

Methanol to olefins using modified SAPO-34 zeolite

BY

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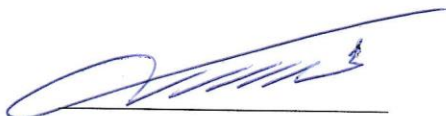
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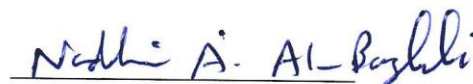
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Dedicated to my father. May Allah forgive him, grant him Jannah, and gather us there. Also, to my mother and sisters for their unmeasurable love and support.

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List of abbreviations

FCC: Fluid catalytic cracking

GTO: Gas to olefins

MTO: Methanol to olefins

SAPO: Silicoaluminophosphate molecular sieve.

SDA: Structure directing agent

TEOH: Tetra ethyl ammonium hydroxide

T: Tetrahedral atom connected by four bonds

Octahedral: Atom connected by six bonds

Py: Pyridine

Mor: Morpholine

Me: Metal

Aq.: Aqueous

IE: Ion exchange

S-IE: Solid state ion exchange

L-IE: Liquid ion exchange

Me/SAPO-34: Metal impregnation

GC: Gas chromatography

TCD: Thermal conductivity detector

Cat: Catalyst.

MeOH: Methanol

DME: Dimethyl ether

WHSV: Weight hourly space velocity

TOS: Time on stream

C₂-C₄: Light olefins

Abstract

Full Name : Hassan Ahmed Salih Hussein
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The modified SAPO-34 catalysts were synthesized for methanol conversion to more valuable products such as light olefins. The effect of the modification on the catalytic performance and physicochemical properties were investigated. The comprehensive characterizations, XRD, EDX, FESEM, FTIR, N₂-BET, NH₃-TPD and DR-UV-Vis have been applied to characterize the modified SAPO-34. The catalytic enhancement of SAPO-34 was performed by either in-situ or post modifications. The in-situ modification is divided into metallic and nonmetallic where alkaline or transition metals and boron were incorporated into the framework of SAPO-34. While, the post-modification was performed either by metallic incorporation or chemical treatment. Eventhough the crystallinity of modified catalysts decreased compared to parent SAPO-34, the diffusion and acidity properties were improved. Good activity and selectivity for olefins production were observed for all synthesized catalysts. The Metallic incorporation to the framework of SAPO-34 enhanced the catalytic lifetime and propylene yield. The methanol conversion was stable for more than 1 h over metallic in-situ modified catalysts with W/F=6.6 g. h/mole at 350 °C, and 1 bar. The IE-MgSAPO-34 catalyst exhibited the best stability for 2 h of TOS. The deactivation rate was higher for the parent SAPO-34 as compared to metallic

modified catalysts. Subsequently, the light olefins yield was increased by metallic incorporation. The in-situ modified catalysts favored propylene production unlike the post modified catalysts which favor ethylene. This olefin preference of catalysts was attributed to the acidity variation. Finally, the post-modification was more efficient to enhance the SAPO-34 catalyst for MTO reaction because of higher incorporation percentage and better acidity adjustment compared to the in-situ modification.

ملخص الرسالة

الاسم الكامل: حسن احمد صالح حسين

عنوان الرسالة: تحويل الميثانول لأوليفينات باستخدام زيولايت SAPO-34 المعدل

التخصص: هندسه كيميائية

تاريخ الدرجة العلمية: ديسمبر 2017

تم توليف المحفزات المعدلة سابو-34 لتحويل الميثانول إلى منتجات أكثر قيمة مثل الأوليفينات الخفيفة. تم دراسة تأثير التعديل على الأداء التحفيزي والخصائص الفيزيائية والكيميائية. تم توصيف الخصائص الفيزيائية والكيميائية باستخدام XRD, SEM, N₂-BET, NH₃-TPD, FTIR, and UV-VIS لسابو-34 المعدل. وقد تم إجراء التحسين الحفز لسابو-34 إما من خلال التعديلات في الموقع أو في مرحلة ما بعد التعديل. وينقسم التعديل في الموقع إلى المعدن وغير المعدنية حيث اضيفت المعادن القلوية و الانتقالية والبورون في إطار سابو-34. في حين، تم إجراء ما بعد التعديل إما عن طريق التأسيس المعدني أو المعالجة الكيميائية. علي الرغم من انخفاض التبلور بعد التعديل بالمقارنة مع الأم سابو-34، تم تحسين خصائص الانتشار والحموضة. وقد لوحظ نشاط جيد وانتقائية لإنتاج الأوليفينات لجميع المحفزات المصنعة. وقد أدى دمج المعادن في إطار سابو-34 إلى تعزيز العمر الوظيفي للحفز وإنتاجه البروبيلين. كان تحويل الميثانول مستقرًا لأكثر من 1 ساعة باستخدام المحفزات المعدلة بالمعادن عند 6.6 غرام. ساعة / مول عند 350 درجة مئوية، وبار واحد. أظهر المحفز إي-مغسابو-34 أفضل استقرار لمدة 2 ساعة من توس. وكان معدل التعطيل أعلى بالنسبة للسابو-34 الأصلي بالمقارنة مع المحفزات المعدنية المعدلة. وفي وقت لاحق، زاد العائد الأوليفينات الخفيفة عن طريق التأسيس المعدني. وفضلت المحفزات المعدلة في الموقع إنتاج البروبيلين على عكس المحفزات المعدلة بعد التعديل التي تفضل الإثيلين. ويعزى تفضيل أوليفين من المحفزات إلى الاختلاف الحمضي. وأخيرا، كان التعديل اللاحق أكثر كفاءة لتعزيز المحفز سابو-34 لرد فعل مو بسبب زيادة نسبة التأسيس وتحسين الحموضة أفضل بالمقارنة بعد التعديل.

