h. Spherical solid formed in the autoclave is recovered by filtration. After crushing with glass rod, it is dried at 333 K for 2 days. Then crushed with a mortar, dried at 443 K for 1 h, and finally calcined at 823 K (or 723 K) for 2 h.

3.3.2.4 Synthesis of ZnO-SnO$_2$ (Zn/Sn = 1)

Preparation of ZnO-SnO$_2$ (Zn/Sn = 1) was achieved when 2.975 g of Zn(NO$_3$)$_2$ 6H$_2$O and 3.506 g of SnCl$_4$ 5H$_2$O were dissolved into 20 ml of 0.1 M HNO$_3$ in a 50 mL beaker. Into the solution, 2.0 g of urea is added and the solution is stirred till urea becomes dissolved. The solution is transferred to autoclave (100 ml) and heated at 373 K for 48 h. The solid formed in the autoclave is recovered by filtration. After crushing with glass rod, it is dried at 333 K for 2 days. Then crushed with a mortar, dried at 443 K for 1 h, and finally calcined at 823 K for 2 h.

3.3.2.5 Synthesis of 2.5 wt% Zn/SiO$_2$-MgO (Si/Mg = 1)

2.5 wt% Zn/SiO$_2$-MgO (Si/Mg = 1) was prepared by dissolving 0.254 g of Zn(NO$_3$)$_2$.6H$_2$O and 5.518 g of Mg(NO$_3$)$_2$.6H$_2$O into 20 ml of 0.1 M HNO$_3$ in a 50 mL beaker. Into the solution, 2.0 g of urea is added and the solution is stirred till urea becomes dissolved. 5 mL of TEOS is added with whole pipette (one-mark pipette), and stirred till the solution become homogeneous. The solution is transferred to autoclave (100 ml) and heated at 373 K for 48 h. The spherical solid formed in the autoclave is recovered by filtration. After crushing with glass rod, it is dried at 333 K for 2 days. Then crushed with a mortar, dried at 443 K for 1 h, and finally calcined at 723 K for 2 h.

3.3.3   Characterization of catalysts

Characterization of catalysts were done comprehensively in other to establish the physico-chemical features of the catalysts' synthesized. Adopted characterization techniques are listed below:

3.3.3.1 BET Surface area

At 77 K, N_2 adsorption measurements was used to characterize the textural properties of the catalysts with the aid of Quantachrome Autosorb 1-C analyzer. Outgassing of the samples were done at 220 ^{0}C under vacuum (10-5 Torr) for 3 hours before N_2 physisorption. The BET surface areas were determined from the adsorption data with an assumption that the cross-section of N_2 molecule is 0.164 nm^2 and that the relative pressure (P/P_0) range from 0.02-0.3.

3.3.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Nicolet FTIR spectrometer (Magma 500 model) was used to measure the transmission FTIR spectra of adsorbed pyridine for all the catalysts, so as to determine the nature of the Brönsted and Lewis acid sites. Wafer (self-supporting) with the dimension of about 50-60 mg in weight and 20 mm in diameter was used as the sample, formed by ensuring that zeolite powder was of uniform layer when compressed. An infrared vacuum cell equipped with KBr windows (Makuhari Rikagaku Garasu Inc.) was used to hold the wafer and pretreated at 450 ^{0}C for 2 hours under vacuum followed subsequently. At 150 ^{0}C, the pyridine vapor was made to come in contact with the pretreated wafer for 5 min and preceded by evacuation at 150 ^{0}C for 2 hours. Cooling of the IR cell to ambient temperature was ensured before placing it in an IR beam compartment whereas

the recordings for spectra transmission under vacuum and were noted. Pyridine desorption at 300-500 ^{0}C was carried out.

3.3.3.3 Scanning Electron Microscopy (SEM) and Electron Diffraction SEM (EDSEM)

Selected samples were used for the SEM and EDSEM mappings so as to determine the catalysts morphology. FE-SEM Nova NanoSEM 230 was used to record these images.

3.3.3.4 X-ray Diffraction (XRD)

The degree of meso porosity and crystallinity of the catalysts were measured via XRD. Rigaku Miniflex II XRD powder diffraction system was used to record low- and high- angle X-ray diffraction pattern over CuKa radiation (1= Ka= 1.54051 Å, 30 Kv and 15 mA). Recording of the XRD patterns in the static scanning mode from 1.2-60^0 (2q) at an angular speed of 2^0/min for detecting and 0.02^0 of step size.

3.4   Calibration of Gas Chromatography (GC)

3.4.1   Retention time determination for compounds

Retention times help in identifying each components in the reaction products. Analysis of all the compounds used in pure forms were carried out in a GC to determine their retention times. The retention times for different compounds are given in table 3-1 below. A flow rate of 20 ml/min was maintained for Helium (The carrier gas) and temperature of the oven is programmed for 25 min. to range between $40\ ^0C\ to\ 250\ ^0C.$ Operation condition is a key factor which can enhance slight variation in retention times.

Table 3-1: Different retention times for compounds in the GC.

Compounds	Retention times (min.)
Gaseous Hydrocarbon	3.019-4.950
Methanol	5.711
Toluene	9.717
Ethylbenzene	12.114
Isomers of xylene	13.300- 14.500
Styrene	17.107
Others	>19.000

3.4.2 Correlation between GC reading and the actual weight percentage of each compound

Standard samples with different compositions of styrene and ethylbenzene were prepared for GC calibration. Carefully chosen sample compositions for the different investigated reaction conditions were considered so that all possible combinations of products reflected. The first injected sample of 0.2 μl to the GC gives output in area % representing the responses for each components. All other samples also were analyzed using the same procedure.

3.5   Evaluation of catalysts

The synthesized basic catalysts (Cs-X, Cs_2O/Cs-X, ZnO/Cs-X, and ZnO/Cs_2O/Cs-X) were used for toluene alkylation with methanol. Reaction temperature of $410\ ^0C$ was used for evaluation of catalysts. Reproducibility of experimental data was ensured by repeating the experimental runs for at least twice for each reaction temperature.

