SURFACE MODIFIED ZEOLITE CATALYSTS FOR THE HYDROUS PYROLYSIS OF HEAVY OIL

BY

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DEDICATION

This work is dedicated to my beloved parents..

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I would like to acknowledge all committee members for their support and guidance throughout my research work. I want to express my sincere and deepest gratitude to Supervisors, **Dr. Adnan Al Amer**, and **Dr. Oki Muraza** for their guidance and also keeping me motivated to achieve this milestone. I would also like to thank Center of Research Excellence in Nanotechnology (CENT), Chairman Dr. Zain Yamani and his team for providing me all facilities and support to complete this work in allocated time. I also thank to Chemical System Engineering Laboratory members Hokkaido University Japan for their sincere contributions in this work.

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LIST OF ABBREVIATIONS

API	:	American Petroleum institute
AR	:	Atmospheric Residue
Atm	:	Atmosphere
BAS	:	Brønsted Acid Sites
BEA	:	Beta Zeolite
cP	:	CentiPoise
DRIFT	:	Diffuse reflectance infrared Fourier transform
EIA	:	Energy Information Administration
FAU	:	Faujasite
FCC	:	Fluid Catalytic Cracking
FID	:	Flame Ionization Detector
GC	:	Gas Chromatography
H/C	:	Hydrogen/Carbon
HDT	:	Hydrotreater
HDC	:	Hydrocarking
IGCC	:	Integrated Gasification Combined Cycle
LAS	:	Lewis Acid Sites

Mol		Mole
MOR	:	Mordenite
MR	:	Membered ring
MW		Molecular weight
OPEC	:	Organization of the Petroleum Exporting Countries
TCD	:	Thermal Conductivity Detector
TPD	:	Temperature Programmed Desorption
WGSR	:	Water Gas Ghift Reaction
USY	:	Ultra stable Zeolite Y
XRD	:	X-ray Diffraction

ABSTRACT

Full Name : Umer Khalil Chaudhry

Thesis Title : Surface modified zeolite catalysts for the hydrous pyrolysis of heavy oil

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Surface of the Beta zeolite catalyst (SiO_2/Al_2O_3=150) was modified to improve its hydrophobicity and stability using organo-silane compound. Triphenyl silane was deposited on external surface of catalysts through two techniques i.e. vapor phase deposition and liquid phase deposition. Characterization techniques such as XRD, TPD, N_2-adsorption and FT-IR pyridine were used to characterize these catalysts. Silane treated Beta catalysts retained its crystallinity after modification however, decrease in acidity were observed in NH_3-TPD studies. These results were confirmed by FT-IR pyridine analysis which showed decrease in both Brønsted and Lewis acid site after modification. Parent Beta and silane treated Beta catalysts were tested in fixed-bed reactor for steam-assisted catalytic cracking of atmospheric residue. Silane treated Beta zeolites exhibited hydrophobic properties; hence the modified Beta catalysts were more stable at high temperature in aqueous environment. It was found that the Beta catalysts modified through both techniques retained their crystallinity and phase purity after reaction. Moreover coke formation was also reduced significantly over silane treated Beta catalysts. This indicates the increase in the stability of catalysts. Furthermore, lighter

hydrocarbons yield from 2 h reaction time were higher as compared to reaction time of 4 h. Yield of gases, gasoline (C_7-C_{13}) and gas oil (C_{14}-$C_{20)}$ over a vapor phase silane treated Beta zeolite catalyst were 11.6 mol %, 55.7 mol % and 3.7 mol % respectively for 2 h reaction time.

ABSTRACT (ARABIC)

الاسم الكامل: عمر خليل شودري

عنوان الرسالة: تعديل سطوح المواد الحفازة الزيوليتية للإنحلال الحراري المائي من النفط الثقيل

التخصص: الهندسة الكيميائية

تاريخ الدرجة العلمية: نوفمبر 2015

تم تعديل سطح المحفز الزيوليتي من نوع بيتا زيولايت (نسبة جزيئات السيلكا إلى الألومنيوم=150) لتحسين سطحه لمقاومة الماء واستقراره باستخدام المركب العضوي السيلاني. تم غرس المركب العضوي ثلاثي فينيل السيلاني على السطح الخارجي من محفزات البيتا من خلال تقنيتين هما الترسب في الحالة البخارية و الترسبب في الحالة السائلة. واستخدمت التقنيات التالية لتوصيف الزيولايت مثل حيود الأشعة السينية، و الإمتصاص الحراري المبرمج، و مقياس مساحة السطوح و حامضية السطوح لتوصيف هذه المحفزات.

محفز بيتا المعدل بالمركب العضوي السيلاني احتفظ بالبلورات الأساسية للمحفز بعد التعديل، ومع ذلك، لوحظ انخفاض في نسبة الحموضة في دراسات مقياس حامضية السطوح. وتم تأكيد هذه النتائج عن طريق تحليل البيريدين FT-IR والتي أظهرت انخفاضا في كل من موقع حمض برونستيد ولويس بعد التعديل.

تم اختبار محفز بيتا الزيولاتي قبل و بعد إضافة المركب العضوي السيلاني في مفاعل ثابت مستمر و في وجود البخار لمساعدة التكسير التحفيزي. و حيث ظهر جليا، أن المحفز المعدل بالمادة السيلانية أصبح يحمل ميزة مقاومة الماء و بالتالي كانت محفزات بيتا المعدلة أكثر استقرارا في درجة حرارة عالية في بيئة مائية.

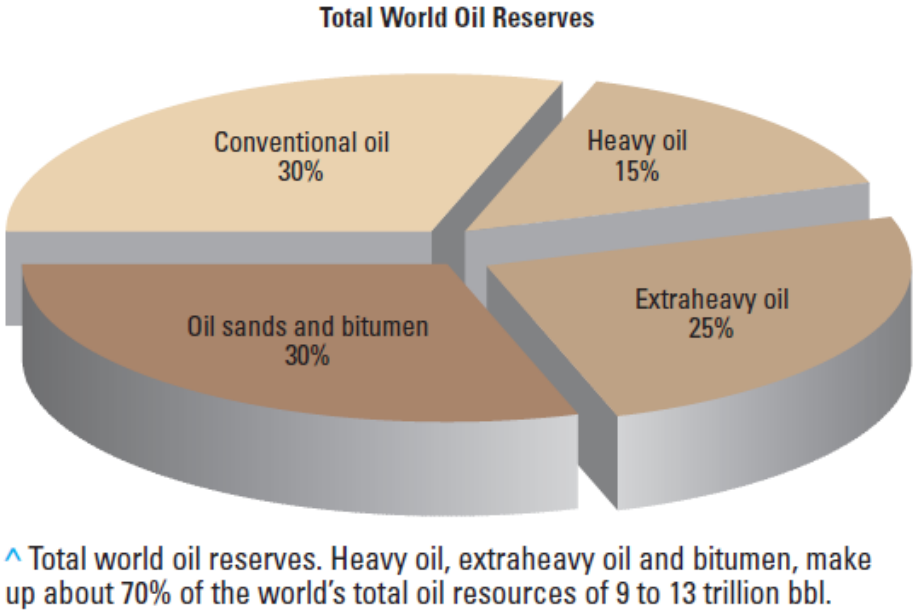
وقد وجد أن المحفزات بيتا المعدلة سواء من خلال التقنيتن احتفظت بتبلورها و نقاء المادة بعد التفاعل. وعلاوة على ذلك تم تخفيض تكون الفحم بشكل كبير في حال التحسين بالمركب السيلاني. وهذا يدل على زيادة في استقرار المواد الحفازة. علاوة على ذلك، كان ناتج المركبات الهيدروكربونية الخفيفة خلال ساعتين من التفاعل كان أعلى مقارنة مع أربع ساعات من التفاعل. وكان الناتج من الغازات، البنزين (C7-C13) والقازولين (C14-C20) في حال وجود المحفز بيتا المعالج بالسيالين هو كتالي، 11.6 مول٪، 55.7 مول٪ و 3.7 مول٪ على التوالي لمدة ساعتين من التفاعل.

CHAPTER 1

INTRODUCTION

The subject of unconventional fossil fuels got more importance in last few decades as conventional fossil fuels reserves are near depletion. Proven reserves which include conventional crude oil are 1.47 trillion bbl and according to study these reserves will sustain up to next forty years at the current level of production [1]. So developing new technologies to utilize unconventional oil resources such as shale oil, tar sand and extra heavy oil is the demand of time.

Unconventional fossil fuel resources makes 70 % of the total world's oil reserves [1] (Figure.1). Fuel from unconventional oil is only accountable for 12 % of total fuel supply [2]. Huge investment and attention should be dedicated towards developing economical and feasible technologies to explore and utilize these unconventional resources.



^ Total world oil reserves. Heavy oil, extraheavy oil and bitumen, make up about 70% of the world's total oil resources of 9 to 13 trillion bbl.

Figure 1. Total oil reserves: an overview [1].

1.1 The World oil scenario

Venezuela, Saudi Arabia and Canada are leading countries in the world with proven oil reserves of 20%, 18% and 12% respectively (OPEC) [2]. According to U.S Energy administration association, Saudi Arabia is the largest oil producing country with the production of more than 10 million bbl/day. Proven reserves of conventional oil are 1.47 trillion barrels which are enough for next 40 years with current rate of production. But considering the increasing consumption of oil, conventional oil resources are depleting and production rate declining 5 % annually. In near future world oil scenario will be shifting towards unconventional oil reserves. According to US-energy administration association study Canada heavy oil reserves are ranked second as compared to conventional oil reserves in Saudi Arabia. While Canada and Venezuela combined have more oil reserves in the category of heavy oil.

Total 30 countries are found to have heavy oil reserves in considerable amount United States (California), Mexico, Brazil, Russia, Indonesia, China, Colombia, Ecuador, Iraq, Kuwait, Saudi Arabia, Chad and Angola (www.halliburton.com). Reserves of heavy oil in these countries make 20 % of total oil reserves of world which is equivalent to 15 years addition of oil supply. Middle East alone have 78 billion barrel of heavy oil reserves which is recoverable and this amounts 3.5 time the U.S total reserves (www.wsj.com). Although Middle East especially Saudi Arabia is depending on easy extracting light oil which is of very high quality but it is expected a transformation from conventional to unconventional oil as lighter oil reserves will not last for too long. Hence, many research on processing and digging out heavy oil is under way in this part of region. According to the International Energy Agency (EIA), approximately 8 trillion dollars will be spent by 2040 in order to develop new oil fields to meet the increasing energy demand in our world. This demand will partially be met by heavy oil and bitumen resources worldwide which are estimated to be approximately 6 trillion barrels.

Saudi Arabia has one fifth of proven conventional oil reserves. Although these reserves are enough to sustain for many upcoming years but after Canada and Venezuela, Saudi Arabia is also targeting to hit heavy oil reserves to enhance their production. Also much advancement is made globally to process heavy oil. Refinery processes are needed to convert heavy crude into valuable products like middle distillates and gasoline.

1.2 Upgrading of heavy oil

Current Oil refining technologies are best optimized to give improved yield and high quality products. Heavy oil have low economic value and more difficult to process as compared to lighter oil. Among all the refining technologies, handling of residue oil is most important and difficult. Economies of an operating refinery majorly depend upon their utilization of heavy oil residues. A substantial investment has been poured into the upgradation of heavy oil processing like Saudi Aramco world largest oil refinery is contributing their efforts to minimize heavy residue. Generally, heavy oil upgrading technologies divided into two categories, Hydrogen addition or carbon rejection. Some technologies based on both carbon rejection and hydrogen addition. Carbon rejection technology because of its low investment presents 56 % of total heavy oil processing capacity. However some countries like Japan largely depends upon hydro treating technologies. Both these technologies are targeted to increase hydrogen to carbon ratio. Carbon rejection technology is oldest and comparatively easier which operates at high temperatures to thermally degrade larger molecules. At the same time molecules combine together to form even heavier molecules resulting in coke formation. These technologies include visbreaking, flexi coking, delayed coking, fluid coking etc. As these processes require less investment and operating cost but on the other hand many disadvantages are associated with these processes such as fewer yields to lighter component, coke formation and presence of other components (S, N) in end products [3]. On the other hand hydrogen addition processes give more product yield as compared to carbon rejection processes. Addition of hydrogen increases H/C ratio hence decrease the density which results in the products of higher commercial values. Hydrogen addition

technologies classified on the type of reactor are fixed-bed, moving-bed, ebullated-bed and slurry-bed processes. Table 1 represents overview of residue processing capacities.

Table 1. Worldwide residue processing capacity (Mbbl/day)

Technology	**United states**	**Europe**	**Canada/ Venezuela**	**Japan**	**Rest of World**	**World total**	**% capacity**
Carbon rejection							
Cracking/Visbreaking	44	2260	331	24	1635	4293	25.8
Coking	2245	673	951	66	1169	5104	30.7
Total	2289	2933	1282	90	2804	9397	56.5
Hydrogen addition							
Fixed-bed, HDT	499	149	30	591	1042	2312	13.9
Ebullated-bed, HDC	102	79	244	23	49	497	2.99
Slurry-phase, HDC			4			4	0.02
Residue FCC	831	681	281	318	1832	3942	23.7
Total	1432	909	559	932	2923	6755	40.6
Others							
Deasphalting	283	46	39	16	75	458	2.76
Total	4002	3889	1879	1037	5801	16609	10000

1.3 Carbon Rejection processes

Thermal processes or carbon rejection processes involves transfer of hydrogen from the heavy molecules to the lighter molecules resulting in coke formation.

1.4 Gasification

This process is carried out temperature above 1000 ^{o}C major products are syngas, ash and carbon. However modified technology named integrated gasification combined cycle (IGCC) has showed great potential for electricity generation due to their minimal effects on environment.

1.5 Delayed coking

This technology is widely used in many refineries because of low initial investments. This technology has an ability to handle any type of residue. Disadvantages of this technology are high coke formation and less liquid yield.

1.6 Fluid coking and flexicoking

These two technologies are developed from fluid catalytic cracking. Flexi coking is the extended form of fluid coking. Liquid yield in these processes are little higher as compare to delayed coking.

1.7 Visbreaking

Visbreaking is developed technology used for both atmospheric and vacuum residues. This is accompanied by thermal cracking to reduce the consumption of fuel oil.in this

process residue is heated upto 500 ^{o}C and then cracked at lower residence time to avoid coke formation.

1.8 Hydrogen addition process

Hydrogen addition process usually involves catalysts. Fluid catalytic cracking is one example of such processes.

1.9 Fluid catalytic cracking

Fluid catalytic cracking offers higher gasoline yield as compare to any other processes. But one disadvantage of this process is the requirement of high quality feed with less metal and sulfur contents. Therefore, atmospheric residue is only suitable for this process. This process use acidic catalyst like USY zeolites. A short overview of heavy oil processing technologies is shown in Table 2.

Table 2. Technologies for processing heavy oil [4]

Catalytic processing technologies	**Thermal processing technologies**
Ebullating bed residue hydroprocessing technology	Visbreaking
Moving/ebullated bed residue catalytic process	Thermal coking
Fixed bed residuum or vacuum residuum desulfurization	Delay coking

	Gasification

1.10 Composition of heavy oil

Heavy oil is differentiated on the basis of high viscosity and low API gravity compared to conventional oil. Definition of heavy oil according to World Petroleum council is oil whose viscosity is between 100 cP and 10,000 cP at reservoir temperature with API gravity between 10 and 20 [3]. Heavy oil has component with complex structure and it is difficult to understand the composition of heavy oil. Many researches have been carried out to understand the heavy oil composition. Asphaltenes are present in heavy oil are most complex and highly aromatic compound. Asphaltenes and resins are usually responsible of high viscosity. In addition to complex compounds heavy oil contains sulfur, nitrogen and other compounds. Composition of these compounds depends upon the origin of heavy oil [4, 5].

Higher viscosity and specific gravity of oil makes it different from conventional lighter oil. Based on viscosity and API gravity heavy oil is divided into three categories as shown in Table 3.

Table 3. Heavy oil feedstocks properties (www.total.com)

	API gravity	**Viscosity (cP)**
Heavy oil	18-25	10 – 100
Extra heavy oil	Up to 20	10000

Oil sands and bitumen	7-9	Above 10000

1.11 Zeolites

Zeolites are subset of molecular sieve family and there structure is based on AlO_4 and SiO4 tetrahedral framework connected to each other by sharing Oxygen atoms. Its frame work structure has voids and channels occupied by cation, water molecules and other quest species.

$$\boldsymbol{Mx(H2O)[Alx\ Si(t-x)O2t]}$$

M is univalent charge balancing cation, x is number of framework aluminum atom, t is total number of framework tetrahedral atom [6]. Zeolites have wide application at industrial scale because of its large surface area, high thermal stability and strong acidity. [7]

1.12 Building Units for Zeolite Frameworks

The building block in a zeolite is a tetrahedron where Si or Al is surrounded by oxygen atoms. Combining these building blocks in different arrangements gives many frameworks of zeolite with different morphologies, pore dimensions and unique characteristics. For example, eight-tetrahedron structure connects by sharing oxygen atoms form a cube (Figure. 2). This cube will be a building unit for more complex structures and form cavities and pore openings. This cube can also be designated as a double four ring structure hence if basic building units combine in a way that it form hexagonal prism like structure, double six-ring will be generated (Figure.3).

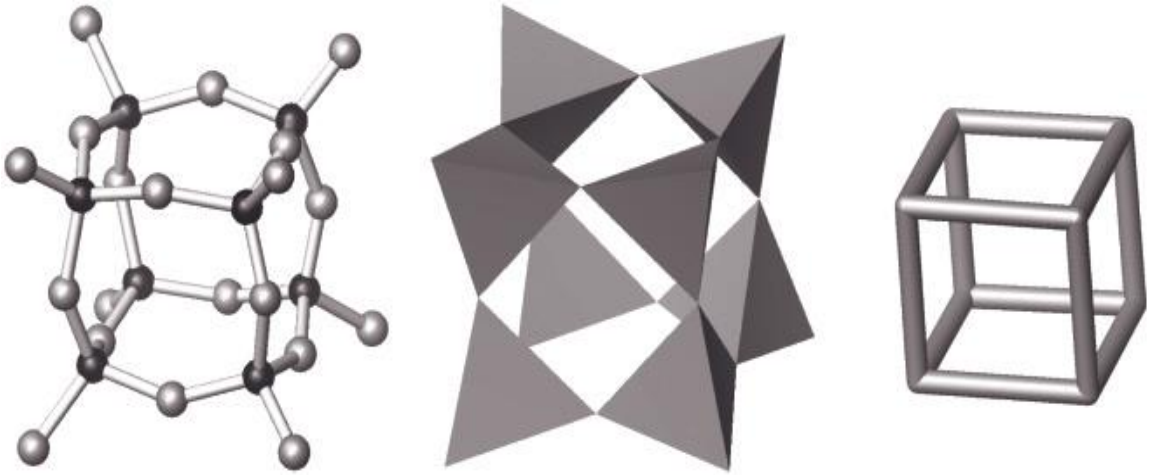


Figure 2. Building units of zeolite structure from eight tetrahedra forming cube [6].

In most literature, framework is represented by Si or Al atom linkages (Si-Si, Al-Al, Si-Al) while oxygen atom is considered at the center of link. The polyhedral building units have unique nomenclature such as sodalite cage or numerical codes i.e cube or 4^6 and hexagonal ring 4^6 6^2. Figure. 3 represent the different building units of zeolite framework with their nomenclatures.

Figure 3. L to R: Double 4-ring, double 6-ring, Sodalite or beta cage [6].