Chapter 1

Introduction

1.1 Background

Light olefins are considered as one of the most important and largest petrochemical products. It is feedstock of various industries such as polymers, olefins oxide, alcohols, organic acids and aromatics [1], [2]. Most of the light olefins production is consumed in polymerization. It is expected in the coming years that supply for light olefins will not be enough to satisfy the industrial demand. So , there is an essential need to develop innovative technologies that can meet the industrial olefins demand especially propylene and ethylene [3]. Normally, production of light olefins is driven by steam cracking and fluid catalytic cracking (FCC), Fisher Tropsch syngas conversion and biomass fermentation. Oil consumption for different domestic and industrial purposes is rising every day producing many liquids and airborne pollutants which are harmful to health and environment so there is a need for other alternatives which have better economic and environmental outcome such as coal and natural gas. Synthesis gas is used as a production source for methanol where natural gas, coal, and biomass waste are converted to gas which will produce methanol under higher pressure and temperature [3], [4]. Therefore, GTO process is considered as a two-step reaction which is more feasible than direct conversion of gas to olefins in terms of cost and energy [5].

1.2 Light olefins demand and supply

The daily growth of light olefins especially ethylene and propylene demand that is driven by industrial and domestic needs for products which intensify regularly with the population explosion of developing countries. This growth is caused mainly by polymers and their applications which needs to be satisfied by more production capacity of different processes. In contrast, the development and new inventions helped to maintain a sustainable supply of olefins for plastics production that is used for domestic purposes in housewares, food packaging, clothing, accessories, industrial and construction applications including automotive parts, surface coating, piping, and insulation. The polymers and olefin oxide industries consume almost 75-80% of the ethylene and propylene production and the remaining percentage was utilized for other chemicals production [6]. The Current ethylene and propylene supply are estimated to be 353 and 252 billion Lbs. respectively as shown in **Fig. 1**. Almost 90% of this supply was provided by conventional steam and catalytic cracking processes. As shown in **Fig. 2**, the demand for ethylene and propylene is estimated to be 320 and 215 billion Lbs. which indicate the flexibility of supply to provide sufficient feedstock for new processes. The demand for ethylene and propylene is estimated to drop by 5% in 2020 compared to the current situation based on several reasons such as economic slowdown and oil prices drop, the fewer petrochemical projects, the increased labor, construction, and transportation cost [6].

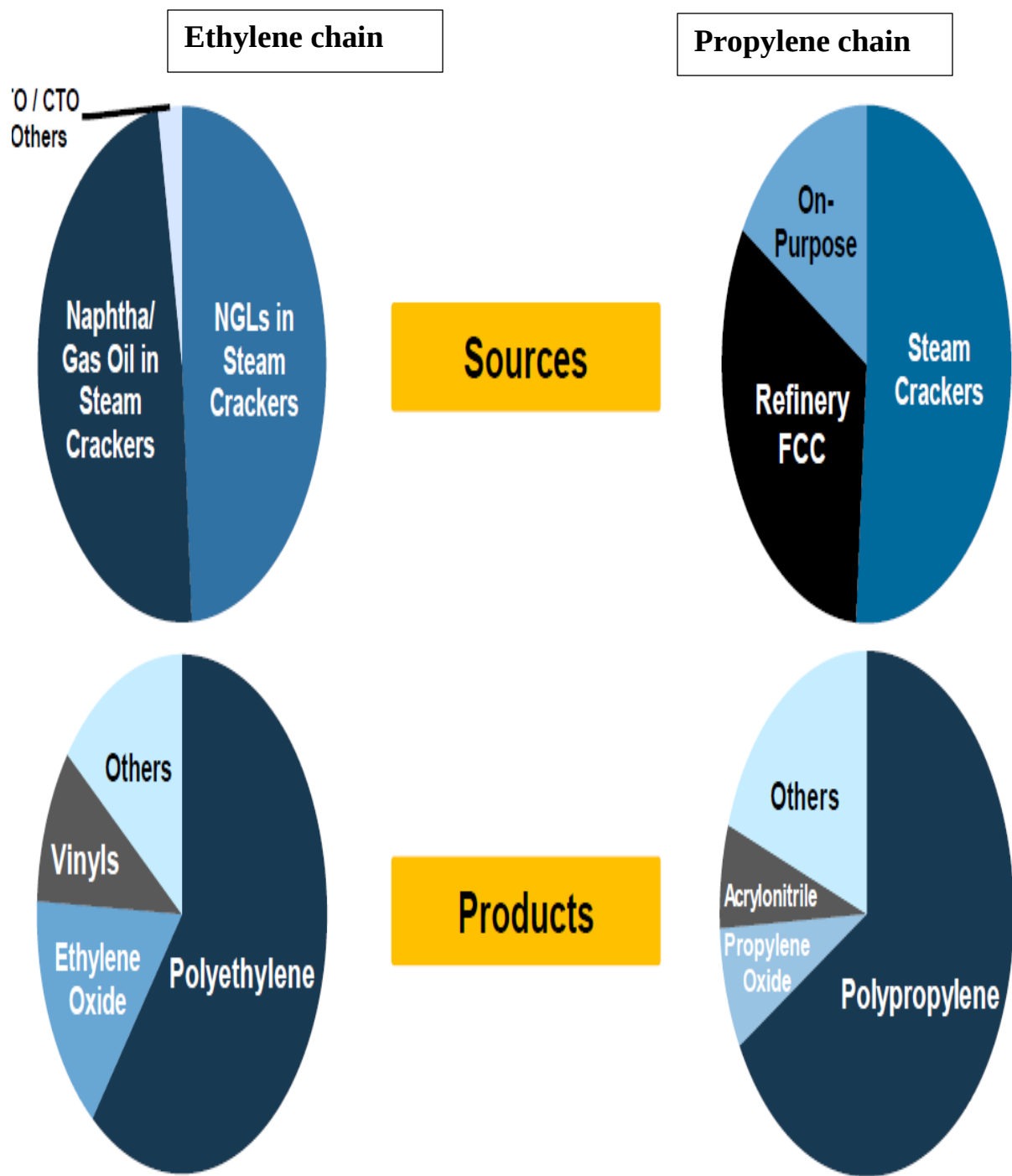


Fig. 1. Statistical presentation of ethylene and propylene in 2016. Adapted from [6]