The definitions for conversion and selectivity are as given below;

$$\text{Methanol conversion} = [1 - \frac{\text{recovered moles of methanol}}{\text{fed mole of methanol}}]\ X\ 100 \qquad (4\text{-}1)$$

$$\text{Toluene conversion} = [1 - \frac{\text{moles of toluene in product}}{\text{fed mole of toluene}}]\ X\ 100 \qquad (4\text{-}2)$$

$$\text{Ethylbenzene selectivity} = [\frac{\text{yield of Ethylbenzene}}{\text{yield of Ethylbenzene} + \text{yield of styrene}}]\ X\ 100 \qquad (4\text{-}3)$$

$$\text{Styrene selectivity} = [\frac{\text{yield of styrene}}{\text{yield of Ethylbenzene} + \text{yield of styrene}}]\ X\ 100 \qquad (4\text{-}4)$$

$$\text{Yields of styrene} = \frac{\text{Toluene conversion X Styrene selectivity}}{100} \qquad (4\text{-}5)$$

CHAPTER FOUR
RESULTS AND DISCUSSION

4.1 Results of characterization of catalysts

4.1.1 SEM

Figures 4-1 and 4-2 below depict the SEM images. Cs-X consists of crystallites ranging in majority between 1~ 3 μm. ZnO/Cs-X is made up of crystallites ranging between 1~ 3 μm with smaller particles ranging between 0.1~ 1 μm attached to them. It is indicated that ZnO particles are the small particles that are attached to the larger crystallites.
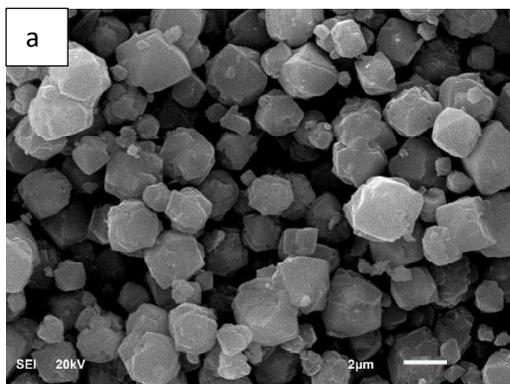
Figure 4-1: Cs-X Catalyst SEM image
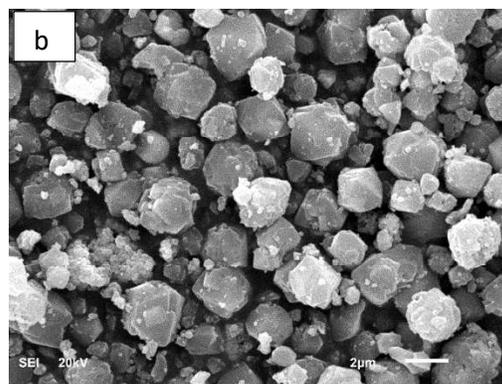
Figure 4-2: ZnO/Cs-X Catalyst SEM image

4.1.2 BET Surface area

Table 4-1 presents the surface areas. Calculation of normalized surface areas as indicated in Table 4-1 using the relation given below was because of an increase in the weight of the zeolite unit cell by ion-exchange of Na with Cs followed by the addition of other components.

Normalized surface area =

$$\frac{\text{(measured surface area) X (unit cell weight of zeolite X containing Cs and zinc oxide)}}{\text{unit cell weight of Na-X}}$$

Retention of crystalline structure was established after Cs ion-exchange since the values obtained for the normalized surface area of Cs-X and Na-X was close. Decrease of about 80 % in surface area was observed for zinc oxide addition preceded by calcination at 773 K to yield ZnO/Cs-X. Likewise, decrease in normalized surface area was also noticed for Cs_2O loading on Cs-X. The measured surface area for ZnO, 10 wt% Sn-SiO_2/ZnO, 2.5 wt% Zn-SiO_2/MgO, SiO_2-ZnO Si/Zn=1 calcinated at 450 ^{0}C, SiO_2-ZnO Si/Zn=1 calcinated at 550 ^{0}C, $Si-SnO_2$ calcinated at 550 ^{0}C, and $Zn-SnO_2$ Zn/Sn calcinated at 550 ^{0}C are 7.8, 52.2, 303.6, 123.0, 56.2, 609.3, and 89.4 m^2g^{-1} respectively.

Table 4-1: Catalysts Surface areas

Catalyst	BET Surface area (m^2g^{-1})	Normalized Surface area (m^2g^{-1})
Na-x	527	527
Cs-X	373	513
Cs_2O/Cs-X	367	507

4.1.3   XRD

Figure 4-2 depicts XRD patterns for Cs-X, ZnO/Cs-X and Cs_2O/Cs-X. The decrease in peaks' diffraction intensity follows a descending form of Cs-X, Cs_2O/Cs-X and ZnO/Cs-X respectively. However crystalline structures of all the samples where retained.
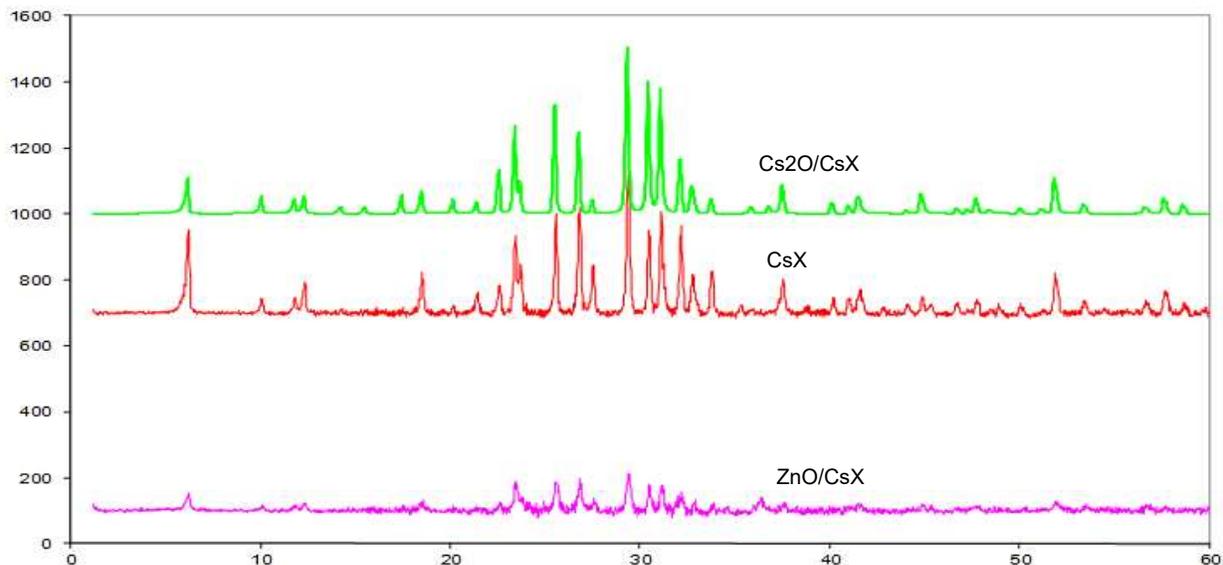
Figure 4-3: XRD Pattern of the catalysts.