'n' Number of rings where n defines the number of Si or Al atoms, defining the face of polyhedral building units are called pores. Pore size less than six-rings are called cages, because larger molecules cannot pass through these cages. If any of the pore size in polyhedral is larger than six-ring it is called cavities. Pores that are extended in one or

multi-dimensions and larger than six-ring are called channels. For instance, LTA structure contains two types of cages i.e. 4^6 and 4^66^8, one type of cavity and eight-ring pore extended in three-dimensions. Diffusion and reaction of molecules in zeolites mainly depend upon pores size and channels dimension. Selection of zeolite is made on the type of reaction, product, reactant and diffusion limitations. Heavy hydrocarbon reactions usually involve large pore zeolite (MOR, BEA or FAU) in order to avoid diffusion limitation. Zeolite pore size distribution is shown in Figure.4 and Figure.5.

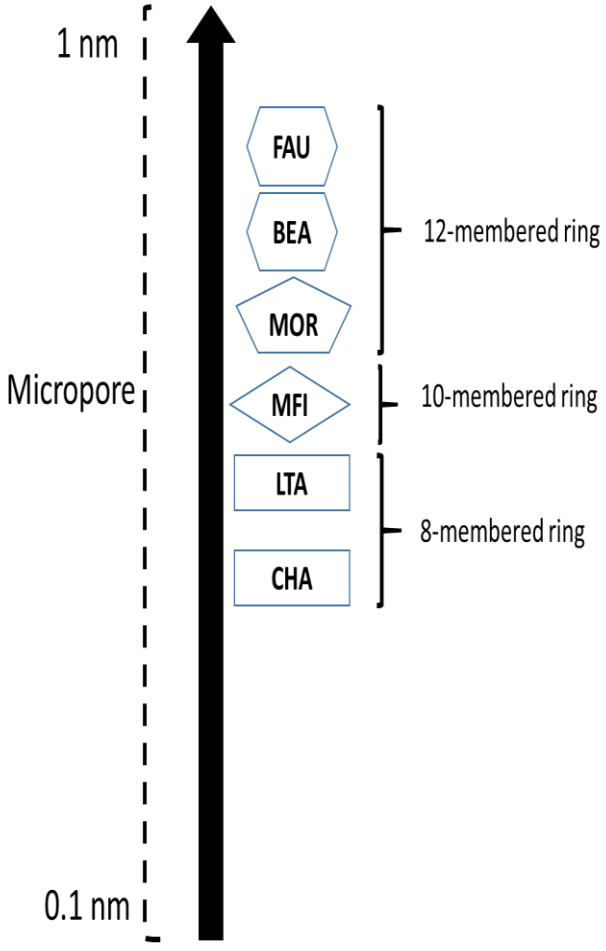


Figure 4. Zeolites pore size distribution.

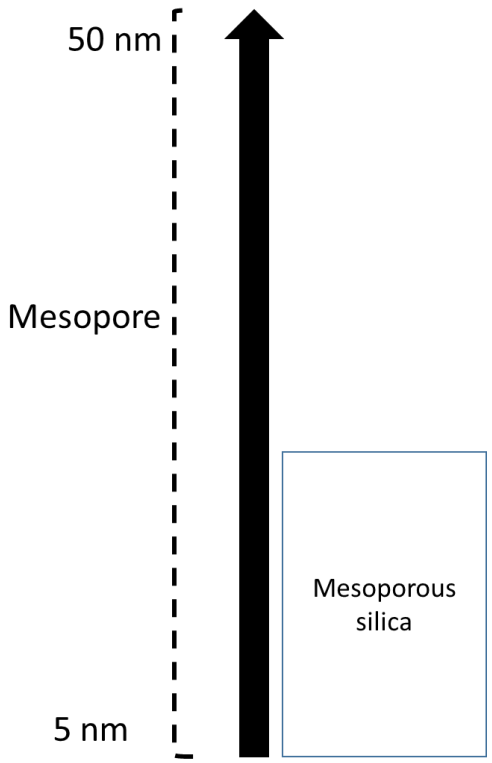


Figure 5. Mesoporous structure pore size range.

1.13 Faujasite (FAU)

FAU has three-dimensional structure connected by 12-ring pore systems. Sodalite cages are connected by six-rings which make a super cavity and FAU one of the large pores structure zeolite (Figure. 6). The unit cell formula of FAU zeolite can be written as | M x (H 2 O) y | [Al x Si 192 – x O 384] where x is the number of Al atoms and M is a monovalent cation. The number of Al atoms can be varying from 96 to 4 (Si/Al ratio 1 to 50). FAU has further two types Zeolite X and Y. Zeolite X ranges between Si/Al ratios 1 to 1.5 and zeolite Y ranges between Si/Al ratios 96 to 77. Zeolite Y has special importance in industry because of its higher Si/Al ratio and higher activity.

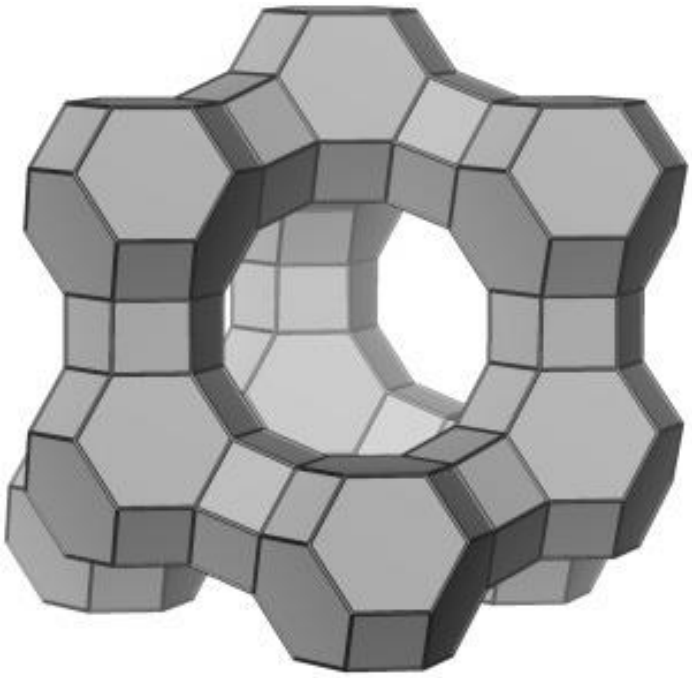


Figure 6. Building unit of FAU zeolite structure [6].

1.14 Mordenite (MOR)

Mordenite is widely used zeolite in practical application such as in catalysis, separation, adsorption, semiconductors, chemical sensors, and nonlinear optics. Mordenite has chemical formula Na_8 (H_2O) $24[Si_{40}Al_8O_{96}]$ and parallel 12-membered ring (MR) channels (0.67 x 0.70 nm) along the c-axis direction, which were interconnected by 8-MR (0.34 x 0.48 nm) along b-axis [8-10]. Due to small size of 8-MR mordenite is considered as a one dimensional zeolite. Especially in adsorption and catalytic application it is treated as one dimensional. In addition high thermal stability and acid strength makes it more useful in industrial applications such as alkylation, hydro isomerization, reforming, dewaxing and cracking processes [10, 11].

1.15 Beta Polymorphs BEA and BEC

BEA refers as beta polymorph A, it has not been synthesized in its pure form yet. BEC refers to polymorph C, although it is synthesized in pure form but only as Ge polytype. Beta zeolite has three-dimensional 12-ring framework structure with elliptical opening 0.76x 0.64 nm (Figure.7). Beta zeolites are considered to be high Si/Al ratio framework zeolites. Its structure is highly disordered and has many internal defects which make its acidity properties more interesting. Table 4 represents the properties of Beta polymorph A.

Table 4. Properties of Beta zeolite.

Type	**Beta polymorph A**
Chemical Formula	[Na7][Al_7 Si_{57} O_{128}]
Pore structure	Three-dimensional 12-ring
Synthetic forms	Beta, Al-rich beta,CIT-6
Type	Beta polymorph A
Pore structure	Three-dimensional 12-ring
Synthetic forms	FOS-5,ITQ-14,ITQ-17

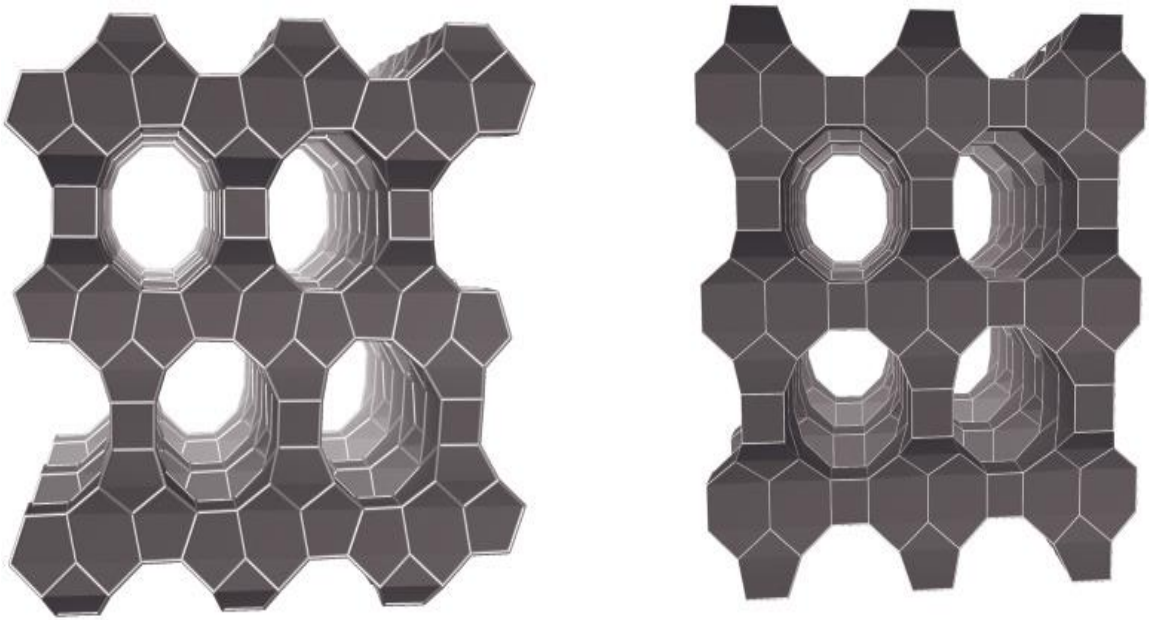


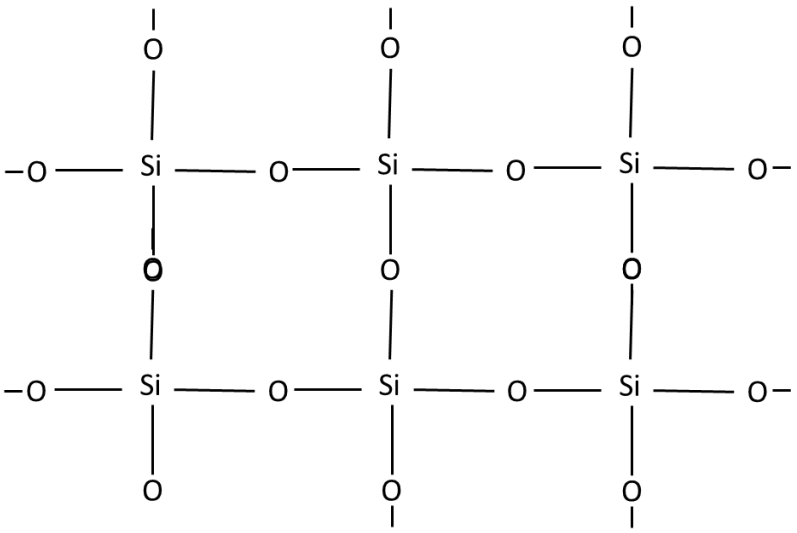
Figure 7. Structure of Beta zeolite.

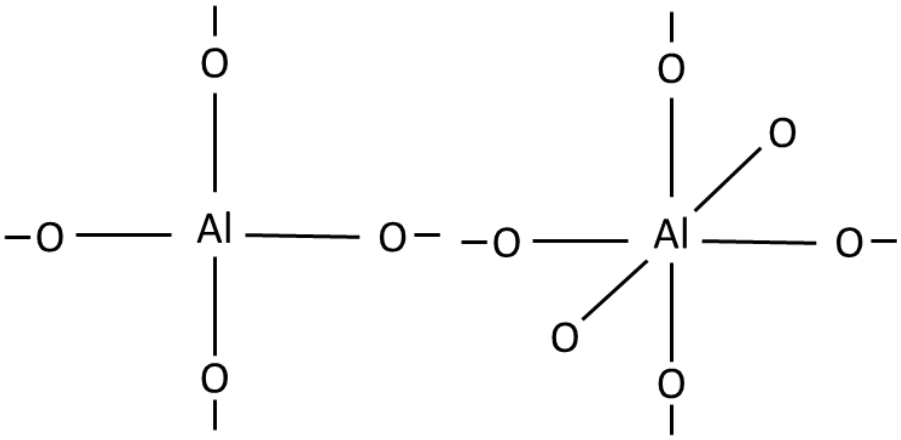
1.16 Chemistry of cracking catalysts

Chemistry of silica and alumina in solid state set a foundation for silica-alumina solid catalysts. Active parts in these catalysts formed when one aluminum atom shares four oxygen atoms and which further shared by four silicon atoms. Their combine structure generates a net positive charge which is compensated by cation which is H^+ in most of the cases. Alone silica is either not active or slightly active. However, alumina alone has more activity than silica in cracking reaction but combination of silica-alumina generates highly active sites and generates solid-acid catalysts. Zeolites are important type solid-acid catalysts which have proven be to be most efficient catalyst in cracking reactions. It is important to first throw a light on the chemistry of silica and alumina in solids states and their role in cracking reactions.

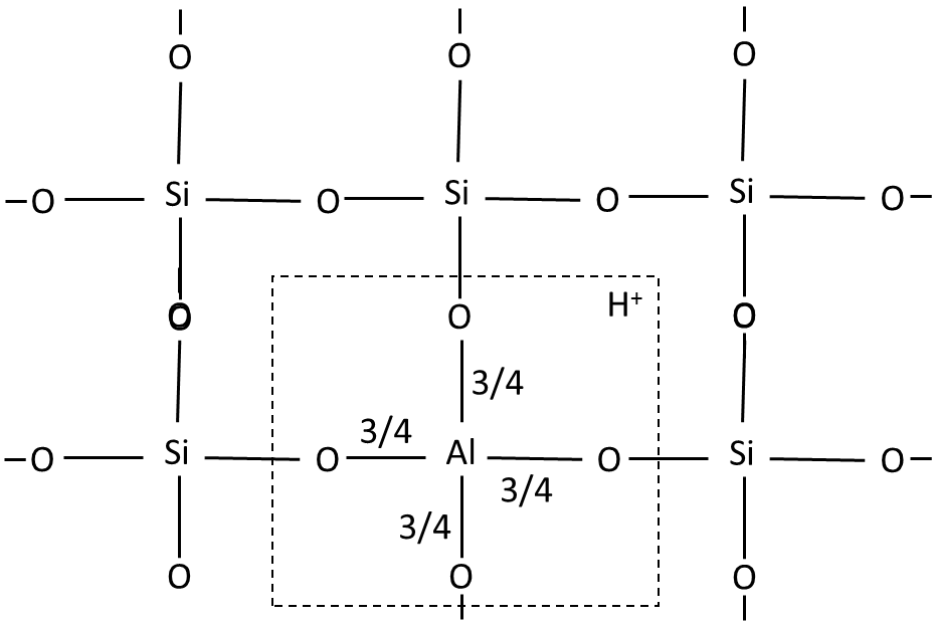
1.17 Solid silica and alumina chemistry

There is no Si=O=Si bond exits in solid state, rather each silicon is surrounded by four oxygen atoms as shown in formula given below. Oxygen atoms are at the corners of tetrahedron and silicon in the center forms a basic building unit of crystalline structure of solid catalyst. Aluminum makes two structures with oxygen i.e. four oxygen atoms surrounding aluminum atom forms tetrahedral while six oxygen atoms generates octahedral structure presented in formula given below. Any of these two combinations may be a building unit of complex polymers. But silica-alumina cracking catalyst is a result of tetrahedrally linked alumina structures with silica tetrahedrons [12].





Cracking reaction mainly depends upon activity of catalyst which comes from H^+ associated with every single unit of silica-alumina structure.

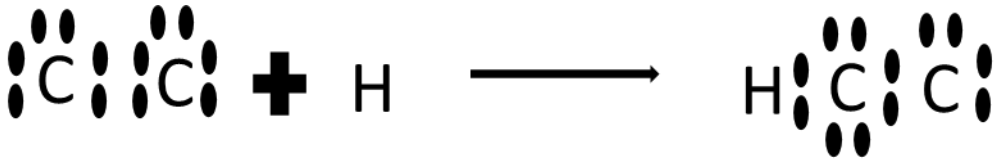


Formula above represents the silicon-oxygen tetrahedron network where each silicon satisfy its valance by sharing four oxygen atom while oxygen atom bonding with two silicon to satisfy its valance. When center silicon is replaced by tetrahedral aluminum atom it creates a net negative charge. Aluminum has valance of three which makes oxygen deficient of charge. Hence, AlO_4 part of structure is unsatisfied by one valance unit. This valance unit is compensated by H^+. So it can be concluded from above discussion that positive charge hydrogen ion is a result of tetrahedral aluminum.

Catalyst activity is associated with its acidity; this means that maximum number of Si-O-Al bond gives higher acidity and hence higher activity. High silica to alumina ratio should give maximum acidity but this it is not possible to get maximum acidity. This is due to the formation of Si-O-Si bonds during synthesis of catalyst. This reduces potential Si-O-Al bond concentration.

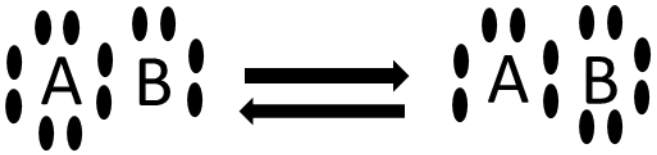
1.18 Mechanism of catalytic cracking reactions

It is well known that an acid catalyst involves carbonium ion reactions. Hydrocarbon cracking reactions in the presence of acid catalysts involve both carbonium ion and carbonions. Carbonium ions are formed from olefins.

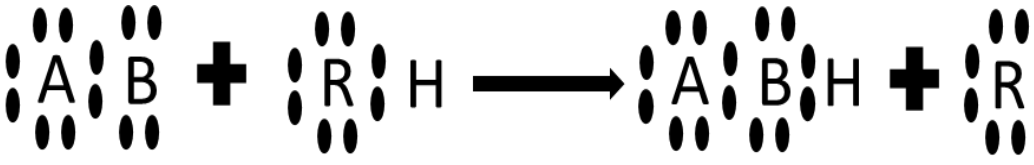


This reaction is the starting of cracking and follows different type of reactions which involves[12]:

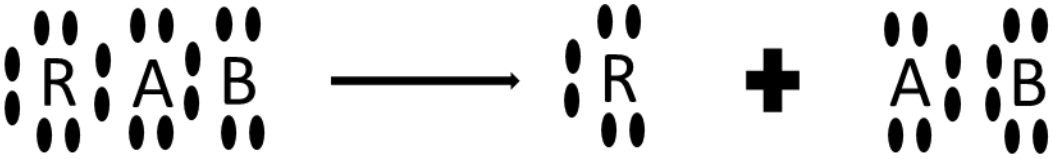
Type 1: When carbonium ion B has greater affinity for electron than other molecule say A. hence electron moves to B and A becomes carbonium ion. This reaction was proposed by whitmore.



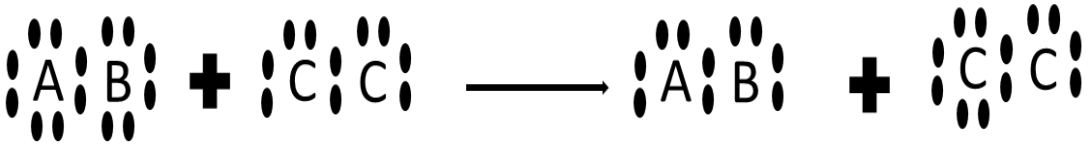
Type 2: carbonium ion reacts with a neutral molecule to become stable and form another carbonium ion. When the molecule is olefin, an unsaturated carbonium ion is formed.