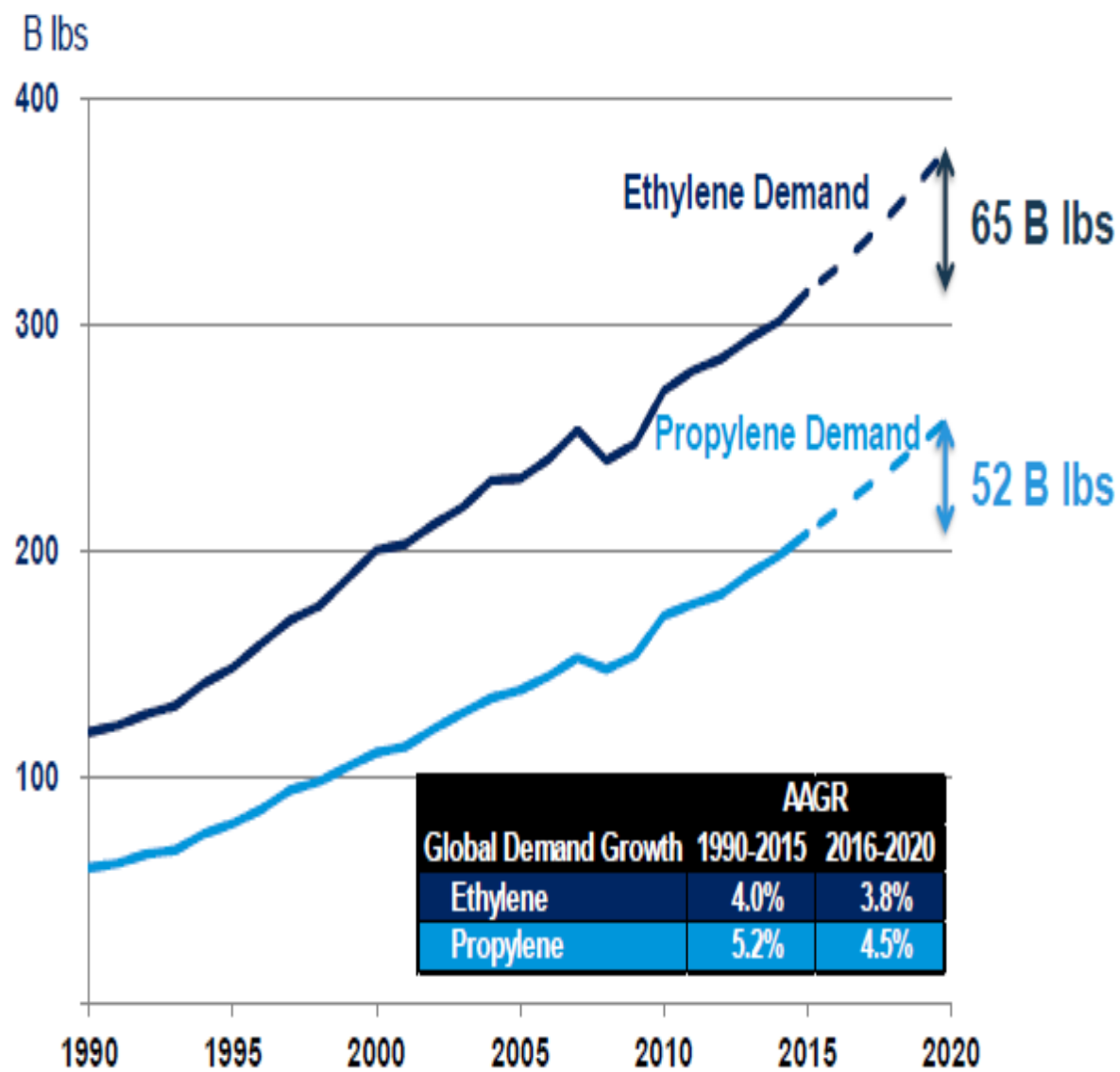


Fig. 2. Supply and demand growth with time. Adapted from [6]

1.3 Light Olefins Production sources

1.3.1 Steam cracking: most of the olefins produced by steam cracking of higher carbon chains compounds naphtha, AGO, natural gas and paraffin to light olefins using heat as shown in **Fig. 3**. Steam cracking is pyrolysis reaction consists of cracking C-C bonds and dehydrogenation of higher chain hydrocarbons to produce smaller olefins molecules. Steam cracking requires less reaction time compared with the other processes due to its high temperature [7].

1.3.2 Fluid catalytic cracking (FCC): normally the feedstock to the FCC unit is heavy and dense ingredients of crude oil including heavy vacuum gas oil (HVGO) or gas oil that has a normal boiling point higher than 340° C and 200-600 average molecular weight. When HVGO was fed to the reactor at moderate pressure and high temperature, subsequently direct contact was conducted between feed and catalyst in the riser where the cracking reaction of the molecular long chain of HVGO to shorter chain molecules such as paraffin, olefins, naphtha, and syngas. The spent catalyst is transferred to the regenerator and activated by hot air.