4.1.4 IR study

Figure 4-3 represents the IR spectra of adsorbed methanol on Cs-X and ZnO/Cs-X at 623 K.
For Cs-X, only one peak was observed at 1610 cm^{-1} while two peaks appeared in ZnO/Cs-X at
1610 cm^{-1} and 1690 cm^{-1}. The study of the adsorption of methanol at 673 K by infrared
spectroscopy on Cs-X and ZnO/Cs-X indicated the formation of formate ions (Unland et al.).
Examination of the Cs-X infrared spectra during the reaction of toluene and methanol at 673 K
showed formation of bidentate formate on the surface during the reaction. ZnO/Cs-X showed
unidentate and bidentate formates formation on the surface during the reaction. Unidentate formate
is suggested to be an intermediate for side-chain alkylation. Palomares et al. (44) showed from
infrared spectroscopy and temperature-programmed desorption of a mixture of toluene and
methanol that the main adsorbed species was toluene.
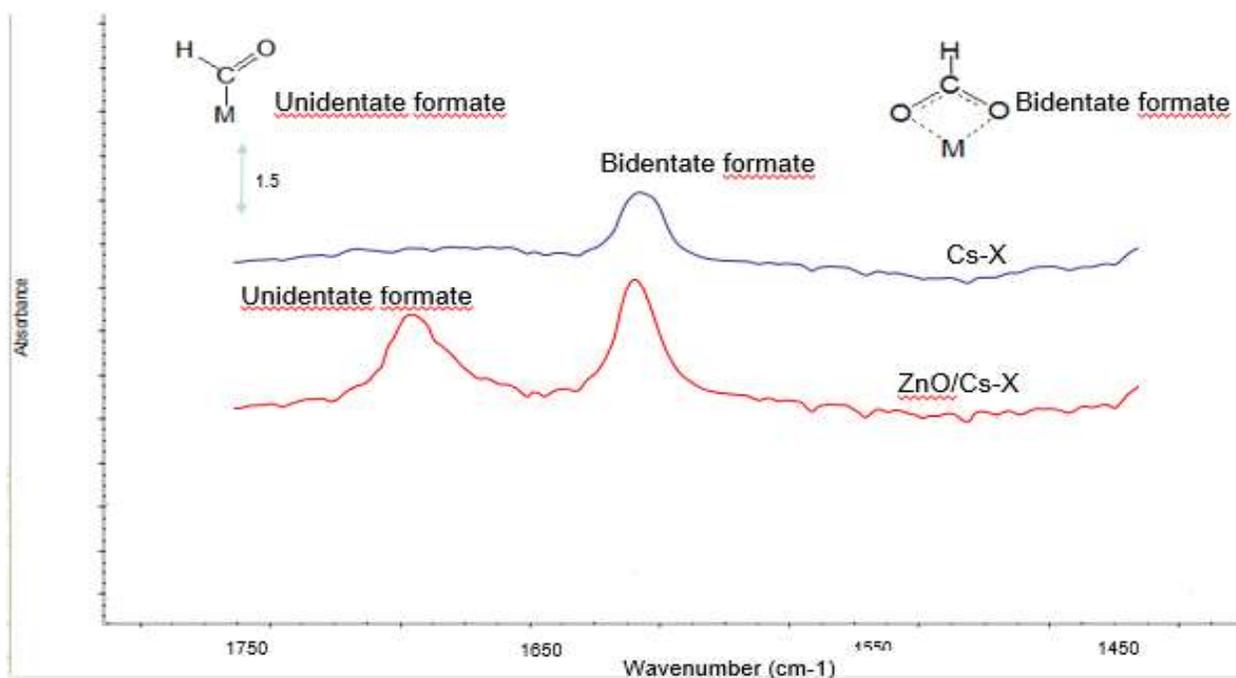
Figure 4-4: IR spectra of adsorbed methanol on Cs-X and ZnO/Cs-X at 623 K

IR spectroscopic studies of adsorbed methanol have depicted that less basic alkali exchanged zeolites (e.g., Na-X) as an alternative sorb methanol over toluene [75]. Lone pair of electron of the oxygen in alcohol and the cation of the zeolite, and the hydrogens present in OH as well as the lattice Oxygen for a methyl group of the zeolite, principally enhances interaction of methanol. Thus, the main products formed are xylenes. Zeolites that are more basic such as Cs and Rb-X, conversely sorb toluene over methanol. The aromatic ring electrons with the zeolite's cation and, the methyl group hydrogens with the lattice Oxygen essentially enhance interaction of toluene. For this, styrene and ethyl benzene are the main reaction products.

These outcomes mean that three parameters are very important for side chain alkylation, and they are; methanol oxidation to formaldehyde, the methyl group of toluene's polarization and the sorption stoichiometry between toluene and the chemisorbed methanol (toluene has to be

preferentially adsorbed over methanol). Rb and Cs-X met all these requirements while K-X met them partially, for situations in which a mechanism of the aldol-type condensation is proposed for the occurrence of the side chain alkylation of toluene.

The direct interaction between Cs^+ (alkali metal cation (electron pair acceptor)) and the methanol oxygen (electron pair donor) is crucial for all zeolites as well as in the adsorption structures.

The interaction of the methanol hydrogen-atoms with the framework increases with increase in the polarity of the oxygen centers in the zeolite framework leading to an isolated methanol molecule coordinately bound to the alkali metal cation. The detailed IR spectra analysis connotes that slight steric hindrance was experienced by the OH group and the methyl group of the adsorbate, with relative to deformational and rotational movements. The higher the negative charge on the oxygen in the zeolite lattice, the more important is the additional hydrogen bonding between the hydrogen of the methanol hydroxyl-group and the oxygen of the zeolite lattice.

Besides, interaction between the methyl-group hydrogens and the zeolite lattice is also noticed. The more the concentration of the zeolites' alkali cations, the more the density of the adsorption sites allow additional hydrogen bonding between sorbed methanol molecules. This work presents IR spectra which indicated that at low MeOH coverage, coordinately bound methanol molecules enhance the hydrogen bonding and not through clustering of several methanol molecules around an alkali metal cation because the chosen conditions in the IR experiments were that irregular MeOH clustering could be neglected.