Type 3: A carbonium ion takes a electron pair from adjacent carbon without sharing a group which shared that electron pair.



Type 4: A carbonium ion react directly with an olefin to convert carbonium ion into olefin and form new ion.



These all four type of reactions are involved in the cracking mechanism over solid acid catalysts. Cracking and isomerization reactions involve same steps only difference is type 3 reaction. Electron pair deficient carbonium ion tries to attract electron pair from beta bond. In the case of cracking only electron pair is transferred to carbonium ion while in isomerization reaction entire group sharing that electron pair is transferred.

It is clear that carbonium ion reactions are initiated in the presence of olefins which cause cracking of paraffin difficult. Thermal cracking during the catalytic reaction allows paraffin to convert into olefin are catalytic reaction proceed.

CHAPTER 2

LITERATURE REVIEW

2.1 Hydrous pyrolysis of heavy oil: background

In the introduction, many techniques have been discussed for the upgrading of heavy oil. All these techniques are already commercialized and contributing to meet the current demand of lighter hydrocarbons. Still many improvements in current technologies are required to meet the current demand for lighter fuels. Hydrous pyrolysis, also known as aquathermolysis, is an efficient technique for the cracking of hydrocarbon in presence of water. Hydrous pyrolysis process involves injection of superheated steam in a reactor to increase H/C ratio and reduces the viscosity of oil. Hyne was the first who reported that reduction of viscosity during hydrous pyrolysis process is mainly due to breakage of C-S bond as the breakage energy of C-S bond is lower than other bonds [13]. Hydrolysis of organosulfur compounds involves water gas shift reaction (WGSR) [14]. Hydrogen from water transfers to oil and results in the release of H_2S after breaking C-S bond.

$$\mathbf{CO + H_2O \leftrightarrows CO_2 + H_2}$$

$$\mathbf{R\text{-}CH_2CH_2\,SCH_3 + 2H_2O \rightarrow R\text{-}CH_3 + CO_2 + CO + H_2 + H_2S + CH_4}$$

It was observed, hydrogen produced was responsible for oil upgrading and hence improve the quality of heavy oil. Carbon dioxide was also produced at steam injection temperature from metal carbonates present in oil reservoirs. Breakage of C-S bond plays decisive role in viscosity reduction and it was investigated that concentration, reactivity

and type of sulfur compounds also effect the viscosity reduction. Hence it is concluded that hydrous pyrolysis has many advantages [15, 16].

(a) Reduction of viscosity and hence improvement of its flow properties.

(b) Desulfurization.

(c) Hydrogenation and hence upgrading of heavy oils.

Purpose of hydrous pyrolysis is to decrease the asphaltenes and resins contents in heavy oil and increase H/C to resin and asphaltenes ratio. Hence reduces the viscosity and improves oil quality [17].

2.2 Catalytic hydrous pyrolysis

During hydrous pyrolysis reaction long change molecules break and form radicals which take part in polymerization reaction and hence further increase viscosity. This problem can be overcome by using catalyst that hinders polymerization. Clark et al [18] first studied hydrous pyrolysis of heavy oil in the presence of catalyst. It was found that minerals present in well act as a catalyst during hydrous pyrolysis process. Higher viscosity reduction was observed in nickel and cobalt reactors than quartz reactor so keeping in this results further research was made in the presence of different catalysts. Kapadia et al reported that reactor material hastelloy also took part in reaction hence cracking results improved in the presence of hastelloy. Previously transition metals were employed as a catalyst for heavy oil cracking at higher pressure where hydrogenation and thermolysis gave conversion up to 56% [19]. Iron napthenate in the presence of cyclohexane (hydrogen donor) was found to be more effective catalyst [20]. In the

presence of nickel and iron, hydrodesulphurization and hydrodenitrogenation are achieved during thermolysis. Hence, hydrous pyrolysis reaction initiated from the breakage of weaker C-S bond and C-O bonds. Moreover, increase in H/C ratio and decrease in O/C ratio was also reported as a result of catalytic hydrous pyrolysis reaction over sulfonic-$H_3Po_{12}O_{40}$ at 280 ^oC and 30 bar [21]. At Liaohe oil field in china, researchers investigated catalytic effect of hydrous pyrolysis on oil containing sulfur content as low as 0.5 wt % [17]. Hydrous pyrolysis catalysts can be divided in mineral water-soluble catalyst, oil-soluble catalysts, and dispersed catalyst. And these catalysts give different degree of viscosity reduction. Mineral < water-soluble< oil-Soluble < dispersed [15]. List of catalysts used for pyrolysis of heavy oil is given in Table. 5 and Table 6 presents the yields of lighter hydrocarbons over metal oxide catalysts during steam-assisted catalytic cracking of heavy oil.

Table 5. Highlight of some catalytic hydrous pyrolysis of heavy oil.

Catalyst	Temperature T (^oC)	Time T (h)	Viscosity Reduction [%]	Conversion into lighter components [%]	References
Alkyl ester sulfonate copper	240	24	90.72	10.12	[22]
Nano-nickel catalyst	280	24	98.9		[23]

Without catalyst	240	24-72	28-42	-	[24]
Amphiphilic catalyst	200	-	96.26	C10< 3.73% to 51.54	[16]
Gemini catalyst	170	24	90	10	
Aromatic Sulfonic Iron and Aromatic Sulfonic Molybdenum	200	24	95.6 and 99.3 respectively		[17]
Dodecylbenzene Sulfonate and Nickel	85	120	73 and 79		[25]
Reservoir minerals	160-280	0-48	25.8	27.8 (saturated HC) and 32.2 (aromatics)	[26]
Ni, W, Mo and C catalysts	240	200	97		[27]

0.8% tetralin	240	24	80		[28]
Nano-keggin-$K_3PMo_{12}O_{40}$	280	24	92.3		[29]
Aromatic sulfonic copper	280	24	95.5	13.72	[29]
Aromatic sulfonic $H_3PMo_{12}O_{40}$	280	24			[30]
Ultra-sonic assistant and XAGD-2 catalyst	200	24	80.5		[31]

Table 6. Steam-assisted catalytic cracking over metal oxide catalysts.

Catalysts	**Conditions**	**Feedstock**	**Conversion into lighter C_7-C_{35}) (Mol %)**
ZrO_2-FeOx-Al_2O_3	500 ^oC for 2 h	Vacuum residue	C_7-C_{18} 56.3 %
FeOx-ZrO_2	500 ^oC for 2h	Atmospheric residue	57 %

FeOx	500 ^{o}C for 2h	Atmospheric residue	50 %
TiO_2-ZrO_2	470 ^{o}C for 2 h	Atmospheric residue	40 %

2.3 Catalyst Selection

As shown in Table 5, various type of catalysts were employed and different extent of viscosity reduction was achieved .Pore diameter, size, morphology and activity plays an important role in the selection of process. Zeolite catalysts as a most important industrial catalyst which have much application in cracking including FCC were not taken into consideration for hydrous pyrolysis up till now. Zeolite catalysts because of their higher activity, crystallinity and selectivity than other catalysts considered superior for many practical application but stability of zeolite in hot aqueous environment is always a question. Hydrothermal stable zeolite will be the breakthrough for the processes in the presence of water. Zeolites are mainly categorized base on Si/Al ratio: low, intermediate, high and silica molecular sieves. Low Si/Al ratio (1-1.5) zeolites have less acidity as compare to intermediate (2-5) and high (10-100) Si/Al ratio zeolites. Thermal stability and hydrophobicity also increases with increase Si/Al ratio. Properties associated with framework of Si/Al allow low and intermediate zeolites to remove water from organics in adsorption and catalysis while high and silica molecular sieves are used to remove organics from water because of their hydrophobic nature [7].

High intra crystalline surface area, uniform porous structure, micro- and meso-porous characteristics, wide range of crystal size, the ion exchange properties, high internal acid density, thermal stability and the ability to absorb chemicals into their structure introduced zeolites in commercial and practical applications [32].

2.4 Applications

Three main properties of zeolites make it commercially important [33];

- Ion exchange capacity for detergents
- Separation and adsorption because of their molecular sieve properties
- Catalysts because of their high acidity

Substitution of tetravalent silicon by trivalent aluminum in the framework gives rise to a net negative charge, which is compensated by cations, *e.g.* H^+, Na^+, and Ca^+. If these cationic sites are exchanged to H^+, strong Brønsted acid sites are formed and these strong acid sites enable zeolite applications in catalysts. Many zeolites especially ZSM-5, FAU, Beta, Mordenite have found many commercial application in catalysts such as hydrocracking, catalytic dewaxing, fluid catalytic cracking, upgrading of naphtha and syn fuel production. Hence zeolite can be used to achieve stability, selectivity and yield [6, 11, 33, 34].

2.5 Stability of zeolites in aqueous environment

Zeolites has numerous applications as a catalyst, adsorbent etc. water-free environment cannot always be guaranteed, many catalytic applications involve steam or water at high or moderate temperature. Although zeolites are considered as stable material at high

temperature but stability in water at high temperature is still questionable. Many recent researches have been conducted to study the zeolite properties in aqueous environment. Zeolites that showed stable structure in water were found to distort in steaming environment. So, still lot of study is required to study the zeolite behavior in water and steam both. It was reported that degradation mechanism in water is hydrolysis of Si-O-Si bond while steaming cause dealumination (Si-O-Al) [35].

Recently extensive study on stability of zeolite Y in hot water shows that Si-O-Si bond is hydroxyl ion (OH^{-1}) catalyzed and generated two silanol groups which further accelerates the degradation. Si-O-Al is attacked by proton but this reaction is dominant in steaming condition (dealumination). Hydrolysis of Si-O-Al extract Al from framework and form extra framework Al, defected structure left with four silanol groups Si-OH but these defects were healed by other silicon atom those were removed in process [35]. It was observed that removal of Al framework mostly occur during cooling step after steaming. Zeolite Y showed increase in degradation of structure with increasing Si/Al ratio which in opposite of other zeolites. It was also observed that EFAl results from dealumination helped to block further hydrolysis of Si-OH groups. This could be the one reason of high stability of low Si/Al zeolite Y. Moreover, Lanthanum incorporated in zeolite structure increased the stability of MTT zeolite in the presence of steam [36].

Five types of OH groups are associated with H-beta namely silanol OH, bridging hydroxyl, two type of AlOH, and hydrogen hydroxyl groups[37]. Brønsted acidity is because of bridging hydroxyl group and has a main role in many catalyzed reactions. Lewis acidity mainly depends upon the Extra framework aluminum (EFAL). Combination of two polymorph in beta zeolite results in the higher concentration of

structural defects [38]. Dealumination was found to be the main reason of structure degradation. Decrease in the concentration of BAS in both untreated and steamed BEA was low as expected. Decrease in the concentration of BAS after steaming was justified by removal of framework Al. However less concentration of BAS in untreated was because of charge neutralization of some AlO^{-4} by positively charge extra framework aluminum (EFAL). It should be clear that one EFAL result in the loss of two BAS, one by itself and other is by blocking framework Al. Moreover, EFAL are important for thermal stability as they cover framework Al and prevent further degradation [37].

In contrary to FAU (zeolite Y) and Beta (BEA), ZSM-5 found stable at 200 ^{o}C and 150 ^{o}C for 6 h [35]. No change in crystallinity and structural changes were observed. Some octahedrally coordinated Al removed which indicates the removal of some (EFAL) from the zeolite structure [35].

2.6 Hydrophobic Zeolites

As discussed earlier, in aqueous environment zeolites leads to deactivation whether irreversible (dealumination) or reversible (deposition of solvent molecules on zeolites). It was also observed that in water, degradation of Si-O-Si bond is the main mechanism while in steam Si-O-Al bond breakage leads to deactivation. Recently many researches have been carried out to improve the stability of zeolite in aqueous phase. One major disadvantage of zeolite is reduction in crystallinity in hot water at high temperature (>150 ^{o}C) [39, 40]. Reducing the hydrophilicity is one solution to enhance zeolite tolerance at elevated temperature. Density of acid sites depends on the Si/Al ratio, framework configuration and type of cation. Similarly their stability is also depending upon these

factors. Increasing Si/Al ratio helps to improve the hydrophobic nature of zeolite but at the same time it also decreases Al framework which results loss of Brønsted acid sites (BAS). Sacrificing Brønsted acid sites which are responsible for catalytic reactions such as dehydration alkylation and oligomerization is not desirable outcome [41].

Studies have shown that purely siliceous surface are hydrophobic and hydroxyl site which includes Si-OH groups and Si-O-Al sites are hydrophilic and can easily attached by water. In the case of microporous materials (zeolites) higher increasing Si/Al ratio decreases water uptake. Mordenite zeolite of varying Si/Al ratio (80-200) showed hydrophobic nature with increasing Si content in structure [42]. Same trend was observed in mesoporous materials, MCM-41 and MCM-48 modified with trimethylsilane showed decrease in water uptake [43]. Large port zeolite e.g. FAU, BEA were found unstable in hot water even at temperature >150 ^{o}C while at the same temperature in vapor phase structure was stable [35, 37]. Zapata et al observed highly hydrophilic structure of H-FAU, degraded in hot liquid water just after 3 h. H-FAU functionalized with organo-silane groups showed remarkable increase in hydrophobicity. Silane groups attached on the external surface of H-FAU prevented water molecules to attach and adsorb on internal surface. It was concluded that oragno silane functionalization prevented contact of water with zeolite which otherwise cause irreversible structural degradation. MCM-41 functionalized with methyl, ethyl and phenyl groups were structurally more stable, indicating that siloxane hydrolysis rates were slower than pure silicious MCM-41.

Surface modification of zeolite with sodium fluoride, lanthanum, phosphorus and organo-silane (silanation) increase hydrophobicity without reducing the density of acid sites [44-49]. Cerqueira et al [47] studies effect of the introduction of phosphorus on H-MFI

zeolite before and after hydrothermal treatment. Introduction of pyridine and sodium fluoride to develop hydrophobic siliceous ferrierite was also reported elsewhere [46]. Impregnation of different Si/Al ratio ZSM-5 with phosphorus in H_3PO_4 form was studied by Corma et al [44]. Figure. 8 shows the different routes to impart hydrophobic character in zeolites, whether by post treatment or in-situ synthesis methods.

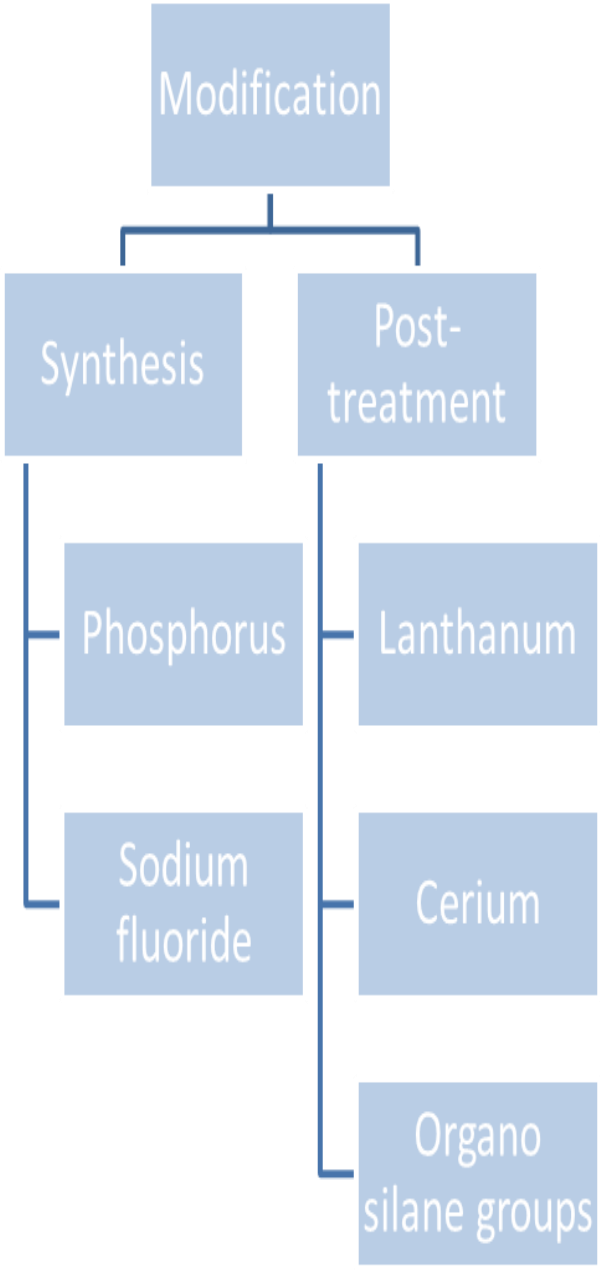


Figure 8. Different ways of zeolite modification.

2.7 Organo-silane treated zeolite catalysts

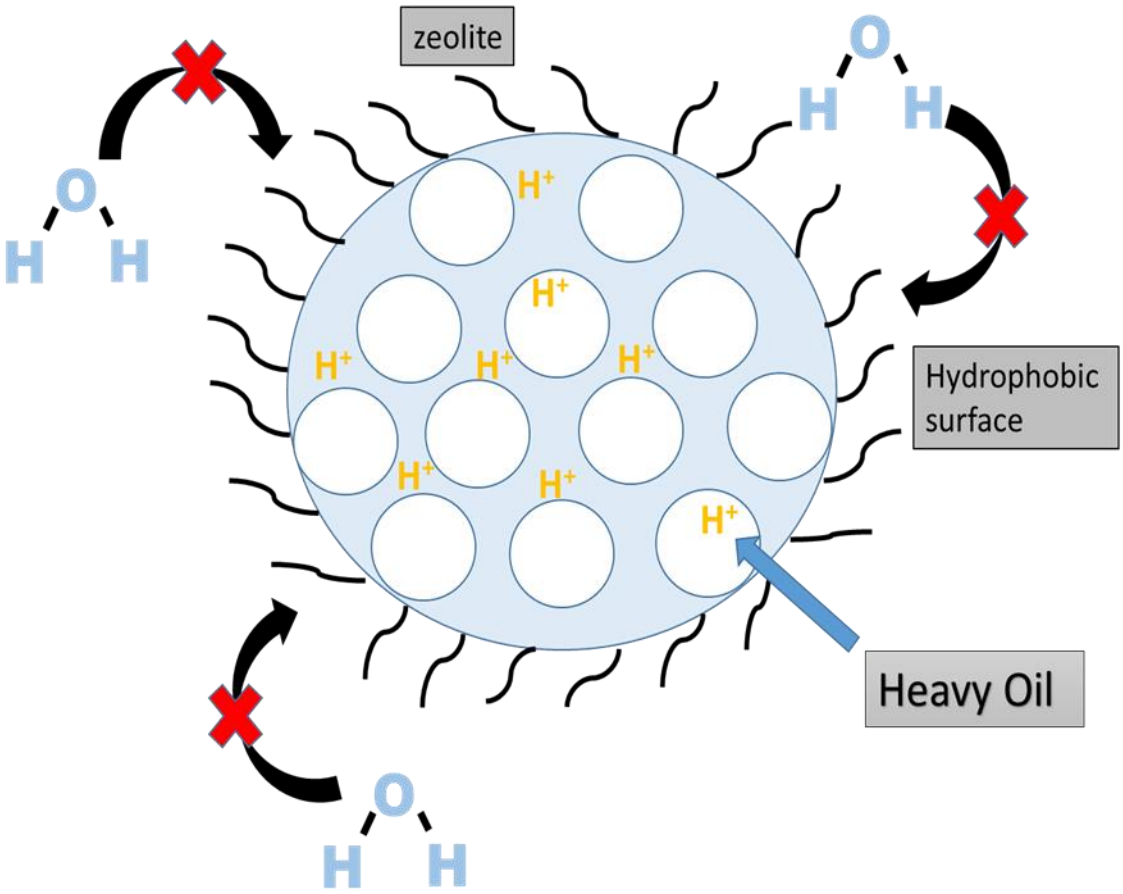


Figure 9. Schematic overview of hydrophobic zeolite in heavy oil upgrading.