1.3.3 Fisher tropesch process: the process can be shortly described by conversion of syngas (CO and Hydrogen) into hydrocarbons such as paraffin and short chain olefins using metal precursors (mostly Co and Fe) as a catalyst for the reaction.

1.3.4 Biomass fermentation: utilization of domestic or industrial biomass waste to produce olefins is one of the alternatives for oil and gas oriented processes that have an environmental impact. The biomass is fermented in a batch reactor to bio alcohols which will be converted catalytically by MTO, dehydration, ODH, Metathesis, and steam cracking to produce C₂-C₄ light olefins as shown in **Fig. 4** [8].

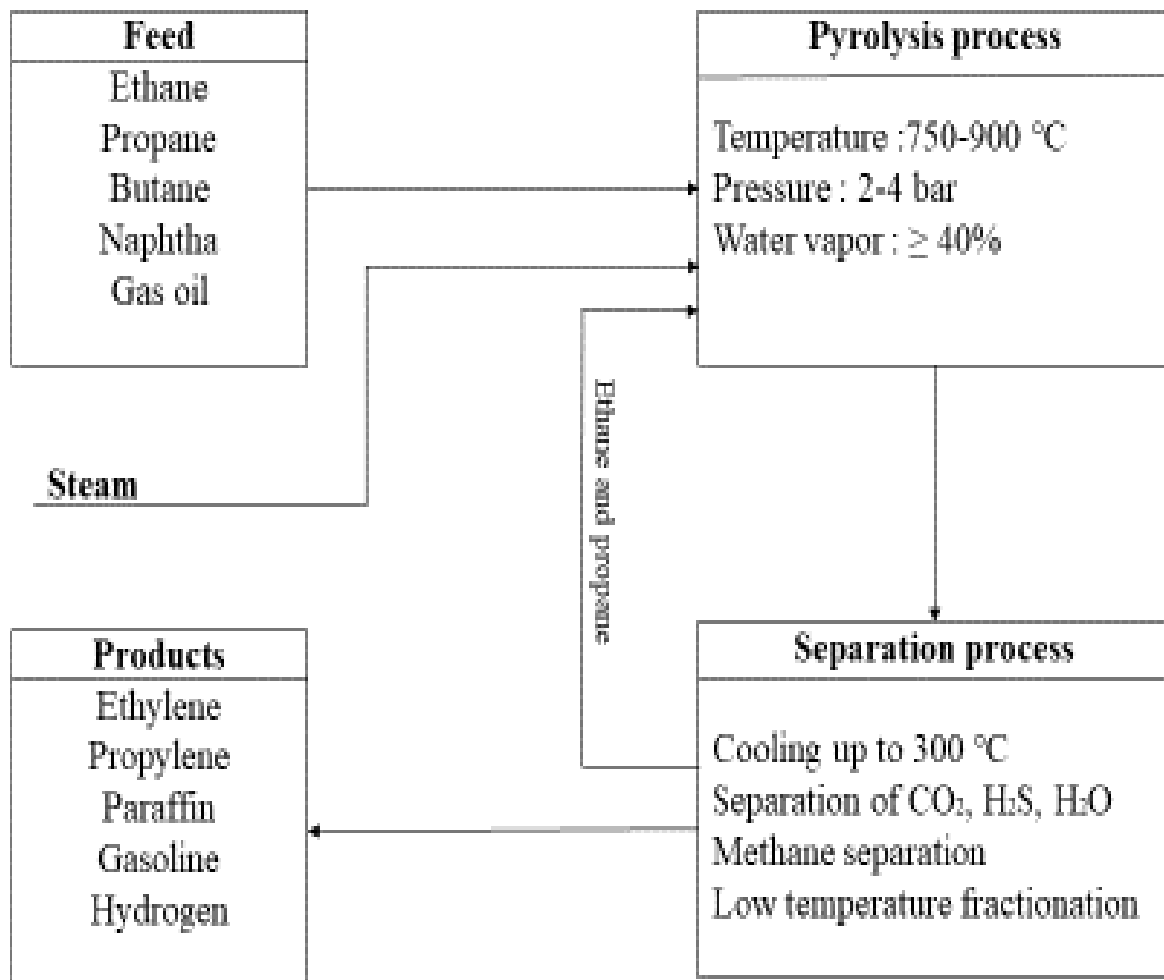


Fig. 3. Steam cracking process for olefins production. Adapted from [7]