4.2   Activity of catalysts

The activities of catalysts for side chain alkylation of toluene and methanol with molar feed ratio of 1:1 (toluene:methanol) at a reaction temperature of $410\ ^0C$, feed rate of 0.12 ml/min, N_2 flow rate of 40 ml/min, catalyst weight of 40 mg over the synthesized catalysts are given in Table 4-2 below. Time on stream of 50 min. will be considered for all discussions. The major products from the experimental results are styrene and ethylbenzene. The reactants, toluene and methanol, as well as hydrocarbons in small quantities less than 5 % of styrene produced, also appear among the products. Thus, the hydrocarbons were excluded from product quantification.

Table 4-2: Activities of catalysts for toluene side chain alkylation with methanol for a molar feed ratio of 1:1 (toluene:methanol) at a reaction temperature of $410\ ^0C$.

Catalyst	Methanol conversion (%)	Toluene conversion (%)	EB selectivity (%)	SM selectivity (%)	SM yield
Cs-X	6.9	3.9	46.2	52.4	7.4
CuO/Cs-X	3.3	2.3	41.0	59.0	1.4
K₂CO₃/Cs-X	6.3	2.5	40.6	58.1	1.5
MoO₃/Cs-X	35.3	1.9	16.2	79.2	1.5
V₂O₅/Cs-X	73.4	0.5	18.4	81.6	0.4
ZnO/Cs-X	42.4	4.6	20.6	76.1	3.5

Cs_2O/Cs-X	23.6	5.7	85.3	9.8	0.6
ZnO/Cs_2O/Cs-X	40.1	7.0	53.2	40.0	2.8
Sn/SiO$_2$- ZnO/Cs-X	19.43	4.37	33.53	75.51	3.3
SiO$_2$- ZnO (45O)/Cs-X	34.2	2.8	11.6	88.4	2.5
ZnO- SnO$_2$ (55O)/ Cs-X	95.4	2.9	78.1	17.5	0.5
Zn/SiO$_2$-MgO/Cs-X	16.7	3.4	21.9	78.1	2.7
SiO$_2$- ZnO (55O)/Cs-X	19.5	1.0	29.4	70.6	0.7
SiO$_2$-SnO$_2$ (55O)/Cs-X	19.1	2.5	39.9	57.5	1.4

Figure 4-4 shows how the catalytic activity of Cs-X/Cs_2O was enhanced by its modification with ZnO. The selectivity to styrene was also increased. Toluene conversion was 5.69 % and 7.02 % for Cs-X/Cs_2O and ZnO/Cs-X/Cs_2O respectively as shown in Figure 4-4 (a). Selectivity to styrene was 9.82 % and 39.95 % for Cs-X/Cs_2O and ZnO/Cs-X/Cs_2O respectively as shown in Figure 4-4 (b). Modification of Cs-X/Cs_2O with ZnO enhanced the increments in toluene conversion and styrene selectivity for Cs-X/Cs_2O.
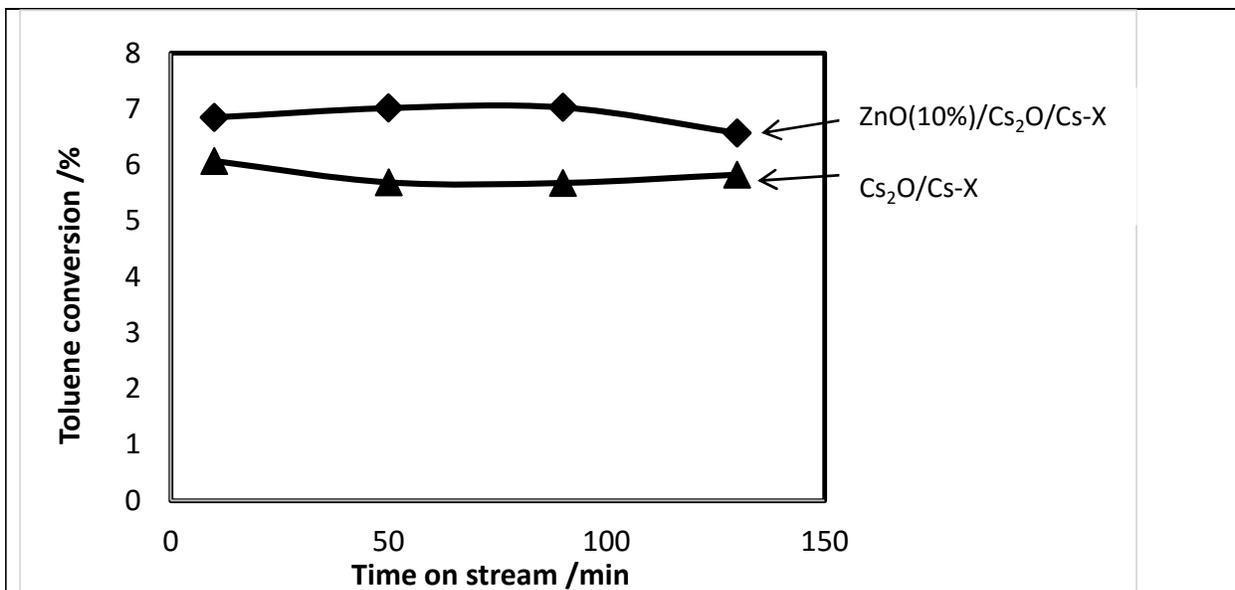
(a)
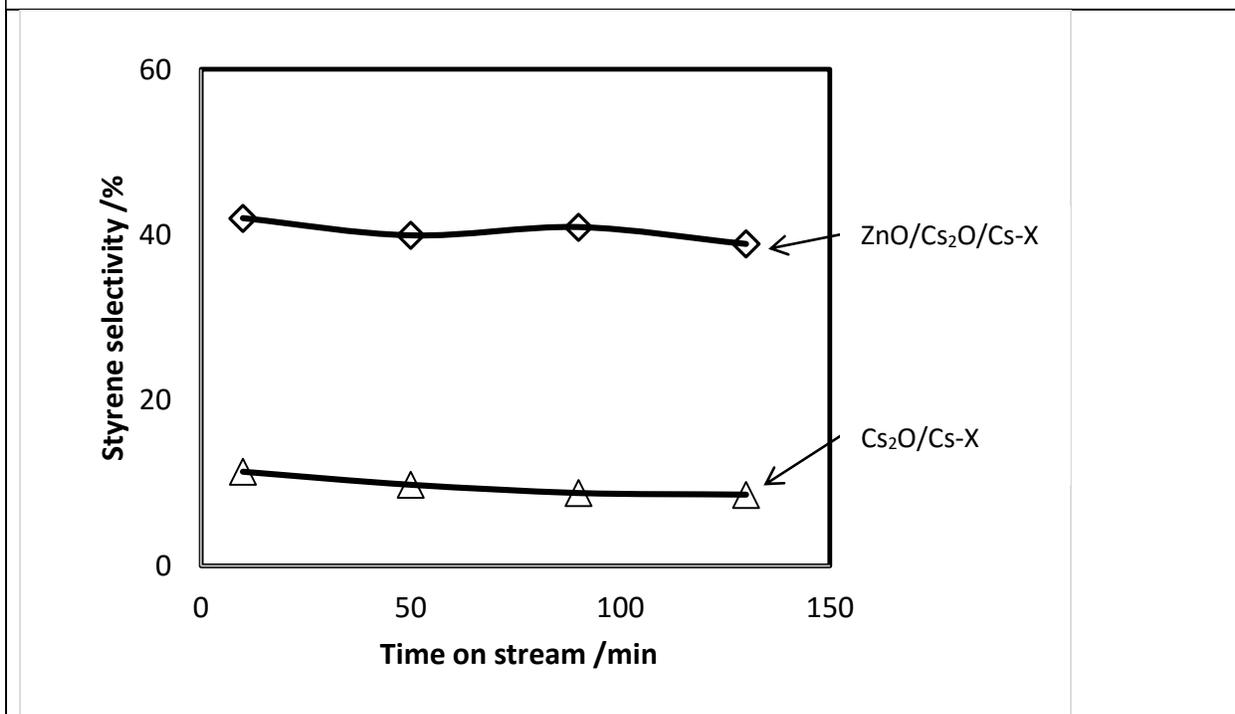
(b)