In general activity, selectivity and stability depend upon composition and structure of zeolite, diffusion of reactants and products and post-treatment of synthesized zeolite. It is important to get desired properties of zeolite to achieve better results. There are many compounds and techniques are available in literature to modify zeolite in order to get desired properties. If application of zeolite is required in hot water then hydrophobicity and stability of zeolite plays an important role [39, 41]. One way to increase the hydrophobicity is to increase Si/ Al ratio or dealumination of zeolite but this also cost the loss of Brønsted acid site and as a consequence reduction in its catalytic activity [50, 51].

There are numerous applications of silane treated zeolites. Recently, silane compounds were used to control the activity of ZSM-5 zeolite catalyst. organo-silane conpunds were employed in catalytic cracking of silane compound on zeolite surfaces. These silane compounds on calcination formed SiO_2 units in external active site hence decreasing the activity but in increase in selectivity of lighter components [40]. Moreover, decreased acidity also caused to reduce coke deposition and increased the stability of ZSM-5. Same technique was used for n-hexane cracking over di-phenyl silane treated ZSM-22. Results showed higher selectivity of propylene and less aromatics [52]. More importantly stability of catalyst increased remarkably after and ZSM-22 found stable even after longer reaction time. This method involved chemisorption of silane compounds vapors on the external surface in N_2 flow flowed by decomposition of silane compounds on surface at 550 ^oC. finally these silane compounds formed SiO_2 units on external active sites in the presence of air [53]. On contrary, Zapata et al used different method for silane treatment where objective was to impart hydrophobic properties to zeolite [41]. Organo-silane groups with different alkyl lengths were adsorbed on surface using liquid phase method where zeolite sample was first dissolved in solvent, followed by the addition of silane compound under stirring condition at room temperature. Sample was recovered by filtrations and washed with ethanol [41]. Main different between two methods were formation of silane compounds on the surface of zeolites. Formation of SiO_2 units on surface was mainly used to achieve selective adsorption and reduce coke formation. HMCM-22 was modified with tetraethoxysilane (TEOS) for selective skeletal isomerization of n-butene to isobutene [54].

H-USY was functionalized by octadecyltichlorosilane (OTS) where silane compounds with their organic part attached with surface to make it hydrophobic, in the application of bio fuel upgrading [41] . Table 7 gives the overview of silane treated zeolites and their applications.

Table 7. Silane treated zeolites and their application.

Zeolite	**Silane groups**	**Application**	**References**
MCM_41	dimethoxydimethylsilane (DMODMS) and dichloromethylphenylsilane (DCMPS)	competitive adsorption of water and toluene	[55]
H-USY	Octadecyltrichlorosilane (OTS), hexyltrichlorosilane (HTS), and ethyletrichlorosilane.	Bio fuel upgrading.	[39]
MCM-22	dichlorodimethylsilane (DCDMS	To improve thermal stability of silylated zeolite.	[56]
HY	octadecyltrichlorosilane (OTS)	Bio fuel upgrading in hot aqua environment.	[41]

HMCM-22	Tetraethoxysilane (TEOS), silicon tetrachloride (SiCl4) and 8-hydroxyquinoline	selective skeletal isomerization of n-butene to isobutene	[57]
ZSM-5	TEOS	shape selectivity	[54]

2.8 Objective

1. Steam-assisted catalytic cracking of heavy oil over surface modified zeolite catalyst to increase the production of lighter hydrocarbons.
2. Surface modification of catalysts using organosilane compound through two techniques i.e. vapor phase deposition and liquid phase deposition
3. Improve the hydrophobicity and stability of catalysts.

CHAPTER 3

Methodology and Experimental

3.1 Surface modification of catalyst using silane compound

Beta zeolite catalyst (BEA) with SiO_2/Al_2O_3 150 was provided by Catalysis Society of Japan. Firstly, BEA catalyst was ion exchanged using convention method [58, 59], typically, 1 g of catalyst was suspended in 20 g of 2 M ammonium nitrate ($NH_4(NO_3)$) solution and the solution was heated under stirring for 3 h. Final solution was centrifuge to remove ($NH_4(NO_3)$) solution from catalyst. This procedure was repeated thrice. Finally NH_4^+-BEA zeolite was dried at 100 ^oC for 12 h. $NH4^+$-BEA was first pelletized to get ca. 0.3 mm in diameter pellets and then calcined at 550 ^oC for 3h in an air stream. After calcination H-BEA was used as BEA-parent catalyst in cracking reactions. While for BEA-silane treated samples, pelletized NH_4^+-BEA were used directly in silane treatment.

3.2 Vapor phase silane treatment

Tri phenyl silane was used as a silane reagent. NH_4^+-BEA pellets in a packed bed reactor were first air calcined at 550 ^oC, then H-BEA zeolite was exposed to vapor of tri phenyl silane at 373-393 K in a N_2 stream. After 1 h feed of silane was stopped to remove the physically adsorb silane compounds on surface. Zeolite brought in the contact with silane compound vapor twice [53]. Finally modified catalyst was used as BEA-silane treated catalyst in heavy oil cracking reaction.

3.3 Liquid phase silane treatment

H-BEA zeolite was modified in liquid phase using procedure described by Zapata et al [41]. As a typical run 1 g of zeolite was dispersed in 20 ml of toluene and sonicated for 20 mins at room temperature. Triphenyl silane (0.5mmol/g zeolite) was added in zeolite/toluene mixture and stirred for 24 h at room temperature. Finally, zeolite was collected by filtration and washed several time with ethanol. Modified zeolite was then dried at 100 ^{o}C overnight.

3.4 Steam assisted catalytic cracking of heavy oil

Fixed-bed type reactor was used for cracking of atmospheric residue (AR) with steam at a reaction temperature of 470 ^{o}C and a pressure of 1 atm for 2 and 4 h. Reactor setup is shown in Figure. 10. AR was diluted with toluene to 10% to reduce its viscosity. Toluene inactivity with catalysts were confirmed in previous study elsewhere [60]. Nitrogen, steam and feed mixture were fed to the reactor simultaneously with the flow rate of 5 mL/min, 5 mL/h and 2.9 mL/h, respectively. The W/F was 4 h, where W was the weight of catalyst (g), F was feed flow rate (g.h^{-1}), F_{H_2O}/F was 2 (F_{H_2O}: water flow rate/ g.h^{-1}). The water injection line was heated to 160 ^{o}C to convert water into superheated steam. Previously, all reaction conditions were optimized to get maximum conversion. The liquid and gaseous products were collected with condenser and gas bag respectively. A quantitative gas product analysis was made using gas chromatography, which was equipped with a thermal conductivity detector (TCD; model GC-8A, Shimadzu, Ltd), a flame ionization detector (FID; model GC-12A, Shimadzu, Ltd), activated carbon and Porapak-Q columns, respectively. The liquid products were analyzed using high

performance liquid chromatograph (model: CTO-10A, Shimadzu, Ltd). Carbon number $<C_6$ was not included in production yield. Toluene detected was also excluded in the calculations. The mass balance error was <5 % in preliminary experiments using AR as feedstock without solvent [60-62].

1 g of catalyst was loaded in reactor along with cotton wool on the top and bottom to support the catalyst bed. 0.02 g of cotton wool, 2 g of marble beads, 1g catalyst and 0.02 g cotton wool were loaded in sequence. Steam input line was wrapped with tap heater to maintained the temperature at 160 ^{o}C. Both steam and feed were injected in the reactor simultaneously. Reactor temperature was maintained at 470 ^{o}C through electrical heater. Outlet temperature of reactor was maintained at 100 ^{o}C. Steam injection continued for 0.5 h after reaction to remove left products from reactor.

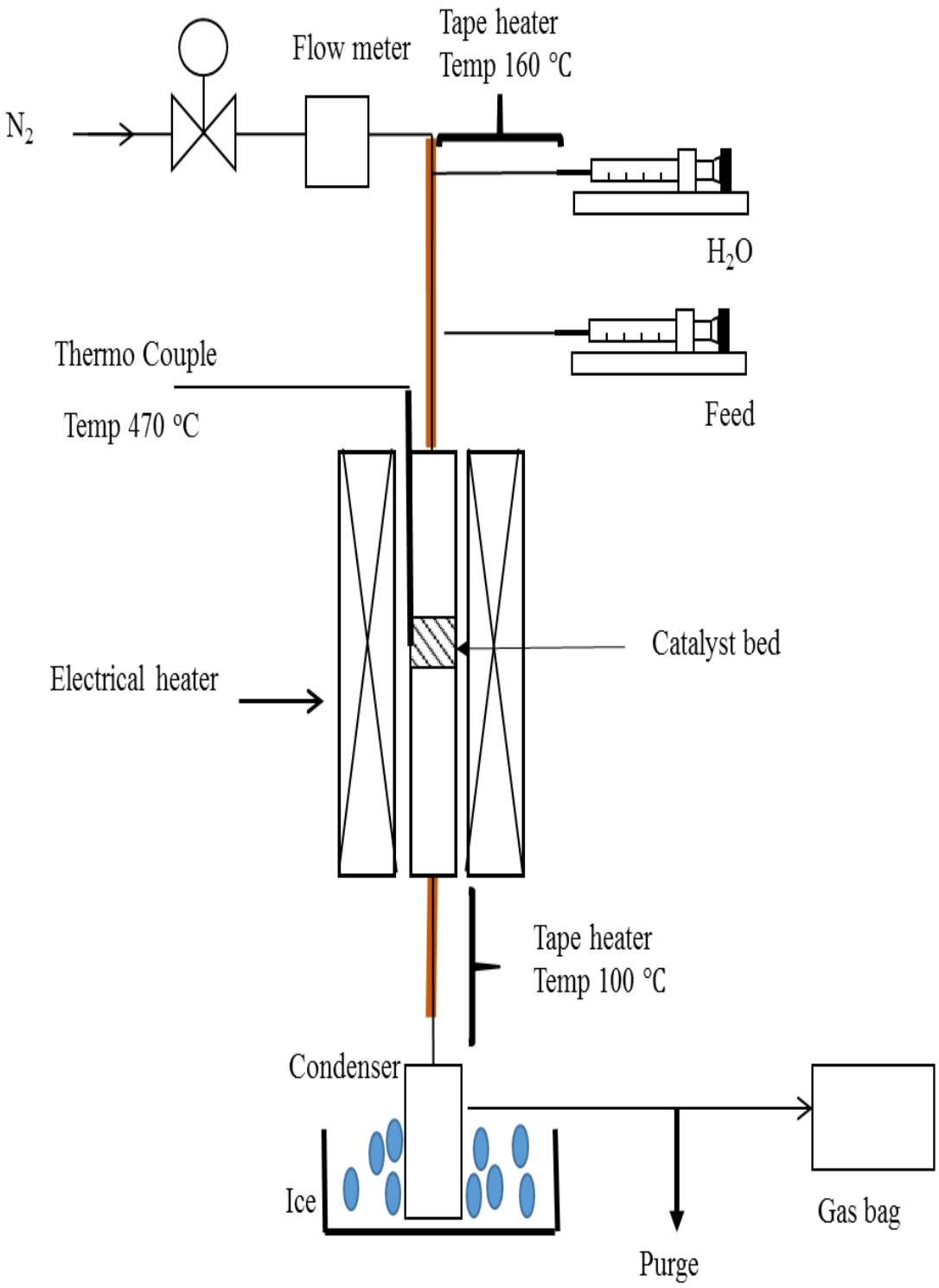


Figure 10. Experimental setup of fixed-bed flow reactor.

3.5 Characterization of catalysts

All BEA zeolite catalysts structure and phase purity was confirmed by using X-ray diffractometer (Ultima IV, Rigaku). Texture properties of catalysts were obtained using an N_2 adsorption isotherm (Belsorp mini, BEL Japan). Acidity was measured using NH_3-TPD method. A 1.0% NH_3 was used as carrier gas at 273-550 ^oC temperature range and 5 $^oC.min^{-1}$ heating rate was maintained. To establish measurement under complete adsorption equilibrium conditions, NH_3 molecules desorption from acid sites of zeolite was performed under a 1.0% NH_3-He atmosphere [63]. Brønsted acid sites (BAS) and Lewis acid sites (LAS) were measured using Fourier transform infrared (FT-IR) equipped with pyridine adsorption support. Diffuse reflectance infrared Fourier transform (DRIFT) spectrometer with mercury cadmium telluride (MCT) detector (FT/IR-4100, JASCO) was used. A total of 200 Scans were averaged for each spectrum. Sample was pre-treated in vacuum at 500 ^oC for 12 h and then pyridine was adsorbed onto the sample at 100 ^oC for 2h. Nitrogen was introduce to remove physically adsorbed pyridine at 100 ^oC for 0.5 h. Lastly, sample acidity was measured via FT-IR analysis at 100 ^oC [64].

CHAPTER 4

Vapor phase silane treated catalysts

Steam assisted catalytic cracking of AR over Beta zeolite catalyst were studied. To enhance the yield of lighter components, BEA zeolite surface was modified using triphenyl silane and catalysts were tested in AR reaction at two different reaction times i.e., 2 h and 4 h. Organo-silane compound was selected on the basis of its kinetic diameter, which should be larger than the pore size diameter of BEA catalyst so that silane compound only modify the external surface of catalyst [41]. As described earlier, vapor phase silane treatment method was employed to modify the catalysts. Protonated BEA catalysts were silane treated and used in the reaction. The cracking products were classified according to their carbon number into six groups: gas, Gasoline + kerosene (C_7-C_{13}), Gas oil (C_{14}-C_{20}, C_{21}-C_{35}), and heavy oil (C_{36}-C_{44}, above C_{45}).

4.1 Effect of silane treatment on catalysts properties

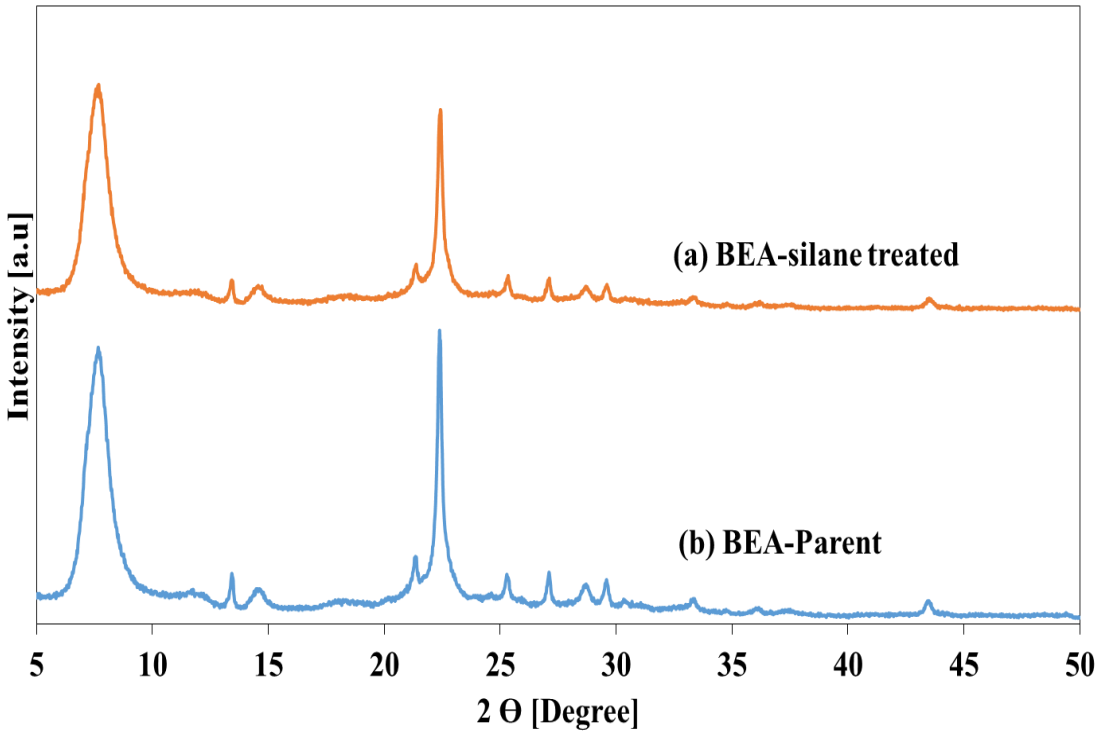


Figure 11. XRD patterns of (a) BEA-Silane treated and (b) BEA-Parent.

Figure. 11 shows the comparison of two XRD patterns: BEA-parent and BEA-silane treated catalysts, which clearly indicates that after silane treatment, catalyst retained its crystallinity and structure. It is important to measure the effect of silane treatment on the acidity and the activity of BEA catalyst. After surface modification, it was expected that the acidity of the catalysts was reduced. This statement is supported by NH_3-TPD results as shown in Figure. 14 NH_3-desorption peak, which is associated with strong acid sites (above 580 K) showed a decline for BEA-silane treated zeolite.

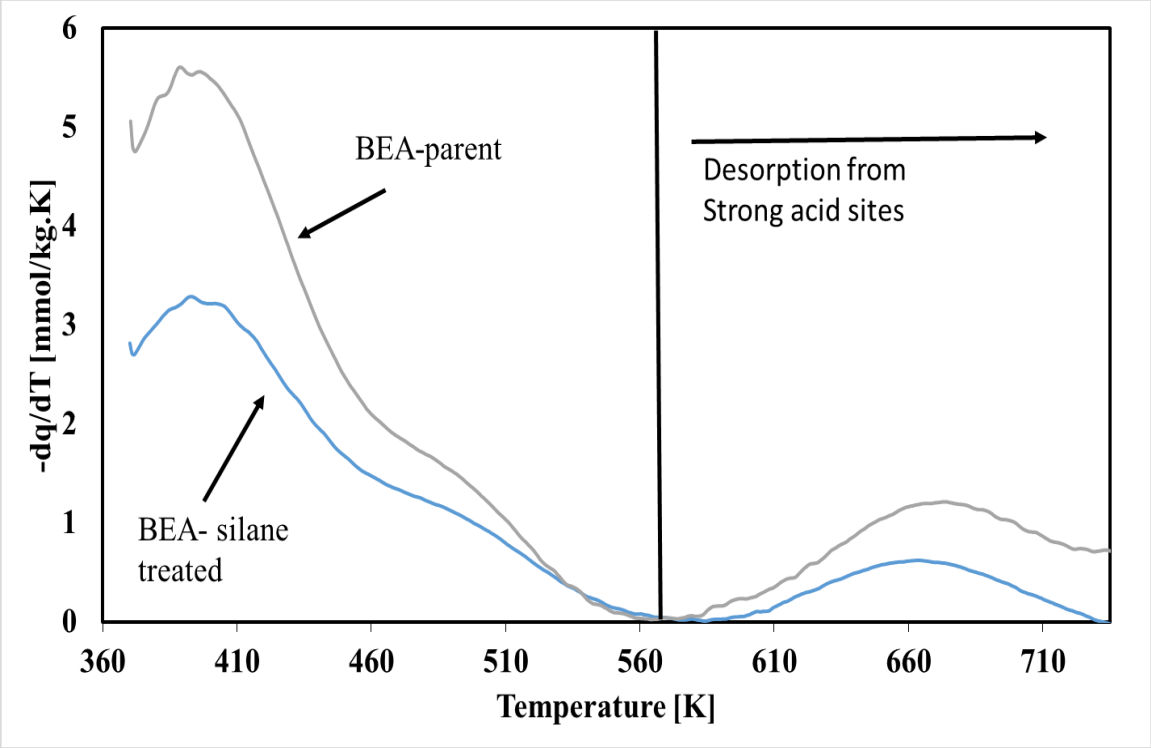


Figure 12. NH3-TPD profiles of BEA-Parent and BEA-silane treated zeolite catalysts.