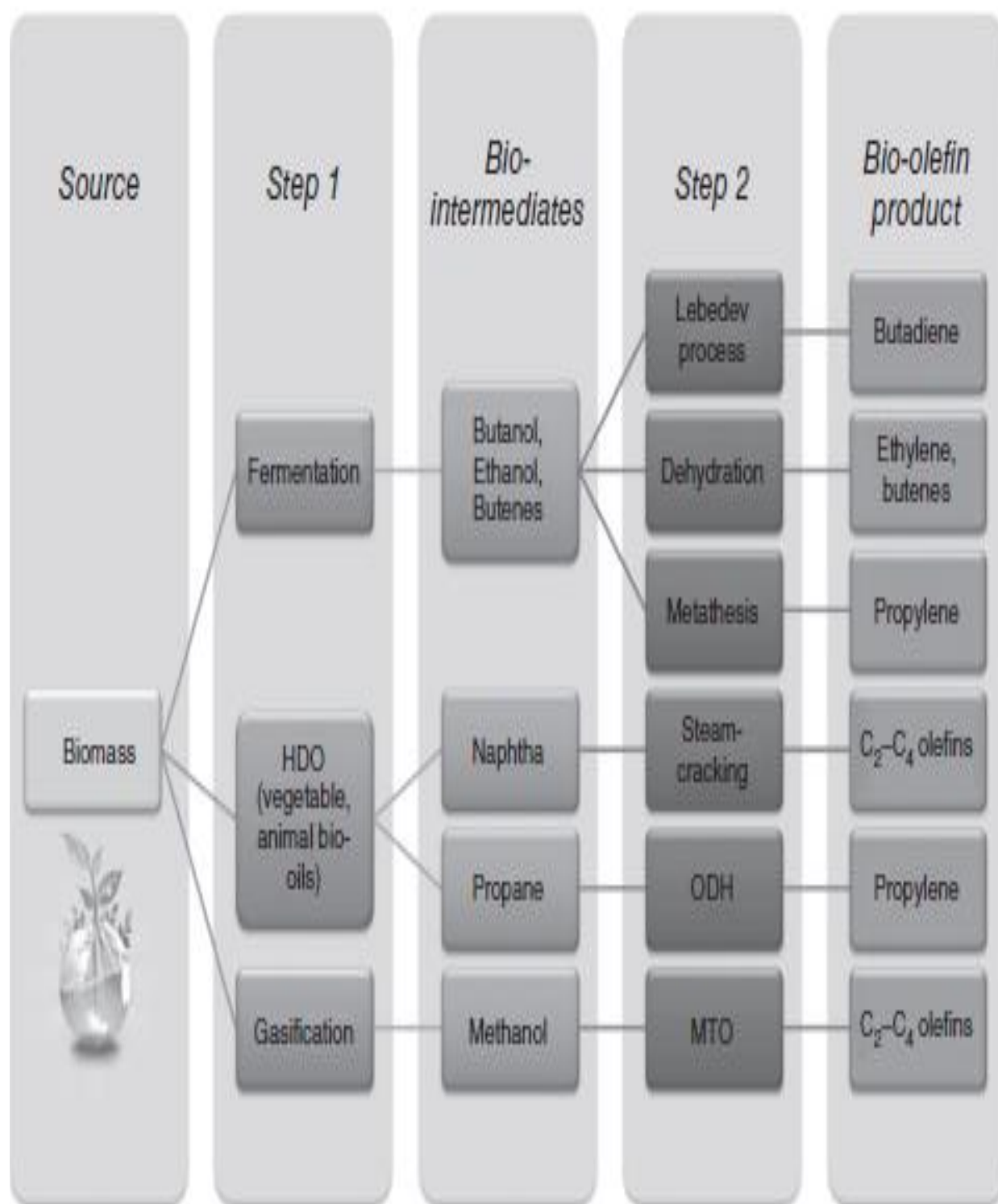


Fig. 4. Bio olefins production through biomass fermentation process. Adapted from [8]

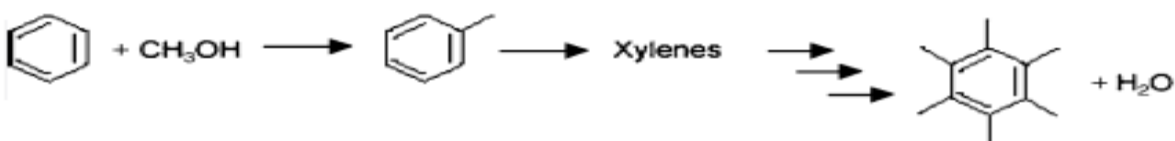
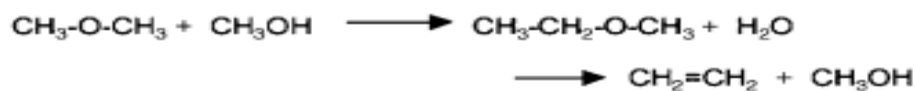
1.3.5 Methanol to olefins (MTO) process:

Methanol has been used as feedstock for MTO reaction to produce olefins by dehydration. Methanol is produced from synthesis gas including carbon monoxide and hydrogen which are generated from coal gasification, natural gas reforming, and biomass fermentation. Synthesis gas is converted to methanol in a fixed bed reactor at a high temperature and pressure. Methanol is suitable as a feedstock for olefins production because it is available to intermediate in different processes and it has limited uses. Also, it has lower economic value as compared with others such as naphtha, LNG, and gasoil [2]. Generally, MTO reaction is considered as a dehydration reaction that has been catalyzed mainly by medium (MFI) and small (CHA) pore zeolite. Firstly, methanol dehydrated to DME after which it will dehydrate to alkyls. Finally, the coupling and hydrogen transfer reactions will occur to produce olefins that can be side reacted to generate paraffin and aromatics which are undesirable industrially as compared to olefins.

1.4 MTO reactions

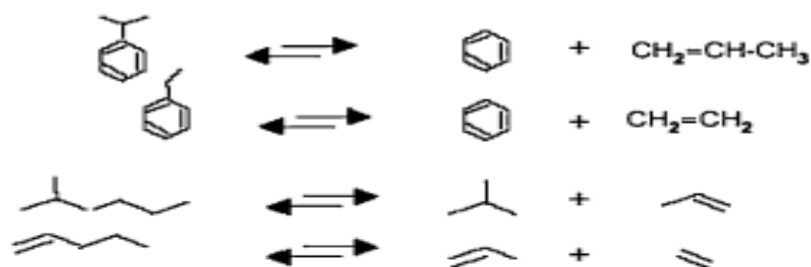
Actually, the olefins are produced by both methanol and hydrocarbon reactions. Initially, they were formed from methanol reactions. Then, the formed hydrocarbons act as reactants for further olefins production. The methanol reactions include methylation and dehydration where olefins and aromatics are formed by repeated methylation and dehydration as illustrated in **Fig. 5**. On the other hand, the hydrocarbons were converted to olefins, paraffin, and aromatics by alkylation/dealkylation, isomerization, cyclization and hybrid transfer reactions as illustrated in **Fig. 5**. The alkylation/dealkylation and isomerization are favorable reactions because of their promotional effect on olefin yield. While, the cyclization and hybrid transfer reactions are considered undesirable due to coke formation by heavy aromatics and consumption of olefins to produce paraffin and aromatics [9].