Figure 4-5: Toluene conversion (a) and styrene selectivity (b) as a function of time on stream in side chain alkylation of toluene with methanol at 683K over Cs-X and Cs-X's modified with zinc oxides.

Figure 4-5 represents the changes in the activity and selectivity to styrene with respect to time on stream under the reaction conditions given above. As seen in Figure 4-5 (a), ZnO modification on Cs-X gave significant changes in the toluene conversion from 3.92 % to 4.6 %. Time on stream of 10 min gave the highest toluene conversion for ZnO/Cs-X, which decreased gradually with time on stream. K_2CO_3/Cs-X gave conversion lower than that of unmodified Cs-X, but remained un-decayed with time on stream. CuO/Cs-X, MoO_3/Cs-X, and V_2O_5/Cs-X showed a decrease in conversion between times on stream of 10 min and 50 min before remaining almost constant up to 130 min.

Cs-X modification with oxides resulted in a unique increase in the selectivity to styrene as indicated in Figure 4-5 (b). In precise, ZnO/Cs-X revealed selectivity higher than 76 % all through the time on stream, unmodified Cs-X gave selectivity below 45 %.

(a)

(b)
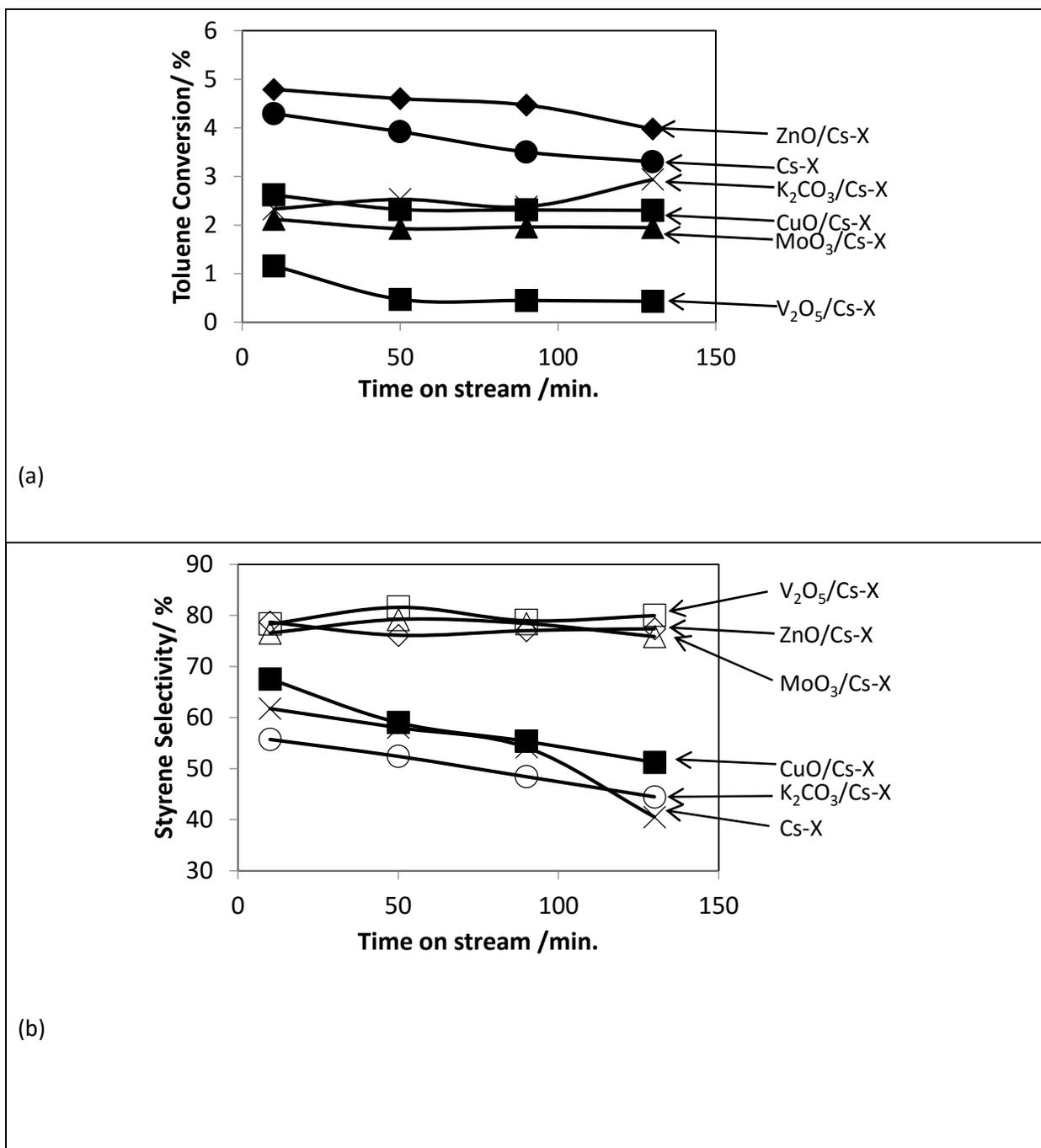
Figure 4-6: : Toluene conversion (a) and styrene selectivity (b) as a function of time on stream in side chain alkylation of toluene with methanol at 683 K over Cs-X and Cs-X's modified with metal oxides.