Previous research on catalytic cracking of alkanes over zeolites already proved the role of strong acid sites, where high acidity provides more sites for cracking but at the same time leads to more coke formation and hence fasten the deactivation of catalysts [65, 66]. In order to take a deeper look into the change in acidity of silane treated catalyst, Brønsted acid sites (BAS) and lewis acid sites (LAS) were measured qualitatively using FT-IR pyridine. The IR spectra in Figure.13 show full agreement with NH_3-TPD results. Decrease in both BAS (1540 cm^{-1}) and LAS (1460 cm^{-1}) were observed after silane treatment. Roles of BAS in cracking reactions were discussed by many researchers [67, 68] but it is also worth mentioning that hydrophilicity of catalysts are also associated with BAS [41, 69]. Hence, the role of BAS in steaming environment during cracking reaction has significant importance. Silane treatment procedure did not include post calcination step unlike catalytic cracking of silane (CCS) in which SiO_2 units were formed on active

sites after calcination [52, 53, 64]. It was expected organic groups of organo-silane compounds attached on outer surface and prohibited the attack of water (steam) molecules on surface [41]. N_2 adsorption analysis supported the concept of outer surface modification of catalyst as only outer surface area measured using t-plot method was increased as shown in Table 8. Moreover, small increase in mircopore volume was observed in Figure. 14.

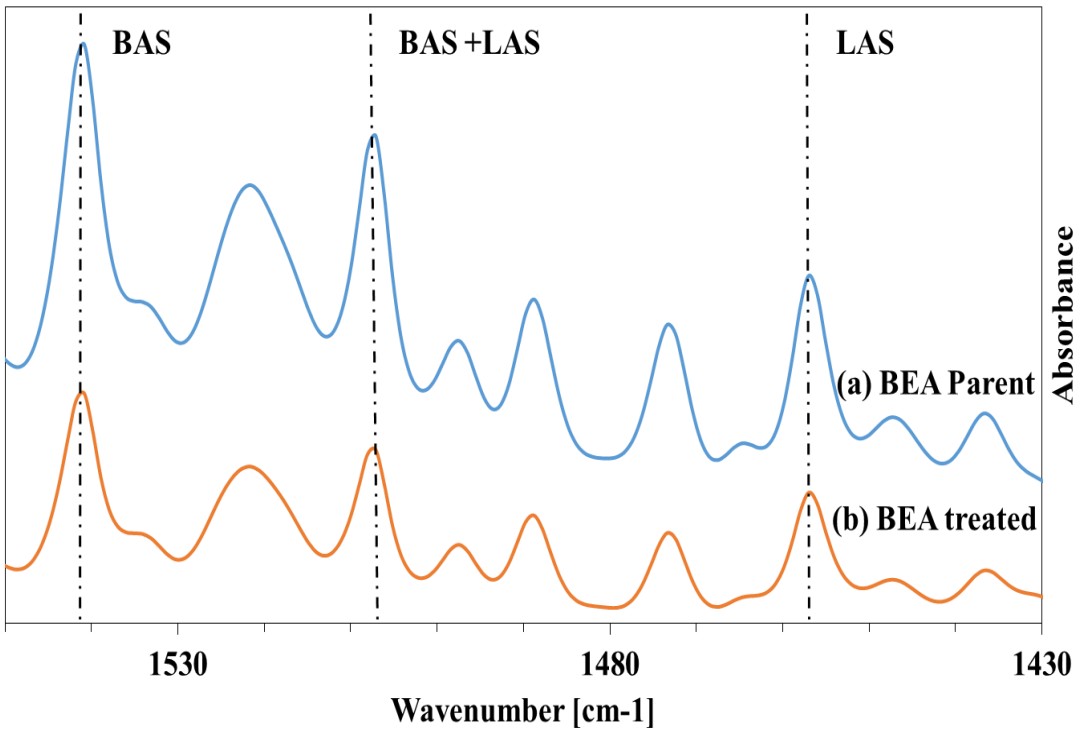


Figure 13. FT-IR spectra of pyridine-adsorbed (a) BEA-Parent and (b) BEA-Silane treated zeolite catalysts.

Table 8. Textural properties of parent and modified BEA catalyst using vapor silane treatment.

Samples	S_{BET} [$m^2\ g^{-1}$]	S_{EXT} [$m^2\ g^{-1}$]	V_{micro} [$cm^3\ g^{-1}$]
BEA-Unmodified	422	62	0.1614

BEA-Vapor Treated	489	136	0.2017

S_{BET} : surface area by BET method;
S_{EXT} and V_{micro} : external surface area and micro pore volume by t-plot method.

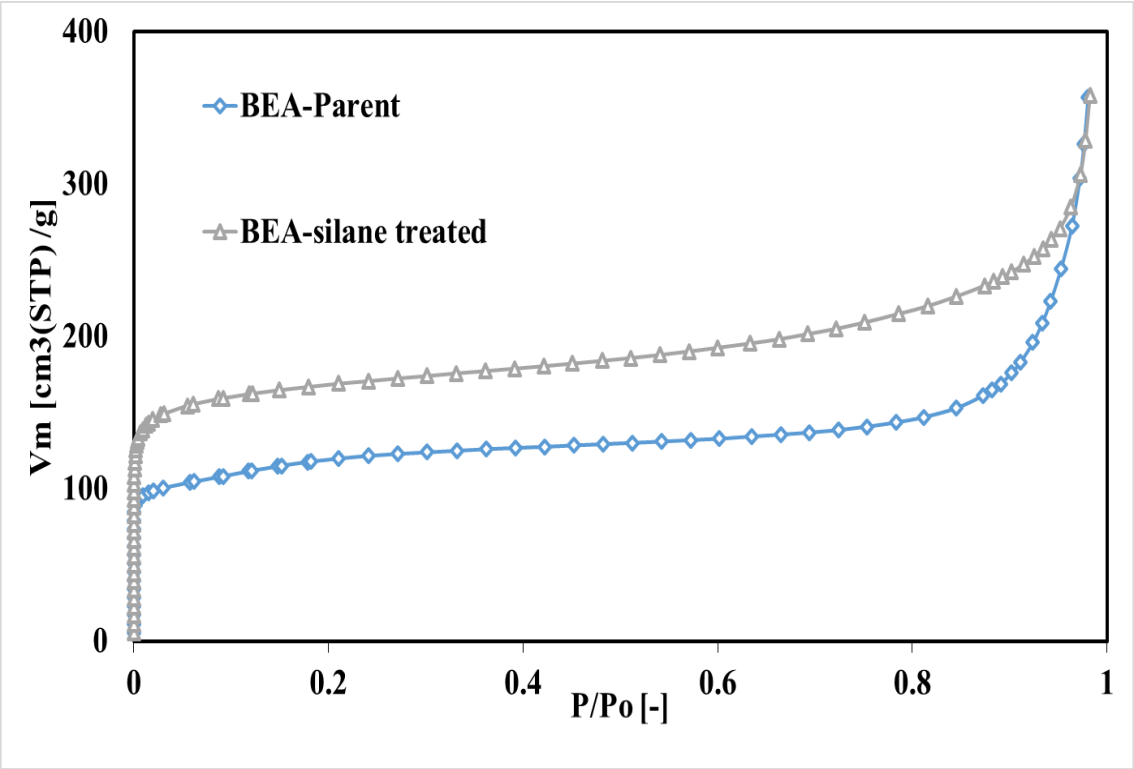


Figure 14. N2 adsorption isotherms of BEA-Parent and BEA-Silane treated.

4.2 Effect of surface modified catalyst on cracking of AR

Steam dilutes the reaction mixture and thus decreases the amount of coke formation [70], but irreversible deactivation (dealumination) of zeolite catalysts is a major problem in the presence of steam [71]. Numerous previous research papers showed a decrease in the dealumination process under steam environment after the incorporation of promoters such as phosphorus, lanthanum, cerium and fluorides [44, 46, 72, 73]. Moreover, other than these problems, zeolite structural changes were also reported in an aqueous

environment [39, 41]. Silane treatment of zeolite catalyst, developed in this work, mitigated the effects of dealumination, coking and structural changes. As shown in Figure. 15, 55.7 mol% of gasoline and kerosene (C_7-C_{13}) were produced over the BEA-silane treated catalyst, which was significantly higher than the 30.9 mol % of same carbon numbers over BEA parent catalyst for reaction time of 2 h. The total yield of lighter component (C_7-C_{35}) over BEA-silane treated catalyst was 59.4 mol%. Yield of lighter component were higher than the ones obtained over metal oxide catalysts used previously in the presence of steam [60-62]. It should be noted that BEA-silane treated catalyst produced negligible amount of heavy hydrocarbon (C_{20}+) as compared to BEA-parent catalyst (26.7 mol% heavy hydrocarbon). Amount of coke formed after 2 h reaction over BEA-silane treated catalyst was 6 wt. % of catalyst as compared to 11.5 wt. % over BEA-parent catalyst. This indicates the formations of heavier hydrocarbons were suppressed in accordance with the surface properties of BEA- catalyst. No hydrogen was formed in the case of both parent and silane treated zeolites as shown in gas composition analysis (Figure. 16), while hydrogen was the main constituent in heavy oil reactions over metal oxides catalysts. This fact also verified the reduction of coke formation in BEA-zeolite catalysts. As it has been shown in many previous reports that zeolite catalysts were preferred over many other type of catalysts for their high tendency of producing olefins and paraffin [70, 71]. This statement was supported with gas composition analysis in Figure. 18 where mainly alkenes and alkanes were formed and no CO_2 evolved which mainly formed in oxidative cracking reactions over iron-oxide catalysts [62].

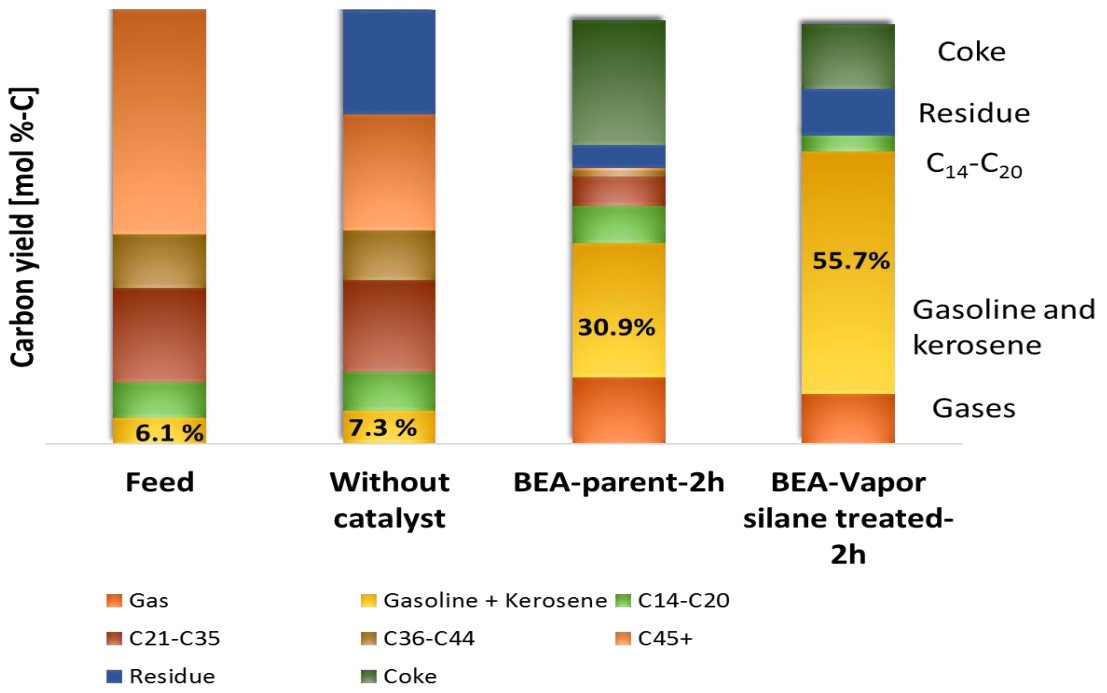


Figure 15. Carbon yield after 2 h reaction of AR with steam over BEA-parent and BEA-silane treated catalysts.

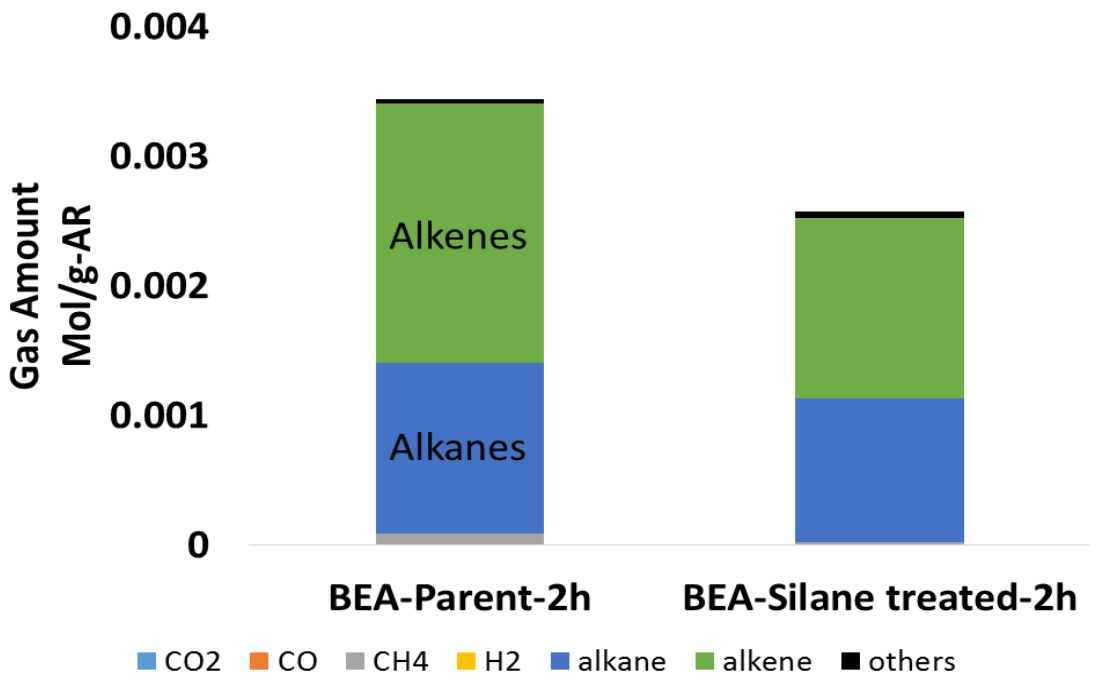


Figure 16. Gas composition (mol/g-AR) after 2 h reaction of AR with steam over BEA-parent and BEA-silane treated catalysts.

Better view on liquid hydrocarbon molecular weight (MW) distribution is presented in Figure. 17. Higher peak of liquid product curve for silane treated BEA catalyst in lower hydrocarbon MW range (less than 200 g/mol) shows considerable amount of lighter component yields. Figure. 18 shows a physical appearance of liquid product obtained after 2 h reaction time. Light green color of liquid product produced over silane-treated BEA catalyst suggests qualitatively the presence of a higher yield of lighter component as compared to BEA-parent catalyst.

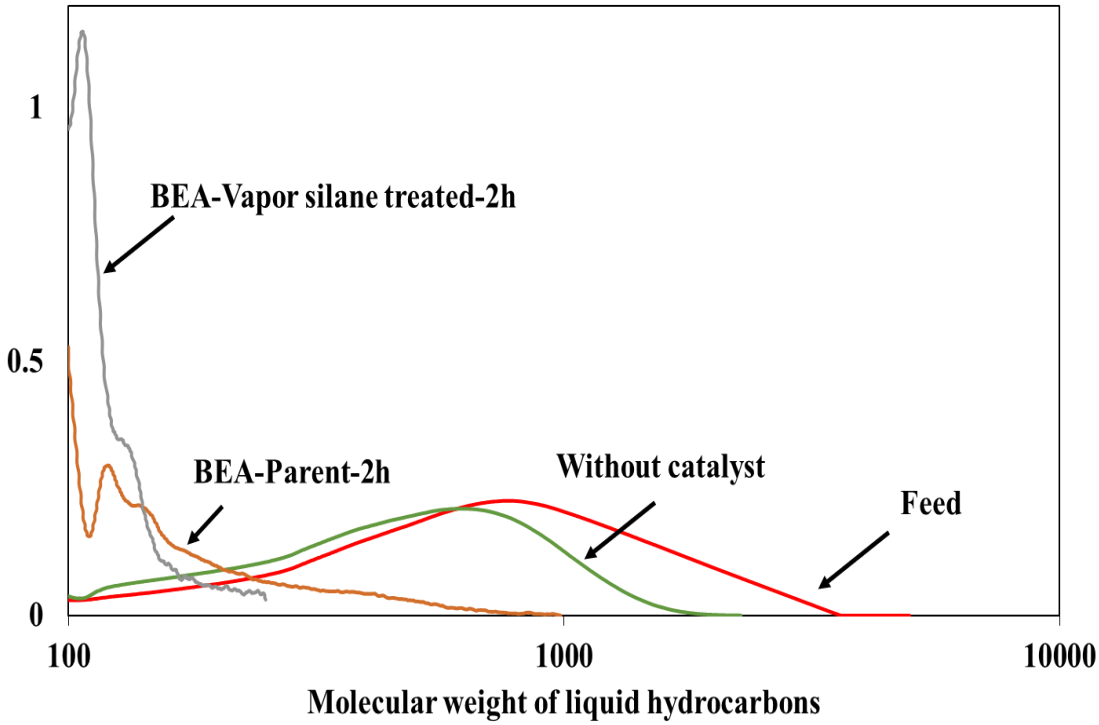


Figure 17. Molecular weight distribution of liquid product after 2 h reaction time.

Figure 18. Physical appearance of liquid product after 2 h reaction time over (a) BEA-parent and (b) BEA-silane treated catalysts.

Structural changes after the 2 h reaction time were observed in N_2-adsorption isotherms as shown in Figure. 19. Prior to N_2 adsorption studies, the spent BEA-parent and BEA-silane treated catalysts were calcined. BEA-parent catalyst showed an increase in surface area which may ascribe to the dealumination during steam-assisted reaction. In contrary, BEA-silane treated catalyst was found to be resistant to the attack of steam. The surface

organo-silane compounds prevented dealumination, which usually occurred under steam environment as shown in Figure. 20, N_2-adsorption isotherms of both BEA-silane treated catalyst before and after reaction shows exactly the same trends. Figure. 21 shows the comparison of XRD patterns for parent and silane treated catalysts. Both samples retained their crystallinity after 2 h reaction under steam exposure. Moreover, no impure phase was observed. This concludes that even though after the 2 h exposure to steam, the BEA catalyst structure was stable.