Methylation reactions

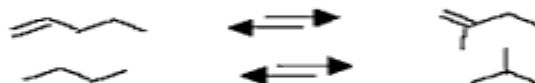


Hydrocarbon reactions

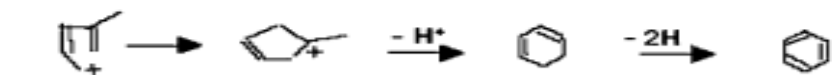
Alkylation/Dealkylation



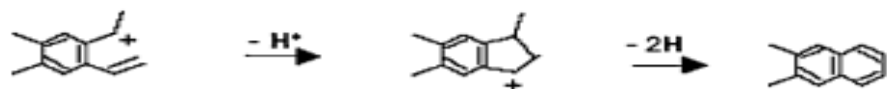
Isomerization



Cyclization
(Aromatization)



(at coking)



Hydride transfer



Fig. 5. MTO reactions to produce light olefins. Adapted from [9]

1.5 MTO process development

Earlier, several works focused on alcohol utilization to produce higher economic value products. In 1970, Exxon mobile succeeded to develop technology that can produce gasoline from methanol using a ZSM-5 catalyst which is considered at that time as a great breakthrough of the petrochemical industry, but the olefins content was very low which is considered as drawback need to be tackled by more research and innovation. Later during the 1980s, the researchers at Union Carbide Corporation (UCC) invented novel zeolite molecular sieves called silico alumino phosphate (SAPO). It was found that SAPO-34 which is a member of this novel SAPO family had excellent catalytic properties that made it suitable to convert methanol to light olefins. In 1988 UCC was merged by UOP Company and SAPO zeolite family development work was progressed and their catalytic activity was evaluated. At that time a Norwegian company called Norsk Hydro collaborating with Sintef Company began the development of their own MTO technology. The Norwegian large oil and gas wealth and energy sector regulations boost their work. They communicated with UOP to learn more about their technical experience and novel SAPO-34 catalyst. In 1992, they signed a partnership with UOP to have their joint UOP/Hydro MTO process [5]. This process had high ethylene rather than propylene compared to medium pore opening ZSM-5 because of the catalytic SAPO-34 structure which prevents higher and complex organic compounds that formed by ethylene and propylene oligomerization as presented in **Table 1**. The preferential production of light olefins was justified by their faster diffusion due to geometrical restrictions that keeps aromatics and large organic molecules inside pores [10].

Table 1. Comparison between most common zeolites used for MTO [11]

Characteristic	Small pore zeolite (SAPO-34)	Medium pore (ZSM-5)
Major Olefins yield	Ethylene and propylene	Propylene
By-products percentage	Low aromatics and C5+	high aromatics and C5+
Deactivation	Fast	Slow
Morphology and acidity	Small size and diameter particles with weak acid site	larger size and diameter particles with the strong acid site

1.6 Research objective

Nowadays MTO process attracts more attention as an alternative to the conventional cracking technologies which consumes a huge amount of energy, have relatively high capital and operating cost for the process complexity and pollute the environment. This preferential advantages of MTO compared to other processes requires more research work on reaction performance using different catalysts. Our selection of SAPO-34 was based on its excellent activity and selectivity towards light olefins. On the other hand, its major drawback of fast deactivation by coking. So, the SAPO-34 catalyst was modified to improve its catalytic performance in terms of catalytic stability and olefins yield. The following tasks will be applied to achieve the research objective:

1. In-situ incorporation of boron and metal.
2. Post modification by metal or acid.
3. Optimization of synthesis conditions.
4. Enhancement of acidity and textural properties.
5. Optimization of reaction conditions.

Chapter 2

Literature review

2.1 The Silico-alumino-phosphate (SAPO) zeolites

Methanol conversion using microporous catalysts is an attractive alternative to meet growing demand for olefins production for its availability as intermediate from different chemical processes [12], [13]. Microporous catalysts with different morphologies, pore structures, and acidities have been studied to be used in the MTO reaction [14], [15]. It has been found that Silico-alumino-phosphate (SAPO) zeolites and especially SAPO-34 molecular sieves exhibited a promising catalytic activity in a lot of studies mainly for their thermal stability, medium acidity and small pores that support olefins rather than aromatics production [16], [17]. On the other hand, it has catalytic stability issue where it deactivates rapidly as space velocity increased due to its high aluminum content and pore structure which prevent aromatics to escape and make them react with other species to form complex aromatic compounds that cause coking [18]. This major drawback of the SAPO-34 catalyst by several techniques including morphological, hierarchical, acidity enhancements. Moreover, the metal modification is used to enhance its stability including impregnation, ion exchange and in-situ incorporation [19]–[21].

2.2 The morphology modification and control of SAPO-34

Catalyst Morphology is an important characteristic that affects its catalytic performance. Normally, SAPO-34 particles have cubic shape but researchers succeeded to manipulate its morphology to produce spherical, plate, and sheet and elliptical particles. The purpose of the morphological modification is to get unique structures that maximize the surface area which eliminates the mass transfer resistance and makes acid sites exposed to methanol molecules. Morphology control by synthesis parameters such as Si/Al ratio, gel PH, template type and concentration, aging time and crystallization conditions have been investigated for MTO reaction as presented in below **Table 2**.