Modifications of ZnO was also done with different oxides as indicated in Figure 4-6 below. It is established that Sn/SiO$_2$- ZnO/Cs-X gave the highest toluene conversion as shown in Figure 4-6 (a). Zn/SiO$_2$-MgO/Cs-X showed a decaying conversion as time on stream increased. ZnO- SnO$_2$ (55O)/ Cs-X showed an increasing conversion for the first 50 min of time on stream which later became almost constant throughout. SiO$_2$- ZnO (45O)/Cs-X and SiO$_2$- ZnO (55O)/Cs-X maintained very close conversion throughout. SiO$_2$- ZnO (55O)/Cs-X gave activity worse than that of unmodified Cs-X.

Figure 4-6 (b) represents the selectivity to styrene the oxide modified Cs-X. SiO$_2$- ZnO (45O)/Cs-X indicated selectivity higher than 86 % for the whole 130 min of time on stream. ZnO- SnO$_2$ (55O)/ Cs-X showed a decaying selectivity. The nature of other catalysts can be noticed from the data given in Table 4-2.
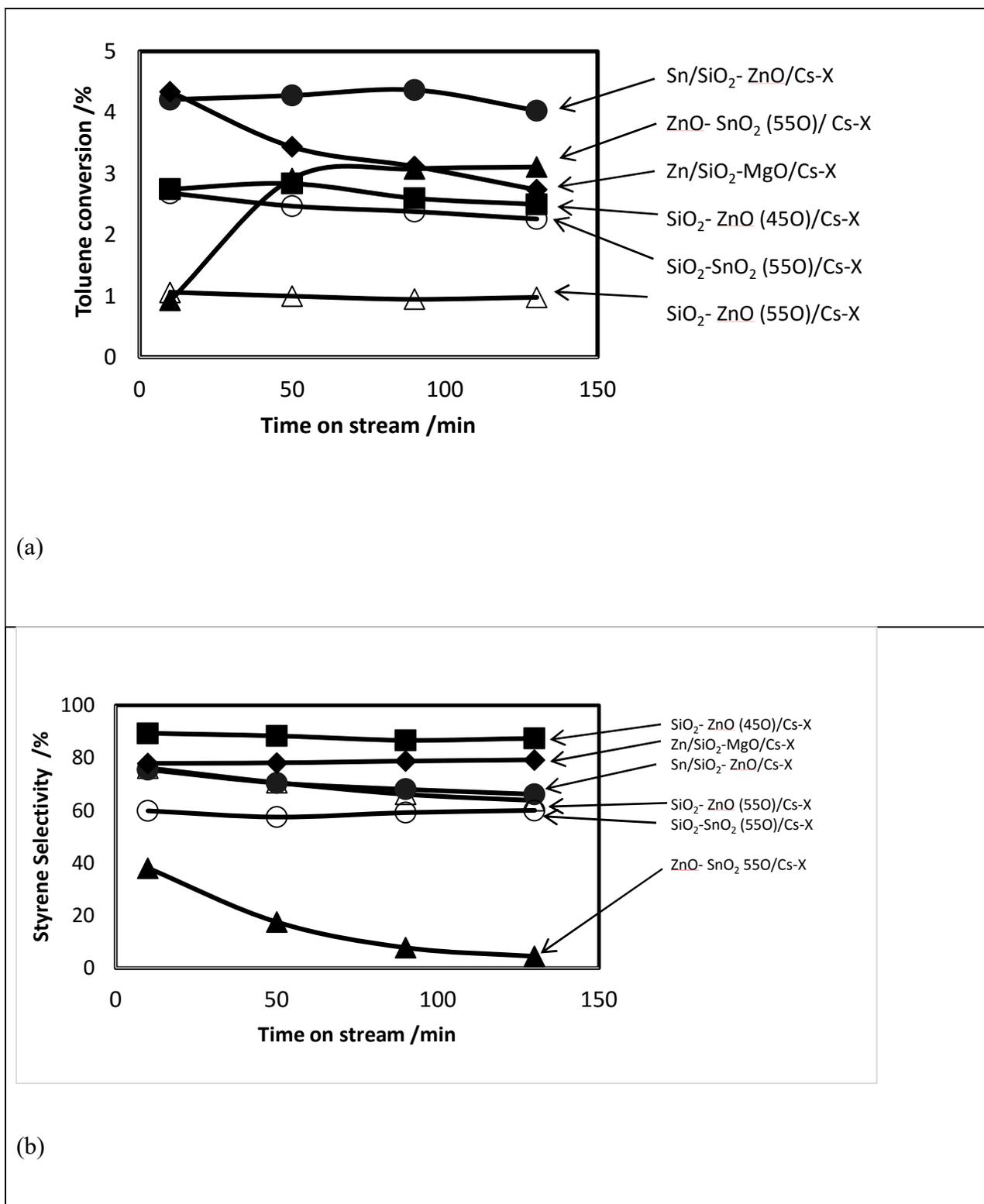
Figure 4-7: Toluene conversion (a) and Styrene selectivity (b) as a function of time on stream in side chain alkylation of toluene with methanol at 683 K over Cs-X and Cs-X's modified with metal oxides.