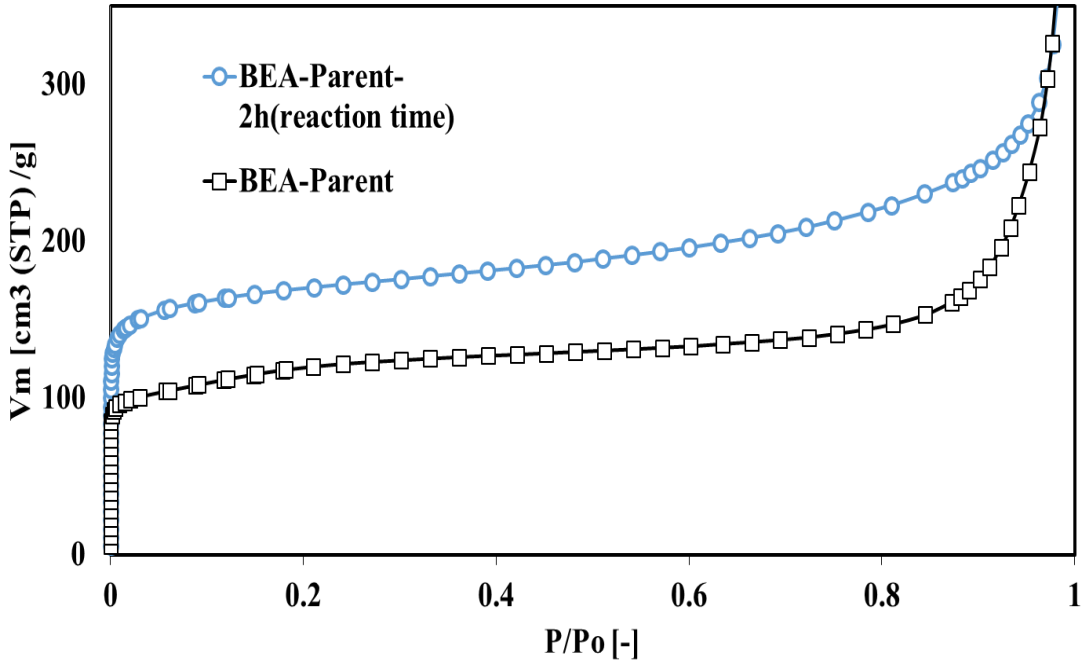


Figure 19. N2 adsorption isotherms of spent BEA-Parent-2h (after recalcination) and BEA-parent.

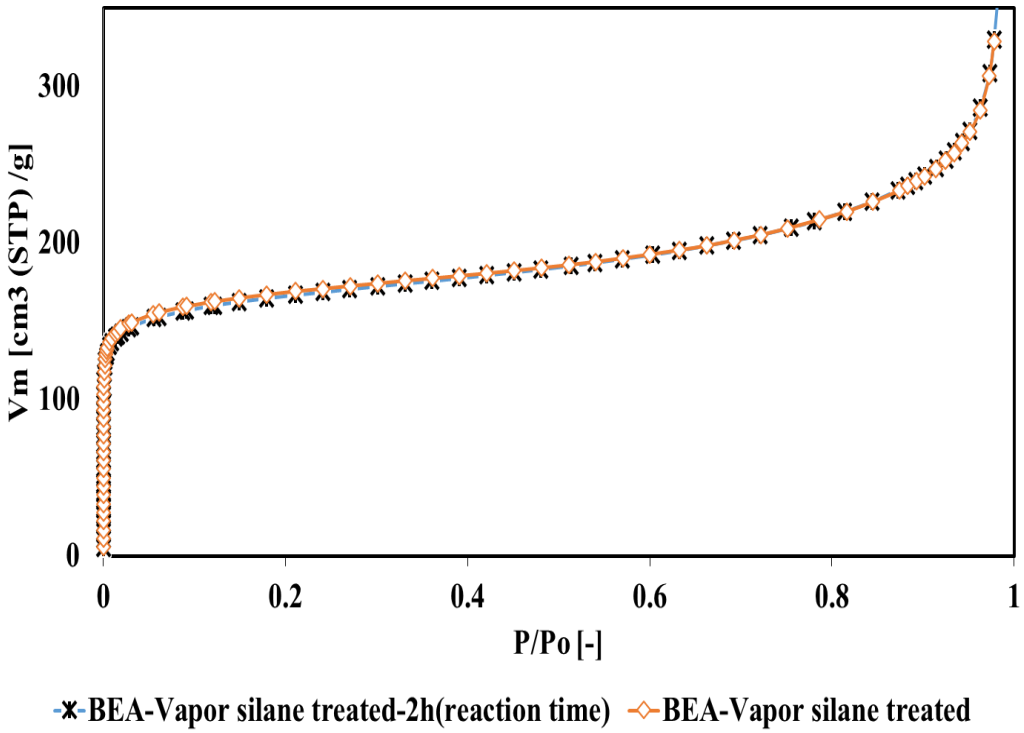


Figure 20. N2 adsorption isotherms of spent BEA-silane treated-2h(after recalcination) and BEA-silane treated

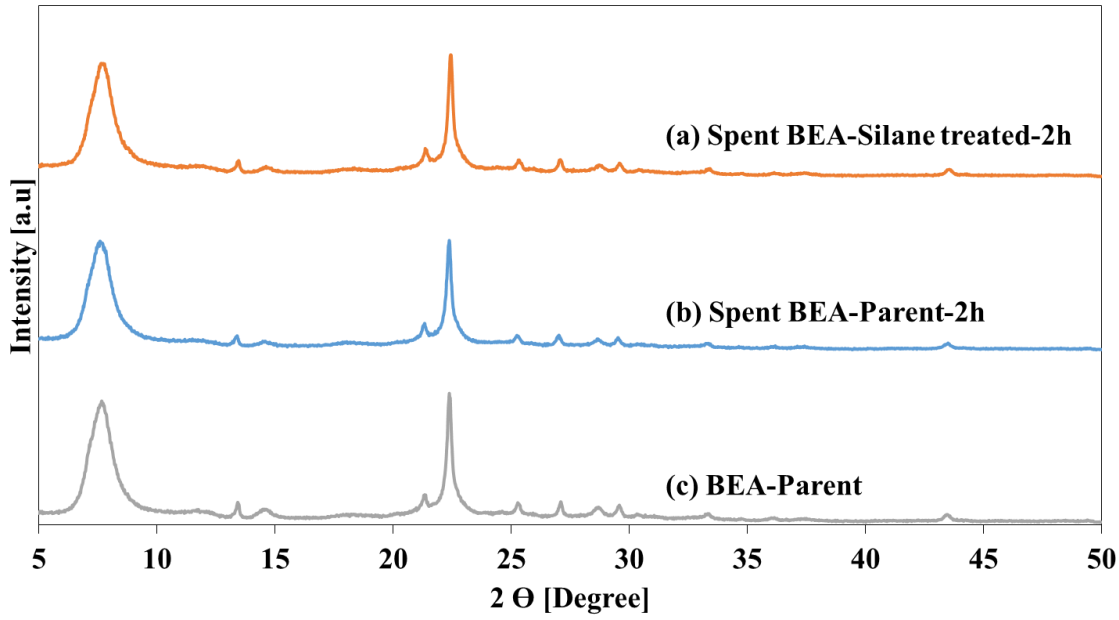


Figure 21. XRD patterns (a) BEA-silane treated-2h (b) BEA-parent-2h (c) BEA-Parent.

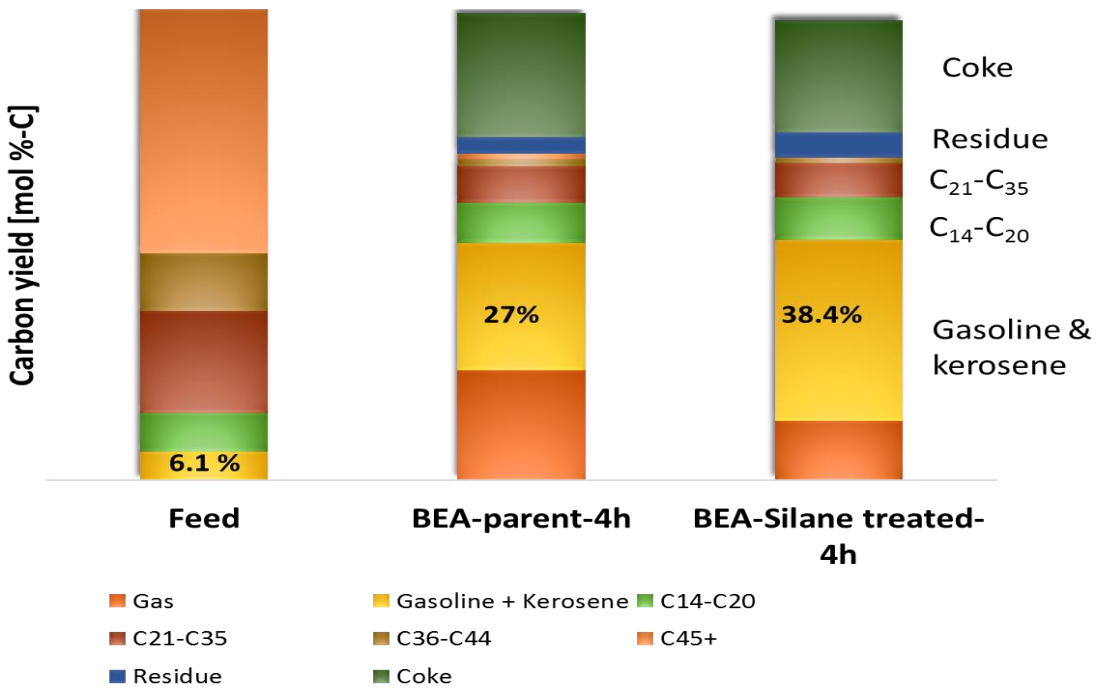


Figure 22. Carbon yield after 4 h reaction of AR with steam over BEA-parent and BEA-silane treated catalysts.

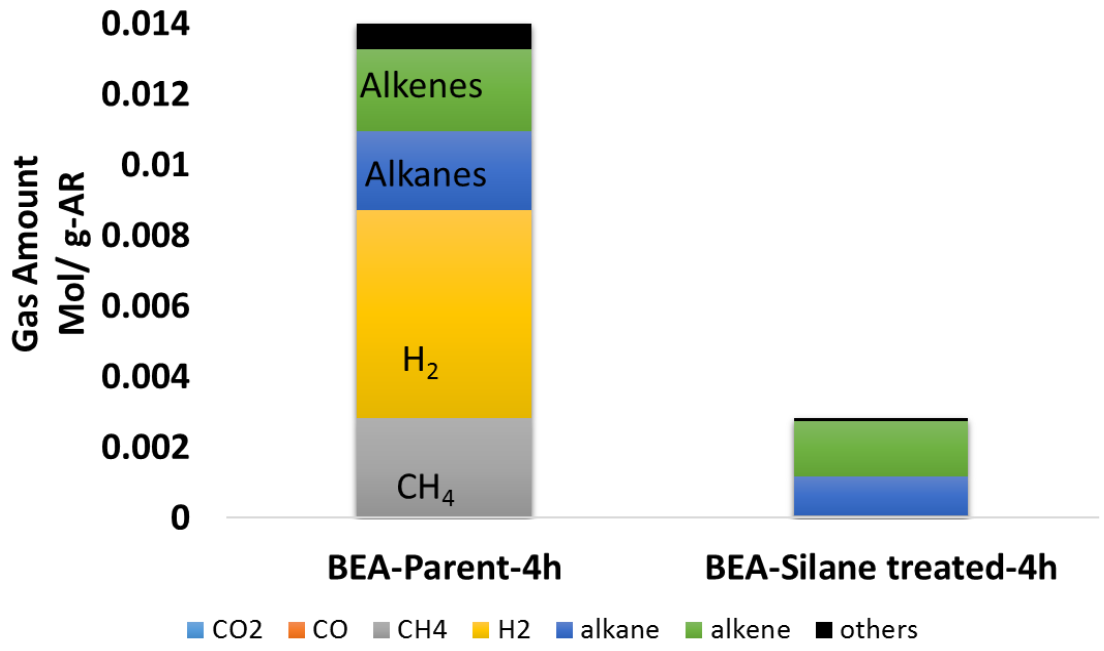


Figure 23. Gas composition (mol/g-AR) after 4 h reaction of AR with steam over BEA-parent and BEA-silane treated catalysts.

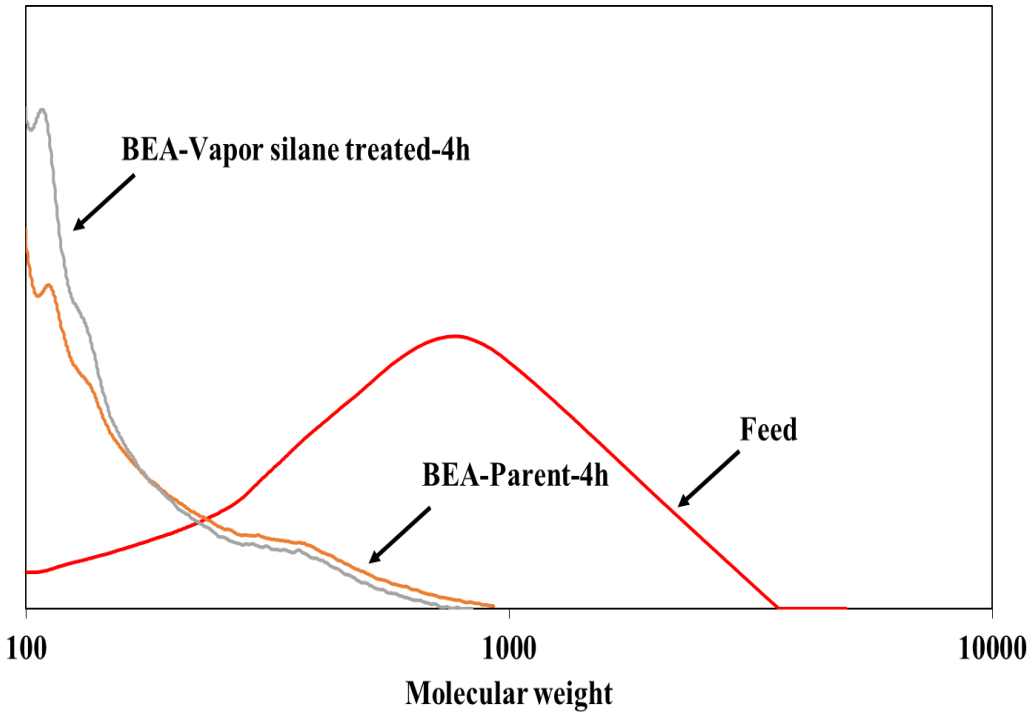


Figure 24. Molecular weight distribution of liquid product after 4 h reaction time.

4.3 Effect of reaction time on the stability of parent and modified catalyst

To investigate the stability of BEA-parent and BEA-silane treated catalysts, reaction time was increased to 4 h and the same sequence of reactions were performed. Product distribution (mol %) was also reported to study the effect of time. It was observed in Figure. 22 that lighter component yield after 4 h reaction decreased for both parent and silane treated zeolites as compared to 2 h reaction time; this finding is obvious as the amount of coke increased with time. Regardless of reaction time, percentage increase in lighter component yield was approximately same after silane treatment. Gas composition analysis in Figure. 23 shows a larger concentration of gas produced (mol per g-AR) over

BEA-parent, in addition mainly hydrogen evolved, which indicates the coke formation. Hydrocarbon MW distribution curves in Figure. 24 shows lighter products were formed over BEA-silane treated zeolite after 4 h reaction. Physical appearance of liquid product after 4 h reaction time in Figure. 25 justifies the results of MW distribution trends. Light yellow color of liquid product over BEA-silane treated zeolite after 4 h indicates the presence of lighter ends. Same color was observed after 2 h reaction over BEA-parent catalyst (Figure. 25).

Figure 25. Physical appearance of liquid product after 4 h reaction time over (a) BEA-parent and (b) BEA-silane treated catalysts.

Change in the phase purity of BEA-parent after 4 h reaction time was studied using XRD analysis. XRD patterns in Figure. 26 shows that an impure phase appears in BEA-parent catalyst, while BEA-silane treated catalyst retained its crystallinity and purity. Two peaks at 9 [2 Θ^{o}] and 24 [2 Θ^{o}] indicates that BEA-parent catalyst loses its purity during 4 h continues exposure to steam at 743 K

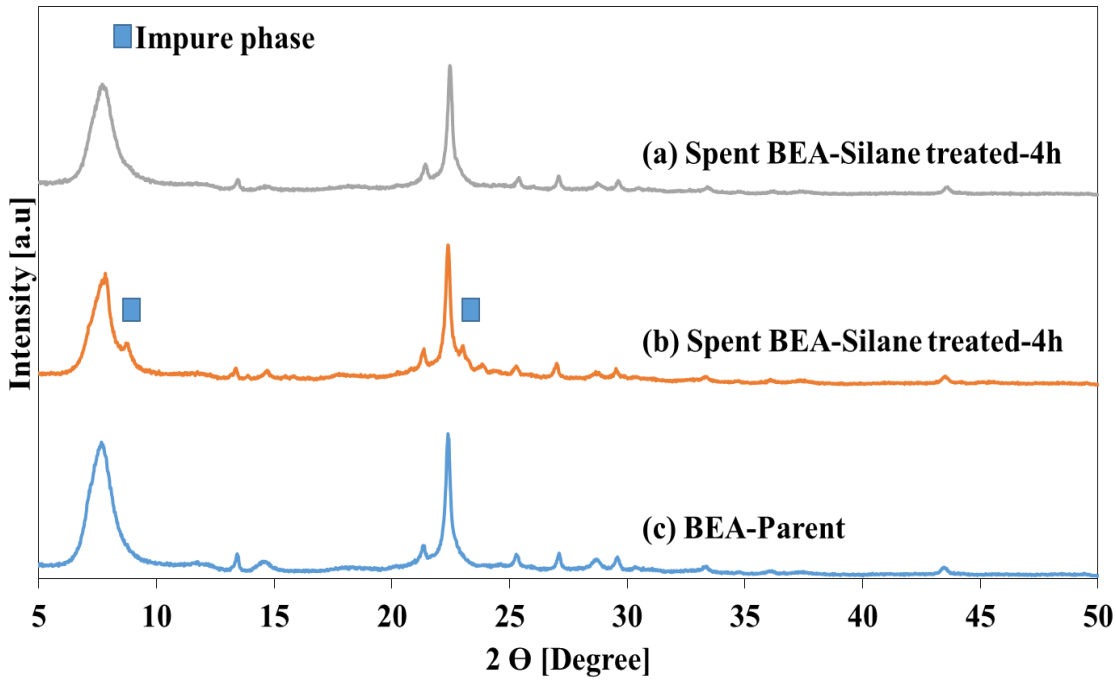


Figure 26. XRD patterns of (a) spent BEA-silane treated-4h (b) spent BEA-parent-4h (c) BEA-parent.

CHAPTER 5

Liquid phase silane treated catalysts

5.1 Effect of silane treatment on catalyst properties

Liquid phase deposition of silane compound on BEA zeolite (SiO_2/Al_2O_3 = 150) was adapted following a procedure reported earlier by Zapata et al [39]. Triphenyl silane as a reagent was selected on the basis of its kinetic diameter, which should be larger than the pore size of BEA. Figure. 27 shows the XRD patterns of parent BEA and liquid phase silane treated BEA zeolites. No change in purity of phase was observed, while a very less change in crystallinity was noted as expected after the surface modification of zeolite N_2-adsorption isotherms in Figure. 28 shows that adsorption over both parent and silane treated catalysts are approximately same. Table 9 presents the change in detailed texture properties after modification which again shows the increase in external surface area, attributes that organosilane compunds attached to the only external surface of BEA catalysts and did not enter into the pore of BEA zeolite. These findings were important because the inner acidity of zeolite remained unaltered and available for cracking reactions. Figure. 29 shows the NH_3-TPD profiles of parent and silane treated zeolites. A decrease in both weak and strong acid sites was observed. NH_3 desorption peak at temperature above 600 K associated with strong acid sites showed a decrease trend after modification. Silane compounds attached to both weak and strong sites, which were located at the outer surface of Beta zeolite. Large number of acid sites increases the activity of catalyst and provides more sites for cracking reaction. However, it was also

found that the coke formation linearly increases with activity of catalyst. Hence, silane groups attached to the selective acid sites also controls coke formation [65, 66].