Table 2. Morphology control of SAPO-34 catalyst by synthesis parameters

Parameter	Morphology effect	Molar composition	ref
Silica source	Colloidal silica produced cubic while TEOS produced Nanoplates crystals	Colloidal Si:Si _{0.12} Al _{0.48} P _{0.4} O ₂	[6]
Crystallization time	Has no effect for Nanoplates and proportional effect for cubic SAPO-34 particle size	TEOS:Si _{0.11} Al _{0.48} P _{0.41} O ₂ 1 Al ₂ O ₃ : 2 P ₂ O ₅ : 0.6 SiO ₂ : 4 TEAOH	[7]
Si source dissolution	Alkaline precursor results in plate-like crystals rather than cubic ones for acidic precursor	Al ₂ O ₃ : P ₂ O ₅ : SiO ₂ : TEAOH 1:2:0.6:4	[7]
Gel solution PH	Amorphous phase was produced for PH below 6 and higher than 9. Highest crystallinity was achieved for PH of 6.8-7.8	1 Al ₂ O ₃ :1 P ₂ O ₅ :x SiO ₂ :2 R (TEAOH+Mor):60 H ₂ O	[8]
P₂O₅/Al₂O₃ ratio	P ₂ O ₅ /Al ₂ O ₃ ratio of 1.5 gave maximum Crystallinity and narrowest pores. Reversible Proportional effect on size.	1.0 Al ₂ O ₃ :1.25–2.5 P ₂ O ₅ :0.6 SiO ₂ :4.0 TEAOH:140 H ₂ O	[9]
microwave heating	Support plate-like SAPO-34 formation by shortening crystallization time	1 Al ₂ O ₃ : 1 P ₂ O ₅ : 0.6 SiO ₂ : 6 TEAOH:110 H ₂ O	[10]
Crystallization time and temperature	165 °C for 0.75 h: results in cubic sapo34. 220 °C for 2 h: results in plate-like sapo34.	1 Al ₂ O ₃ : 1.1 P ₂ O ₅ : 0.44 SiO ₂ : 1.65 TEAOH: 56.9 H ₂ O	[11]
Template concentration	SAPO-34 Crystal size and micro pore area is proportional to X	1 Al ₂ O ₃ : 1.1 P ₂ O ₅ : 0.44 SiO ₂ : 1.65 TEAOH: 56.9 H ₂ O 1 Al ₂ O ₃ :1 P ₂ O ₅ : 0.4 SiO ₂ : X Mor:(2-X) TEAOH:60 H ₂ O	[12]

2.3 The Synthesis parameters effect on catalytic performance

The synthesis parameters such as Si/Al ratio, gel PH, template type and concentration, aging time and crystallization conditions affect the physicochemical properties which have an impact on both stability and selectivity as illustrated in **Table 3**.

Table 3. Synthesis parameters effect on catalytic performance of SAPO-34

Parameter	Heating procedure and recipe	Effect on MTO reaction	Ref
Templates	Hydrothermal	-Cat = 0.49 g, WHSV= 1 h ⁻¹ , T = 450 °C.	[14]
Mixing	1Al ₂ O ₃ :1P ₂ O ₅ :0.6SiO ₂ :x morpholine:2-x TEAOH:52H ₂ O	-C ₂ selectivity is proportional to x and inversely for C ₃ . -Catalytic stability for 12 h and 90% C ₂ -C ₄ yield.	
Particle size	Hydrothermal 1 P ₂ O ₅ :1 Al ₂ O ₃ :0.1 SiO ₂ :0.4 TEAOH:15.7 H ₂ O (1µm) 1 P ₂ O ₅ :1.2 Al ₂ O ₃ :0.4 SiO ₂ :0.6 morpholine:38.5 H ₂ O (5µm)	350 °C, WHSV = 6.2 g/g h and P = 140 hPa -higher stability for smaller size SAPO-34. - C ₂ selectivity is proportional to size. - C ₃ selectivity is inversely proportional to size.	[15]
pH	Hydrothermal S1:1 Al ₂ O ₃ :0.8 P ₂ O ₅ :0.6 SiO ₂ :50 H ₂ O:3 TEA (10.3 S2:1 Al ₂ O ₃ :1 P ₂ O ₅ :0.6 SiO ₂ :30 H ₂ O:1 TEAOH (6.8 S3:1 Al ₂ O ₃ :1 P ₂ O ₅ :0.6 SiO ₂ :20 H ₂ O:2 DPR (7.3 S4:1 Al ₂ O ₃ :0.8 P ₂ O ₅ :0.6 SiO ₂ :50 H ₂ O:2 DEA(7	WHSV=14.22h ⁻¹ , T=723 K, cat weight=0.5 g. -S1 and S2 had the worst and best stability. -S2 and S4 had a conversion of 78 and 52% for 8h. -S2 had highest ethylene and propylene selectivity of 20.8 and 20.2% for 1 h.	[16]
Catalyst morphology	Microwave 1Al ₂ O ₃ ·2P ₂ O ₅ ·4TEAOH:0.6SiO ₂ ·140H ₂ O	WHSV = 2 h ⁻¹ , T = 673 K, cat = 100 mg. -Spherical SAPO-34 had the best stability. -Spherical SAPO-34 had the highest C ₂ selectivity of 42%. -Nanosheet SAPO-34 had the highest C ₃ selectivity of 38%.	[6]
Organic Amine type	Hydrothermal xR:1.2Al ₂ O ₃ :0.9P ₂ O ₅ :0.5SiO ₂ :14.6 H ₂ O	450 °C, WHSV =2 h ⁻¹ , 40 wt.% MeOH DIPA: high stability and selectivity TMEDA: medium stability and selectivity HMI: low stability and selectivity	[18]
Silica ratio	Hydrothermal 3TEA:1Al ₂ O ₃ :1P ₂ O ₅ :xSiO ₂ :50H ₂ O	30 wt.% MeOH and WHSV=1.2 h ⁻¹ at 450°C -Stability is inversely proportional to Si ratio. -Highest selectivity was for x =0.2.	[19]