Finally, examination of ZnO loading effect performed on Cs-X and Cs_2O/Cs-X while the results are presented in Figure 4-7. Figure 4-7 (a) depicts that 5 wt% zinc oxide loaded on Cs-X gave the maximum toluene conversion whereas 10 wt% gave the maximum selectivity to styrene. 5 wt% zinc oxide loaded on Cs_2O/Cs-X (meaning ZnO/Cs_2O/Cs-X) gave the maximum toluene conversion, while the maximum loading required for selectivity to styrene was not obvious as given in Figure 4-7 (b).
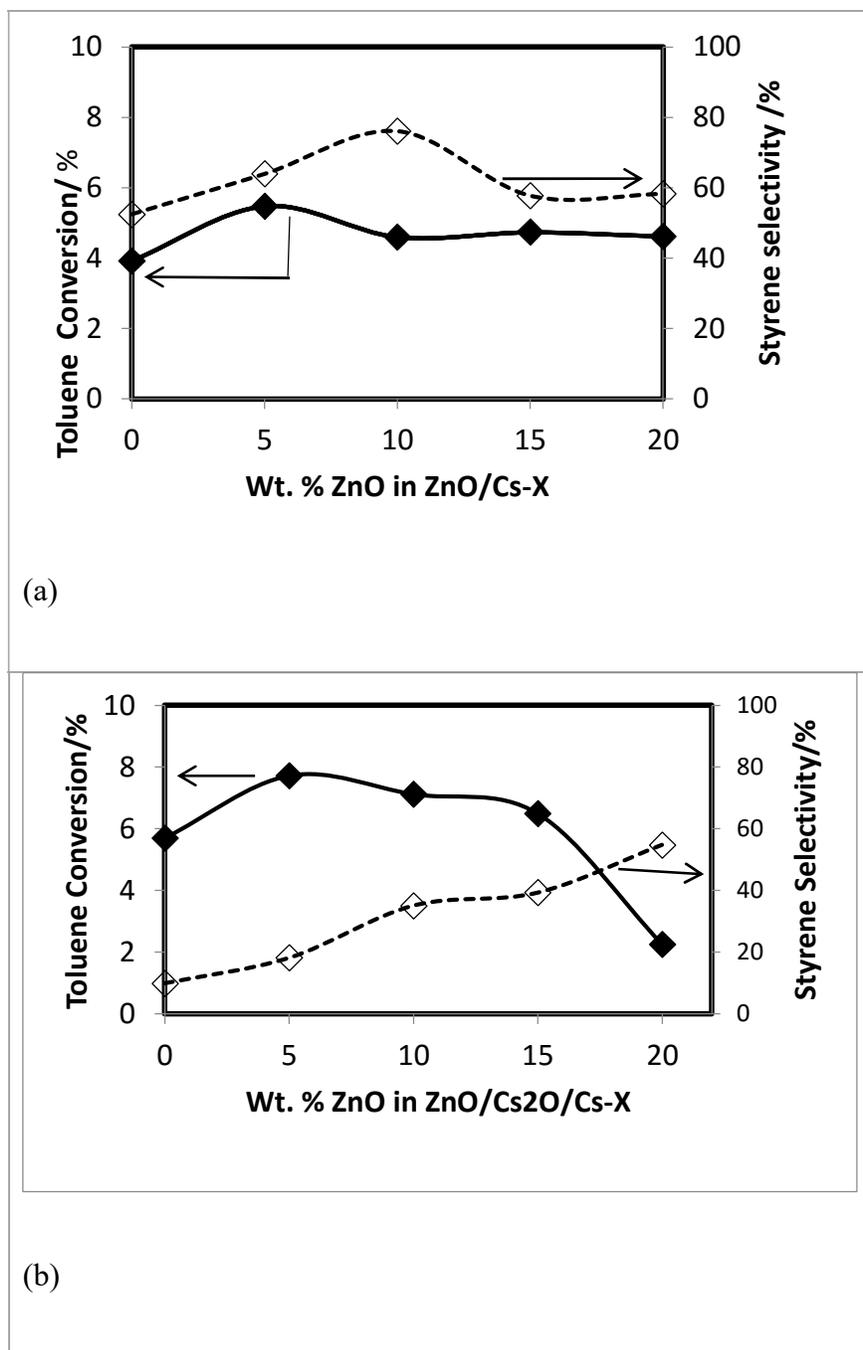
Figure 4-8: ZnO loading effects on the catalysts activity and selectivity to products for Cs-X (a) and Cs_2O/Cs-X (b).

4.3 Basicity of Catalysts

Study of IR of adsorbed pyridine showed the changes in acidity of modified Cs-X. Figure 4-8 below depicts IR spectra of adsorbed pyridine on Cs-X, Cs_2O/Cs-X and ZnO/Cs-X. Due to carbonate ion species because Presence of strong band below 1450 cm^{-1} as a result of species of carbonate ion, the band at 1450 cm^{-1} attributed to pyridine matched to Lewis acid site for Cs_2O/Cs-X and ZnO/Cs-X was not noticeable. Absence of the band at 1540 cm^{-1} for the three catalysts implied that no protonic acid sites were present on the three catalysts. For the three catalysts, temperature of evacuation has an effect on the changes spectra indicating that addition of ZnO and/or Cs_2O/Cs-X to Cs-X does not cause much change in the acid sites. It is worthy of note that the surface of the three catalysts is responsible for the acid sites adsorption of pyridine after evacuation at 423 K.
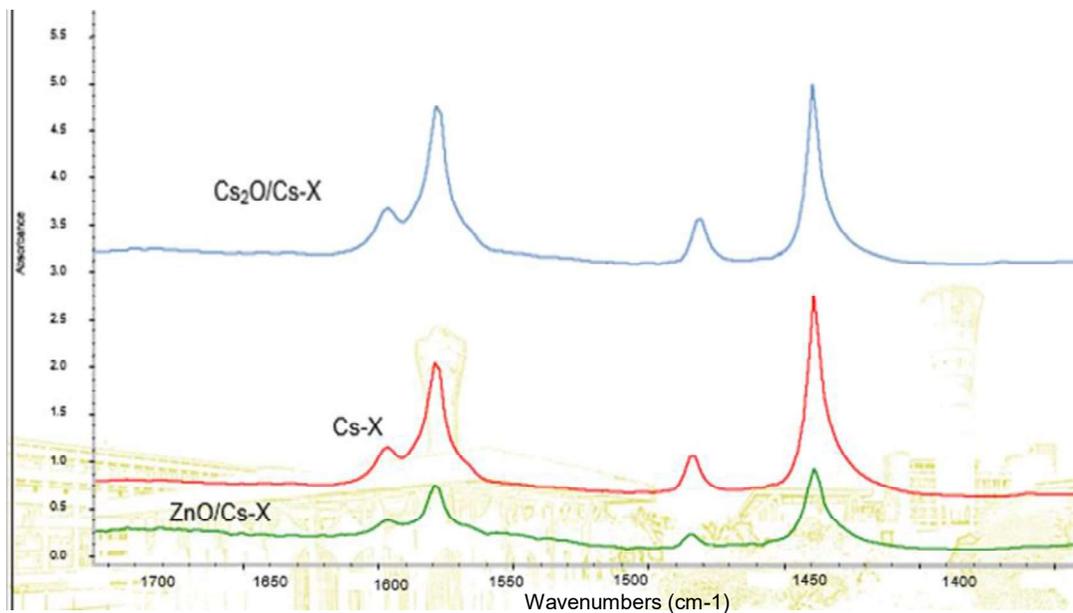
Figure 4-9: IR spectra of adsorbed pyridine on Cs-X, Cs_2O/Cs-X and ZnO/Cs-X at room temperature and evacuated at 423 K for 30 min.