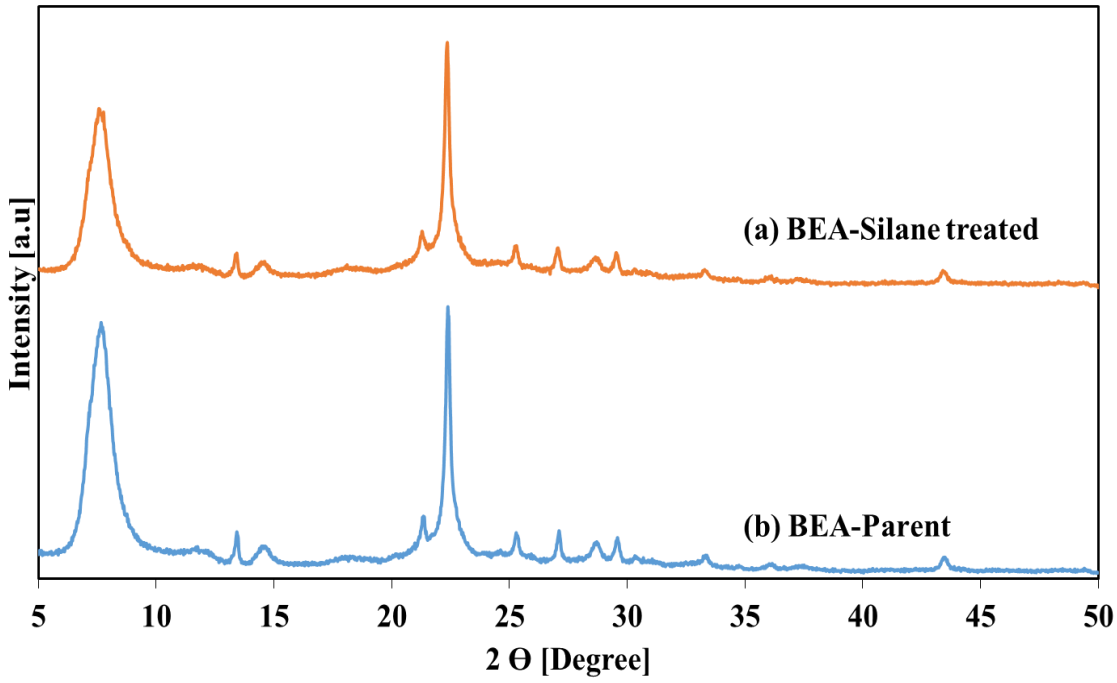


Figure 27. XRD patterns of (a) BEA- Liquid Silane treated and (b) BEA-Parent.

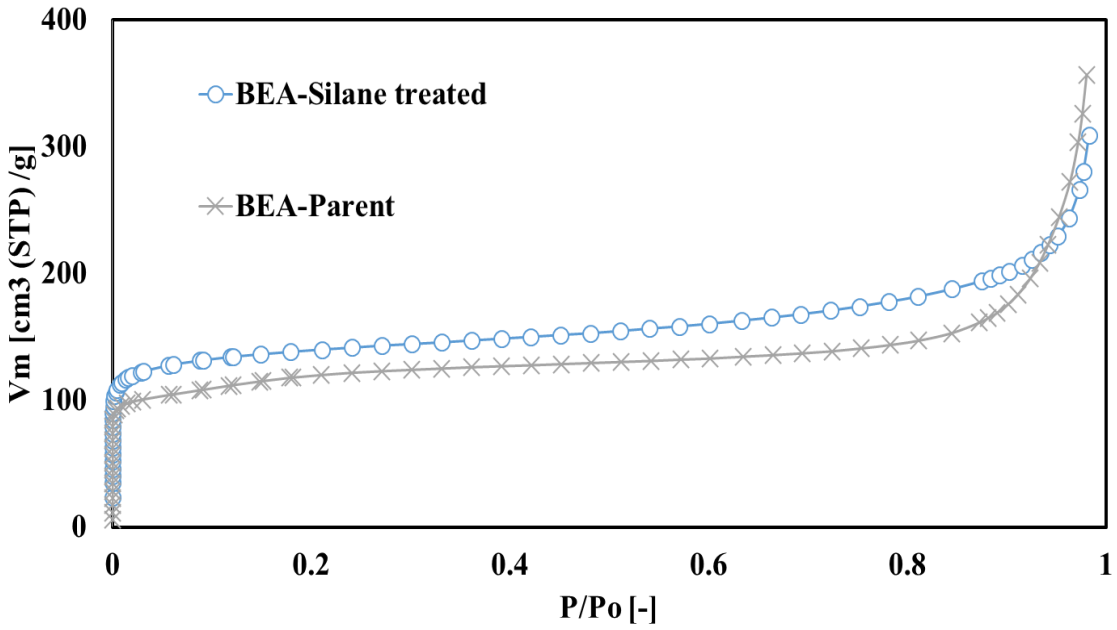


Figure 28. N2 adsorption isotherms of BEA-Parent and BEA-Liquid silane treated.

Table 9. Textural properties of parent and silane treated BEA catalysts.

Samples	**S_{BET} [$m^2 g^{-1}$]**	**S_{EXT} [$m^2 g^{-1}$]**	**V_{micro} [$cm^3 g^{-1}$]**
BEA-Parent	422	62	0.1614
BEA-Silane Treated	415	114	0.1652

S_{BET} : surface area by BET method;

S_{EXT} and V_{micro} : external surface area and micro pore volume by t-plot method.

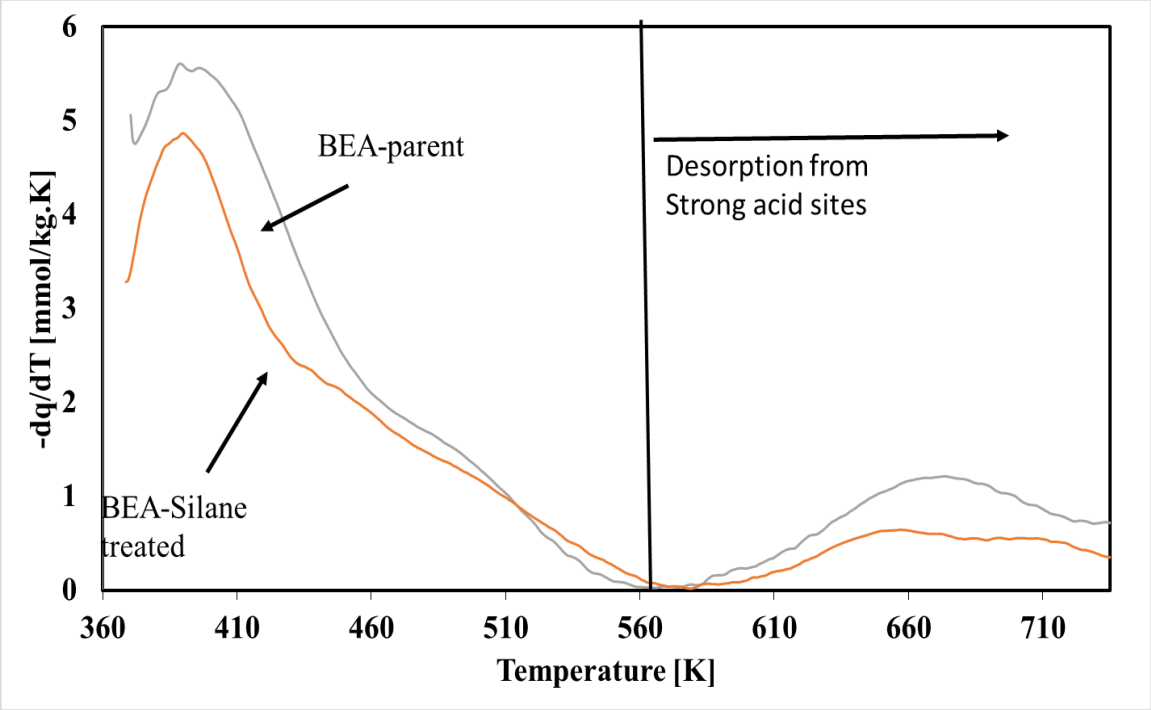


Figure 29.NH3-TPD profiles of BEA-Parent and BEA-Liquid-silane treated zeolite catalysts.

5.2 Effect of surface modified catalyst on cracking of AR

Surface modified BEA zeolite was tested in heavy oil cracking reaction for 2 h and 4 h reaction time. The products were classified according to their carbon number into six groups: gases, gasoline + kerosene (C_7-C_{13}), gas oil (C_{14}-C_{20}, C_{21}-C_{35}), and heavy oil (C_{36}-C_{44}, above C_{45}). To investigate the effect of surface modification on the cracking of atmospheric residue oil, silane treated catalyst was evaluated for 2 h reaction time and liquid as well as gas product distribution was analyzed. Steam plays important role in the cracking reactions over zeolite catalysts as it helps to decrease the amount of coke formation but at the same time dealumination of zeolite catalyst in the presence of steam is a major problem [47, 70, 74]. Reducing the rate of dealumination using silane treated zeolite tends to increase conversion of heavy feedstock into lighter hydrocarbon. This

assumption is verified in Figure. 30 which represent the increase in gasoline (C_7-C_{13}) yield over silane treated BEA zeolite catalyst as compared to the parent BEA catalyst. Also the yield of lighter hydrocarbon products (C_7-C_{35}) increased up to 50.3 mol%. These results indicate that silane treated BEA catalyst retained its activity after 2 h reaction time. Moreover, a decrease in coke formation over the silane treated BEA catalyst was also observed. It is worth mentioning that C_{35+} yield over modified catalyst was negligible as compared to the one for parent catalyst. Gas composition analysis after 2 h reaction time in Figure. 31 shows no hydrogen formed in both parent and modified BEA catalysts. While it was reported that considerable amount of hydrogen was produced over metal oxide catalysts, which indicates the formation of coke [23, 60-62]. Problems involving dealumination caused in the presence of steam and coke formation were mitigated using silane treated zeolite catalysts. Major constituents of the gases produced were alkenes and alkanes in the case of BEA-zeolite. Molecular weight distribution curves in Figure. 32 showed full agreement with above mentioned results. A sharp increase in peak was observed in the lighter hydrocarbon area over silane treated BEA catalyst. The higher amount of the lighter hydrocarbon over silane treated catalysts showed less coke formation. Figure. 33 showed the physical appearance of liquid product after reaction over parent and the modified BEA zeolite catalyst. Light yellow color of product over silane treated catalyst results indicates the presence of lighter components.

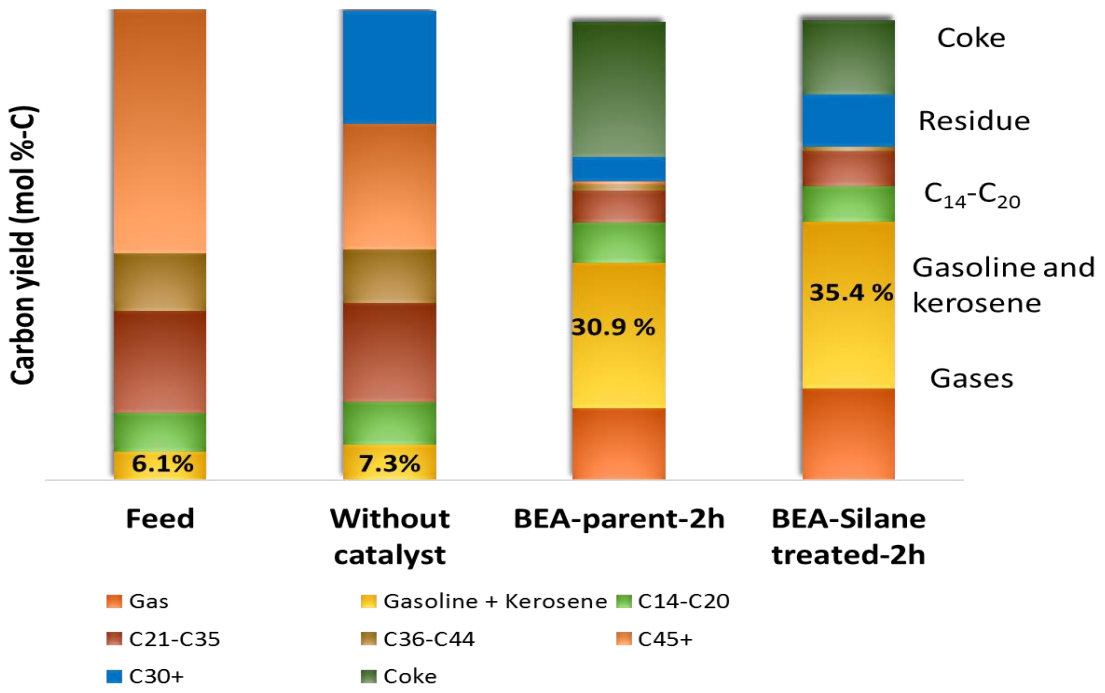


Figure 30. Carbon yield after 2 h reaction of AR with steam over BEA-parent and BEA-Liquid phase silane treated catalysts.

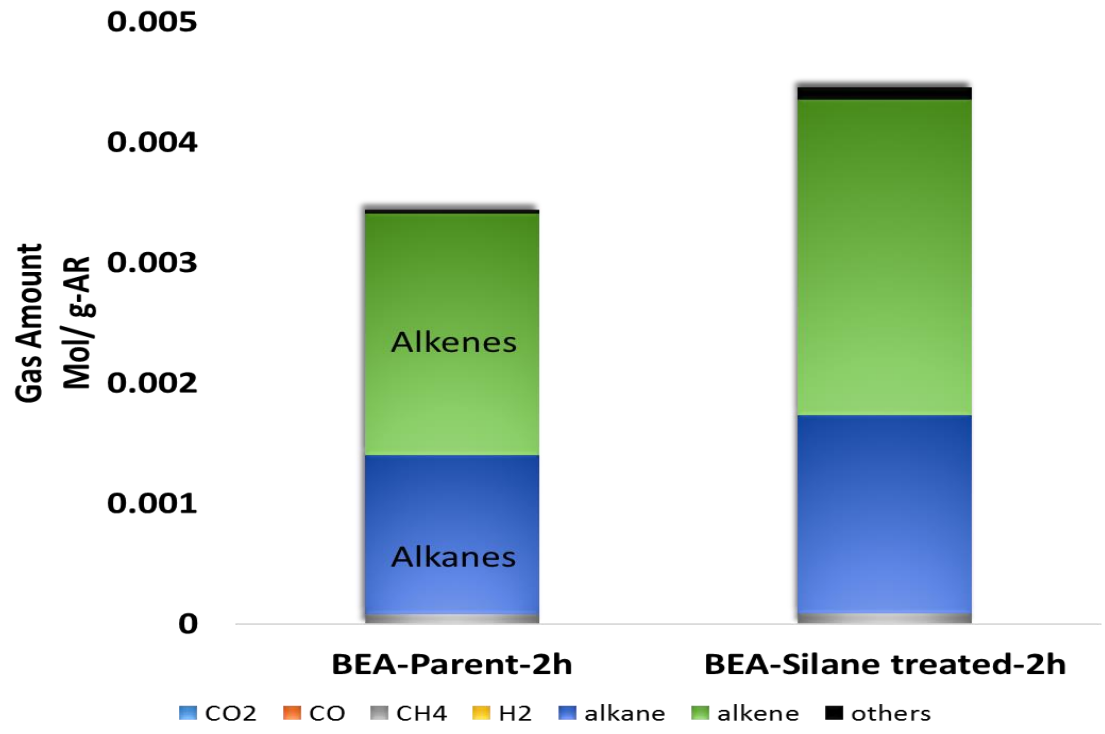


Figure 31. Gas composition (mol %) after 2 h reaction of AR with steam over BEA-parent and BEA-Liquid phase silane treated catalysts.

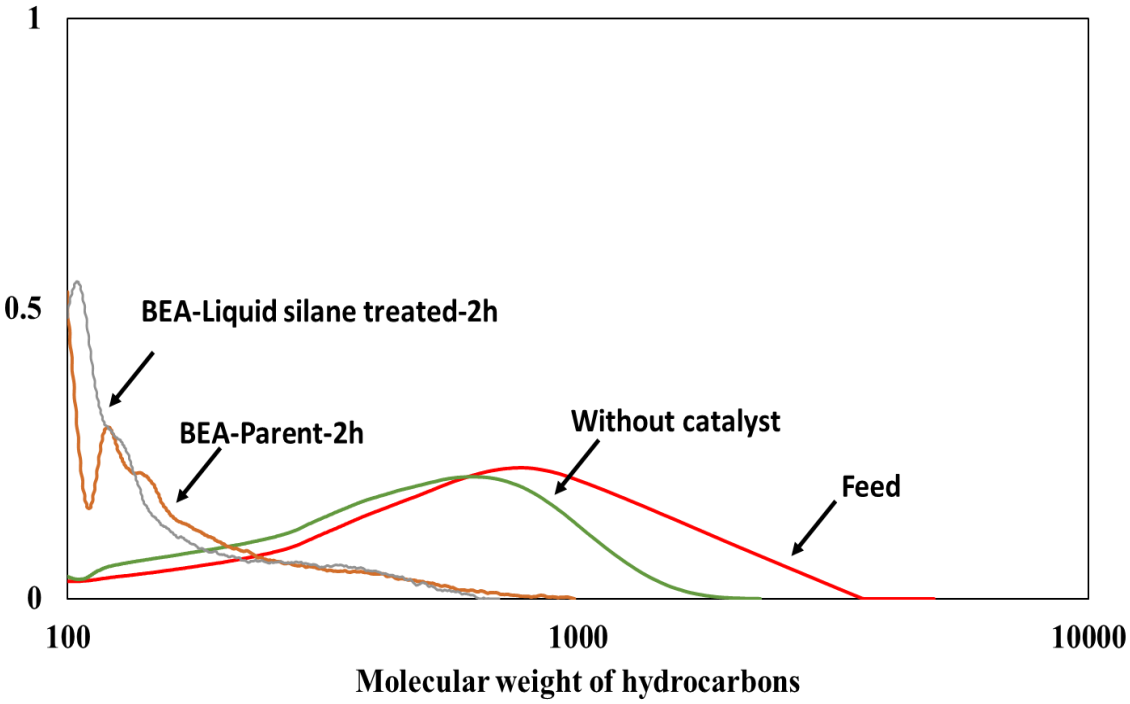


Figure 32. Molecular weight distribution of liquid product over BEA-Parent and BEA-Liquid silane treated catalysts after 2 h reaction time.

Figure 33. Physical appearance of liquid product after 2 h reaction time over (a) BEA-parent and (b) BEA-Liquid silane treated catalysts.

5.3 Effect of reaction time on cracking of AR

Stability of parent and silane treated BEA catalyst was measured after a prolonged reaction time for 4 h. Reaction test was repeated for 4 h over parent and silane treated catalyst and product distribution was carefully studied. Figure. 34 represents an increase in lighter component yield over silane treated BEA-zeolite catalyst. Gasoline (C_7-C_{13}) yield increased up to 34.1 mol% as compared to 27 mol% over parent BEA-zeolite. Relatively less amount of coke formed over silane treated BEA catalyst showed partial

coverage of the external sites by silane compounds. Less amount of coke leads to the improved stability of catalyst and higher yield of lighter components. Gas composition analysis in Figure. 35 show a high percentage of hydrogen gas produced over the parent BEA catalyst after 4 h reaction, which indicates that after longer reaction time, significant amount of coke was deposited on the parent BEA catalyst while there was no hydrogen gas was formed over silane treated BEA catalyst, even after 4 h reaction time. Major gas constituents in the gas of silane treated zeolite were alkanes and alkenes. High percentage of alkenes was obtained over silane treated zeolite. Figure. 36 represents the better view of liquid product distribution according to their molecular weight. Large area under the graph of silane treated zeolite in the low molecular weight region showed a high percentage of lighter components.