4.4   Effects of ZnO addition on the Catalytic Activity and Products selectivity of Cs-X and Cs_2O/Cs-X
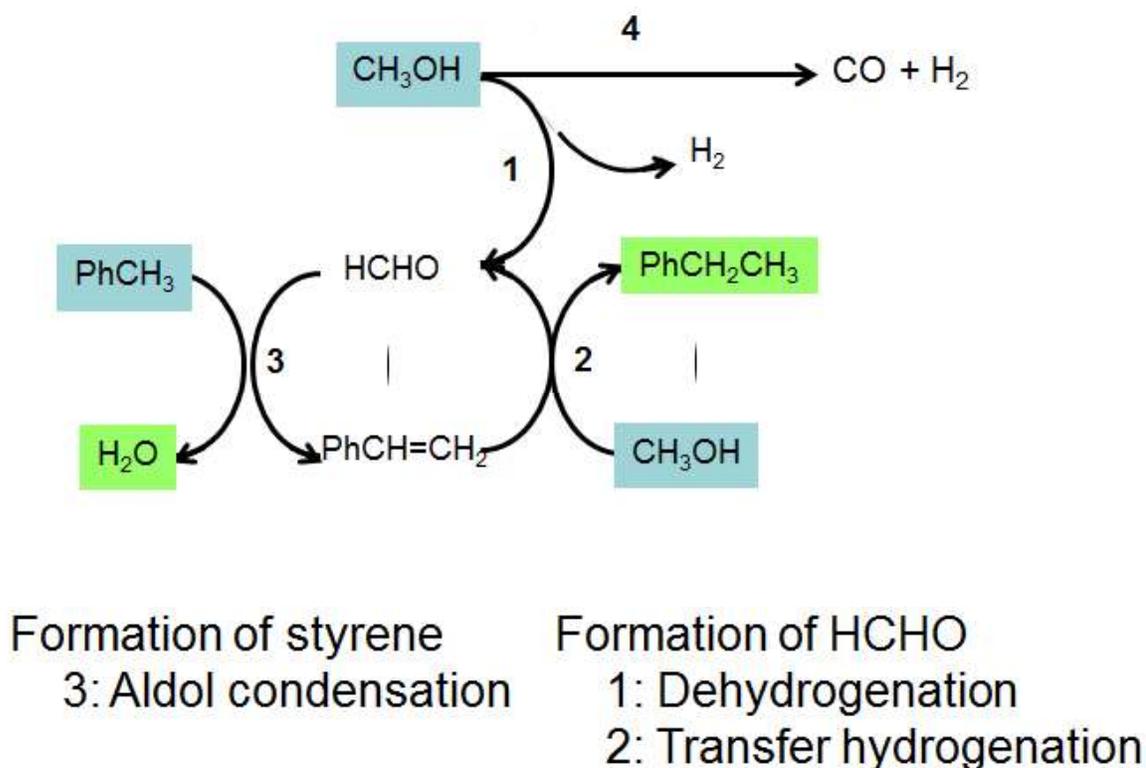
Figure 4-10: Effects of ZnO addition

The enhancement of the catalytic activity and selectivity to styrene were respectively increased due to the addition of ZnO to Cs-X, whereas Cs_2O loading on Cs-X increases catalytic activity and enhanced selectivity towards ethylbenzene. For side chain alkylation, activity of ZnO(10%)/Cs-X in terms of conversion and styrene selectivity was high. In order to increase the activity further, knowledge about ZnO distribution over Cs-X is to be investigated. So to learn more about ZnO impregnation over Cs exchanged Zeolite X, TEM characterization was used. The SAED pattern shows that phase of ZnO nanoparticles are crystalline in nature. Each particle is composed of many crystals. The diffraction lines clearly indicate the regularly oriented nanosized ZnO crystalline particles.

The effects of Cs_2O loading on Cs-X along with selectivity towards the products are correspondingly shown with Figure 4-4 above. Selectivity to styrene and its activity increased as well due to addition of ZnO to Cs_2O/Cs-X. Figure 4-7 (a) established that 10 wt% of ZnO addition is the optimum amount. 10 wt% ZnO has catalyst activity of about four times as high as Cs_2O/Cs-X catalysts without ZnO loading. Figure 4-7 (b) showed that selectivity to styrene with ZnO/Cs_2O/Cs-X is more than when Cs_2O/Cs-X was loaded without ZnO. 10 % ZnO loading on Cs_2O/Cs-X recorded an increment in toluene conversion and selectivity to styrene by 75.5 % (from 10.40 % to 42.50 %) and 16.7 % (from 6.0 % to 7.2 %) respectively, because of the increase in acidity of the catalysts active site which enhances formaldehyde conversion to styrene [35, 38].

Loading effects of ZnO on activity and product selectivity of Cs-X and comparison with other oxides modifications of Cs-X are depicted in Figure 4-5 above. Both catalyst activity and selectivity towards styrene are increased by the addition of ZnO. Toluene conversion increased by 70 % (from 1.5 % to 5.0 %) due to 10 % loading of ZnO on Cs-X (Figure 4-5 (a)) whereas a diminishing trend was noticed for loading above 10 % due to blockage of catalyst pore from excess loading. The selectivity to styrene increased by 31.25 % at 10 % loading of ZnO to Cs-X (from 55 % to 80 %).

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1   Conclusions

This study presents that various conditions must be met for catalysis of the side chain alkylation of toluene and methanol to be successful. The expected features of the catalyst are that it must (i) possess base strength which is adequate for formation of formaldehyde from methanol dehydrogenation, (ii) be able to enhance methyl group activation and maintain toluene stability surface-wise or within the pores, and (iii) create sufficient sorption stoichiometry between toluene and methanol. Catalytic activity can only be recorded to be significant using materials with these characteristics.

Several combinations of modified Cs-X catalysts were studied for side chain alkylation of toluene with methanol, whereas ZnO produced from zinc nitrate resulted to an increase in the catalytic activity of styrene and an increase in the selectivity to styrene; Catalytic acqtivity of Cs-X is increased with reduced selectivity to styrene when modified with Cs_2O. The following conclusions can also be reached;

๑ ZnO increases both the activity (from 3 % to 7 %) of the catalysts and the selectivity towards styrene (from 50 % to 80 %).

๑ The ZnO gave good catalytic performance:

❖ Enhances the formation and selectivity of styrene via side chain alkylation reaction.

❖ Enhances styrene formation by forming unidentate formate from methanol. Also, transfer hydrogenation of styrene was suppressed.

5.2   Recommendations

◦ Catalytic activity and selectivity to styrene must be studied for other sources of zinc oxide and comparison should be made.

◦ Study of the kinetics for the side chain alkylation of toluene and methanol should be performed.

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