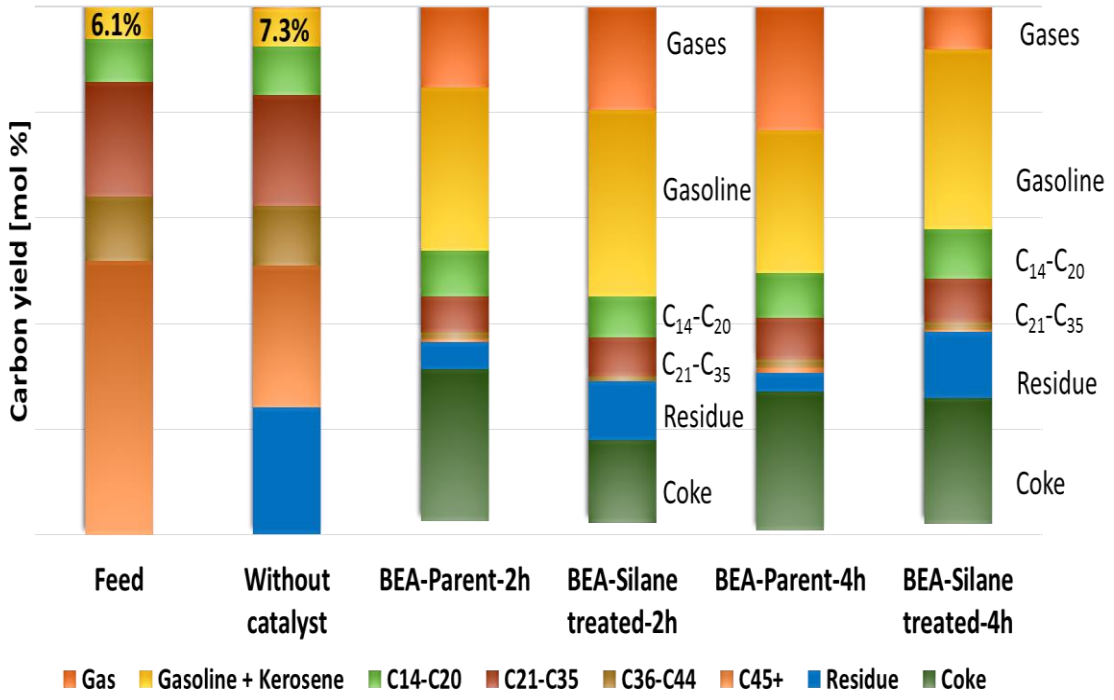


Figure 34. Physical appearance of liquid product after 4 h reaction time over (a) BEA-parent and (b) BEA-Liquid silane treated catalysts.

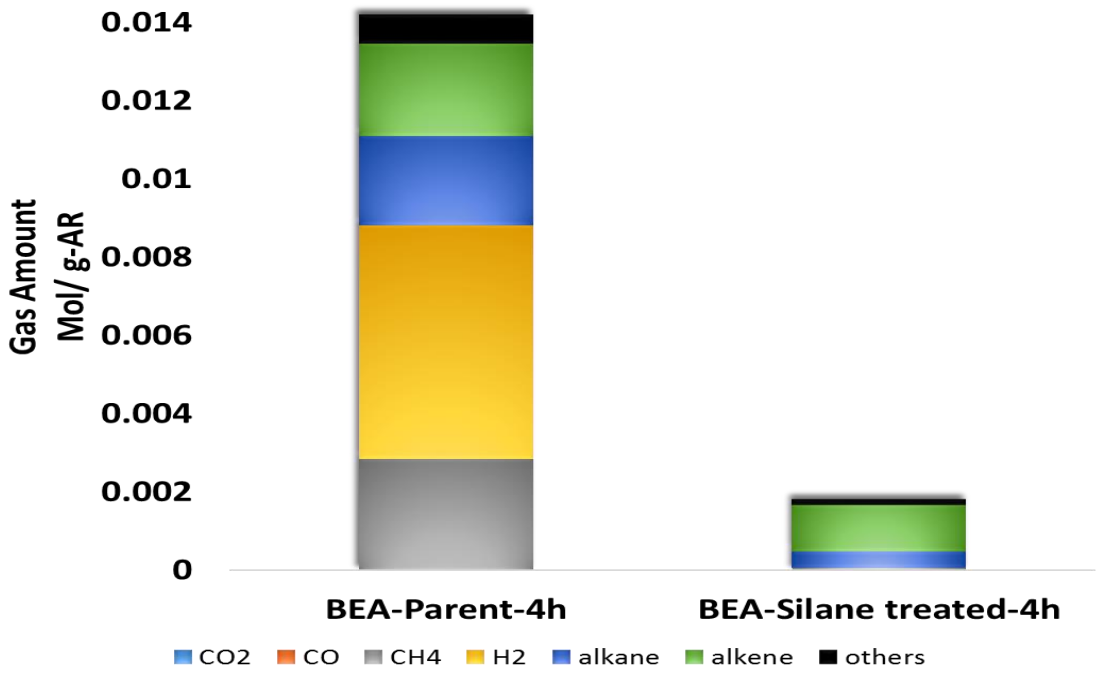


Figure 35. Gas composition (mol %) after 4 h reaction of AR with steam over BEA-parent and BEA-Liquid phase silane treated catalysts.

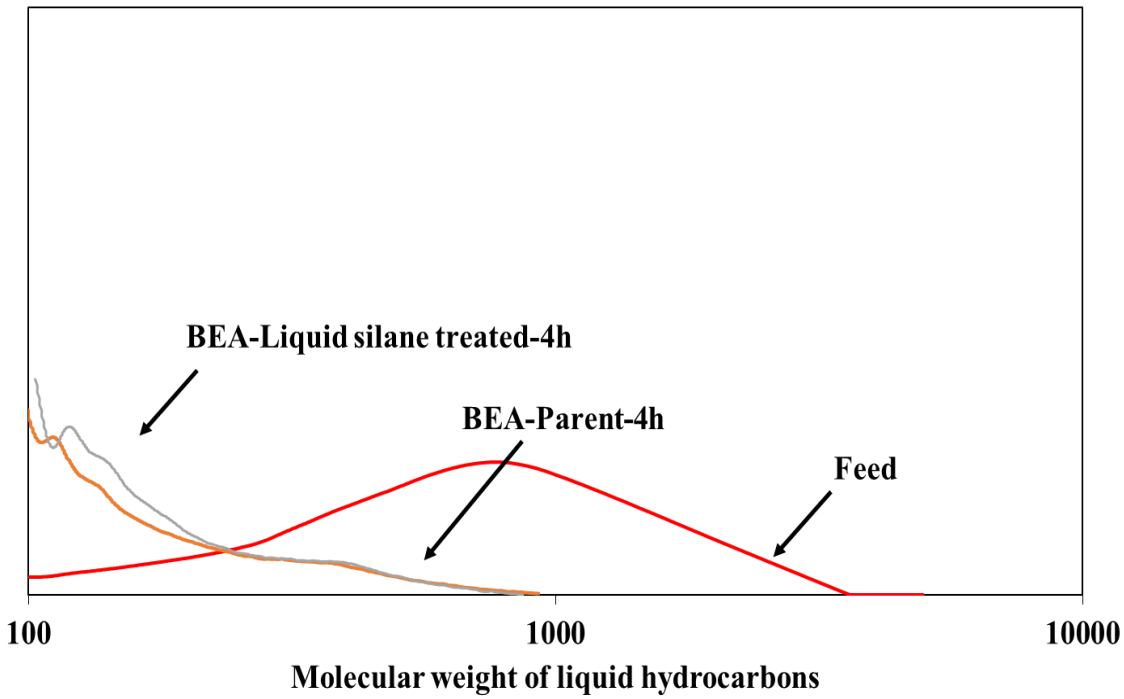


Figure 36. Molecular weight distribution of liquid product over BEA-Parent and BEA-Liquid silane treated catalysts after 4 h reaction time.

Change in the crystallinity of parent and a modified catalyst was studied from XRD patterns. Figure. 37 (XRD patterns) shows that the BEA catalyst retained its crystallinity, even after 2 h reaction and phase purity were still intact. Despite no structural changes were observed after 2 h for parent BEA catalyst, some changes in phase purity were clearly observed after 4 h reaction. Impure phase was appeared after a longer reaction time in parent catalyst, which indicates changes in the structure of zeolite. On the other hand, the silane treated BEA-catalyst exhibited stable structure even after 4 h. Silane compounds attached to the external surface of zeolite prevented the structure from the attack of water and made stable hydrophobic catalyst.

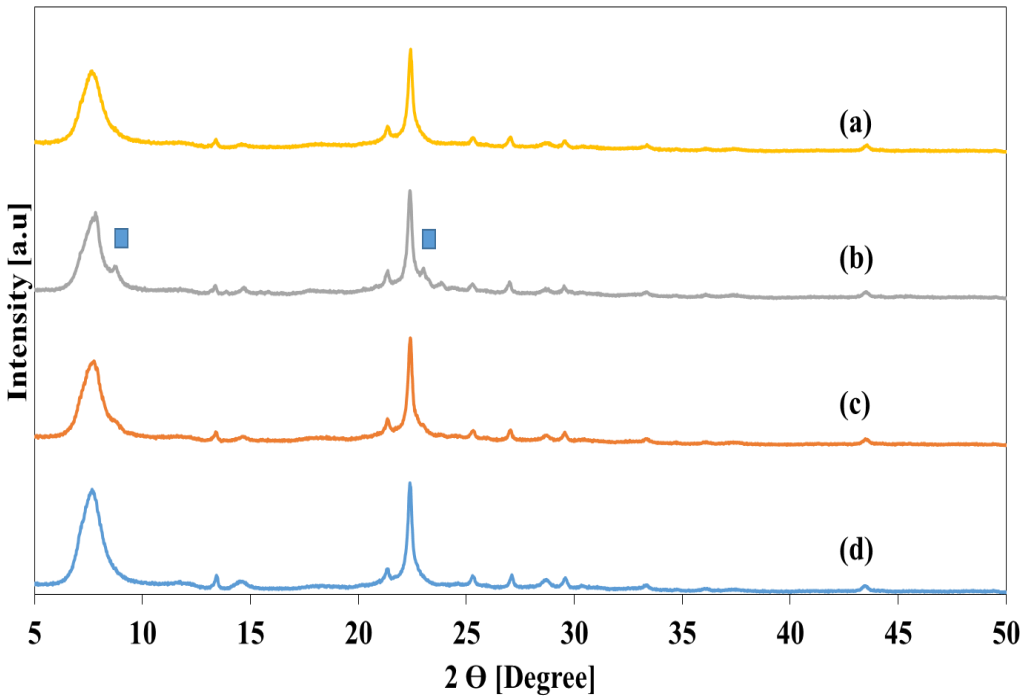


Figure 37. XRD patterns of (a) BEA-Vapor silane treated-4h (b) BEA-Parent-4h (c) BEA-Liquid silane treated-2h (d) BEA-Parent.

5.4 Comparison between Vapor phase and liquid phase silane treated catalyst

It was observed that high percentage of lighter component was obtained over vapor phase silane treated BEA catalyst as compare to liquid phase silane treated BEA catalyst. Reason may be the uniform coverage of catalyst surface when it was modified in vapor phase. In liquid phase there may be agglomeration of silane compound on catalyst surface. Uniformly modified surface more effectively repel the water molecules and make the catalyst more stable. Figure. 38. shows that after 2 h reaction remarkable increase in gasoline from 30.9 mol % over parent to 55.7 mol % over vapor silane treated catalyst. In the case of liquid silane treated catalyst this increase was up to 35.4 mol %.

Moreover, comparatively less coke formed in later case. When XRD patterns of both silane treated and parent catalysts was observed there was no considerable change in crystallinity was observed this indicates the stable structure after 2 h reaction. All three catalysts retained their crystallinity and phase purity. On contrary to this, after 4 h reaction XRD analysis showed structural changes in parent catalyst while vapor and liquid phase silane treated catalysts were stable. After 4 h reaction gasoline yield was higher over vapor phase silane treated as compare to parent and liquid silane treated catalysts. It was also observed that large percentage of hydrogen was produced over parent catalyst while no hydrogen was formed in both modified catalysts. Major constituent of gas product over silane treated catalysts were alkenes and alkanes.

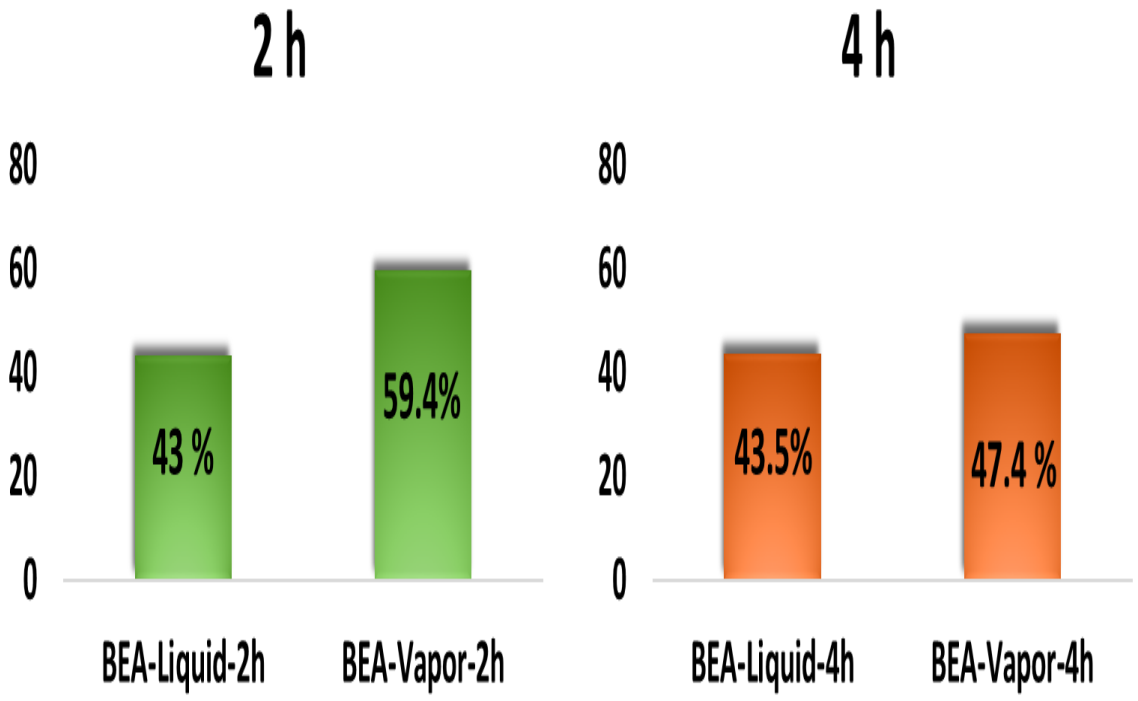


Figure 38. Comprison of lighter hydrcaron yield over vapor silane treated and liquid silane treated catalysts for 2h and 4h reaction times.

Physical appearance of liquid product over all catalysts were observed in Figure 39 after 2 h and 4 h reaction. Lighter color was observed over vapor phase silane treated catalyst as compare to parent and liquid silane treated catalysts this indicates the lighter components were formed over vapor phase silane treated catalyst. This trend was observed in both 2 h and 4 h reaction time.

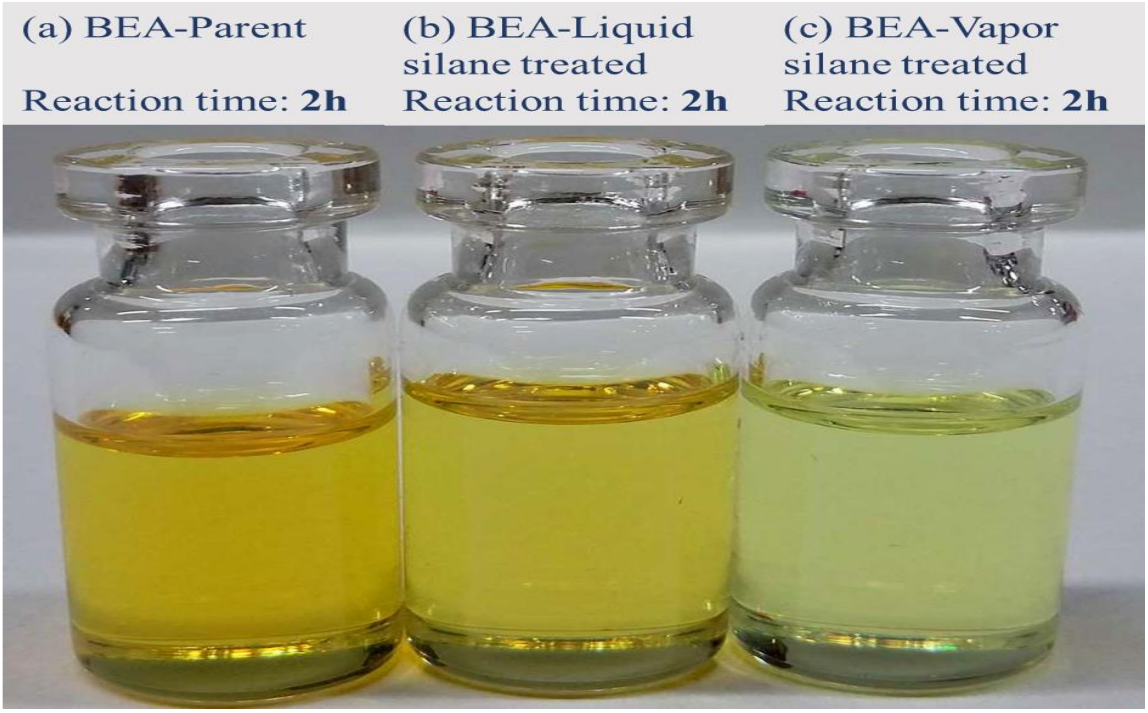


Figure 39. Physical appearance of liquid product after 2 h reaction time over (a) BEA-parent (b) BEA-Liquid silane treated and (c) BEA-Vapor silane treated catalyst.

CHAPTER 6

6.1 Conclusions

Organosilane compound (triphenyl silane) was used to modify the external surface of beta zeolite catalysts.

Two different techniques i.e. vapor silane deposition and liquid silane deposition were used to modify the Beta catalyst.Both parent and modified BEA catalysts were characterized using XRD, NH_3-TPD, FT-IR pyridine and N_2-adsorption.

XRD patterns showed no change in crystallinity and phase purity of catalysts after modification. While NH_3-TPD and FT-IR pyridine analysis showed decrease in acidity of silane treated BEA catalysts. Small increase in external surface was reported after silane treatment through both techniques.

Parent and silane treated BEA catalysts were tested in fixed-bed reactor for steam-assisted catalytic cracking of heavy oil for 2 h and 4 h reaction times.

Yield of gases, gasoline (C_7-C_{13}) and gas oil (C_{14}-C_{20}) over a vapor phase silane treated Beta zeolite catalyst were 11.6 mol %, 55.7 mol % and 3.7 mol % respectively for 2 h reaction time while negligible amount of C_{20+} hydrocarbons were produced.

After 4 h reaction time, XRD analysis showed impure phase in BEA parent catalysts while there was no change in purity of silane treated BEA catalysts after reaction.

These findings indicate that organo-silane groups attached to the external surface of catalysts protect the surface from water attack (dealumination) and made the zeolite stable in the aqueous environment.

6.2 Recommendations

Modified catalysts should also be test for cracking reactions in the presence of liquid water.

Different chain length of silane compounds may have

Study the effect of increasing reaction time on the stability of catalysts.

Different zeolite catalysts should be tested after modification.

Other modification routes such as impregnation of fluoride, phosphorus and lanthanum on zeolites should be studied for cracking reactions in the aqueous environment.

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