2.4 The In-situ modification of SAPO-34 catalyst

In-situ modification of SAPO-34 can be performed either by metal or nonmetal precursor to enhance its physicochemical properties where they will be added to gel solution during synthesis like other components such Si, Al, P precursors and SDA and stirred to form a homogeneous solution. The catalytic performance was enhanced clearly by metallic in-situ incorporation due to acidity adjust as presented in **Table 4**. Cobalt, manganese, and nickel have been incorporated in the SAPO-34 framework by Dubois et al to investigate their effect on conversion, selectivity, and stability. Best catalytic stability was reported for Mn, while Co had highest light olefins selectivity [22]. Sedighi et al studied MeAPSO-34 [Fe, Ni, Co, La and Ce] molecular sieves for MTO. Better catalytic performance was reported for metal modified samples as compared to the parent. Ceria (Ce) had 7 h lifetime which is the best stability and 35.6 wt. % light olefins selectivity. While, iron (Fe) exhibited the lowest selectivity and lifetime among modified samples. Moreover, coke formation analysis was performed to compare the deactivation of MeAPSO-34 catalysts. The metal incorporation was confirmed by characterization techniques to ensure metal presence into the framework [23].

Kang et al have investigated the effect of [Ni, Co, and Fe] on catalytic performance of SAPO-34 molecular sieve for a range of temperature and time on stream. It is reported that catalytic stability and conversion were not improved by this modification. In contrast, the light olefins selectivity has increased almost by 10%. The highest selectivity of 93% was recorded for Co [24]. Co, Mn, and Fe were incorporated successfully into the SAPO-34 framework by Wei et al. Metal presence in the SAPO-34 framework was confirmed by different characterization techniques and they achieved a good activity of methanol conversion towards light olefins [25]. Another work made a comparison of incorporation of alkaline and transition metals into SAPO-34. They reported that

both conversion and selectivity have been enhanced by Ni and Mg presence. Also, coke formation was reduced due to its lower acidity which prolonged catalyst lifetime [26].

Zirconium has been incorporated inside SAPO-34 by Aghaei et al for MTO reaction. $\text{ZrO}_2/\text{Al}_2\text{O}_3$ ratio varied from 0.01 up to 0.15 to optimize synthesis conditions. Zirconium was reported to favor propylene formation over ethylene due to its acidity contribution. Zirconium enhanced selectivity towards light olefins and catalytic stability for ratio up to the 0.05. Further addition of zirconium has led to worse catalytic performance compared to parent SAPO-34 [27]. Another work studied GaAPSO-34 synthesis with different Ga/Al ratio. Gallium addition showed no modification either for conversion or selectivity. Ethylene production was reported to be favorable for GaAPSO-34 samples [28].

Zeolite acidity is an important factor in the catalytic performance of MTO reaction. It was reported that nonmetal incorporation such as boron enhances catalytic stability by increasing weak acid sites where it substitutes aluminum atoms into zeolite framework. Several works studied the effect of boron presence and ratio in zeolite frameworks such as for MTO reaction in terms of methanol conversion, selectivity and lifetime. B-CHA catalyst was developed by Q Zhu et al where boron was detected by FTIR and B-NMR techniques [29]. Catalytic stability was improved by boron addition compared to instant deactivated parent sample. Also, boron presence enhanced slightly conversion and light olefins selectivity. Moreover, boron exhibited better reaction modification compared to transition metals. Another work investigated In-situ incorporation of boron into the H-ZSM-5 framework. The boron effect on physicochemical and catalytic properties was studied. It was observed that ($\text{B}_2\text{O}_3/\text{SiO}_2=0.05$) tripled the catalyst lifetime and increased total olefins selectivity by 10%. This performance boost can be justified by acidity adjustment as proved by Py-FTIR and NH_3 -TPD characterizations [30].

H [B, Al] MFI catalyst was synthesized with different Si/B and Si/Al ratios and evaluated for MTO reaction. Chemical structure and boron presence were identified by NMR and FTIR characterization techniques[31]. The proportional relation was observed between boron ratio and propylene selectivity and lifetime due to acidity reduction as shown by NH_3 -TPD. Chen et al modified MCM-22 zeolite with boron for MTO reaction and B/Al ratio was varied from 0-30. The synthesized catalyst showed declining catalytic stability and light olefins selectivity as boron ratio increased due to weak and Bronsted acid sites reduction [32].

Vanadium was introduced to Boron-Beta zeolite by solid-state ion exchange. The acidity and thermal stability of synthesized samples compared before and after boron removal to understand boron effect on catalytic properties using different characterizations [33]. Qiu et al synthesized SAPO-5, BAPO-5, and LiAPO-5 catalysts and investigate the effect of substituting silica source by boron and lithium on physicochemical properties using XRD, FE-SEM, XPS, NMR, FTIR and Py-FTIR characterizations [34].

Table 4. Metallic in-situ modification of SAPO-34 catalyst

Catalyst	Catalyst performance for MTO	Ref
NiSAPO-34	0.5 g cat, 400 °C and 80% MeOH	[4]
CoSAPO-34	- Mn had the best stability for 30 h.	
MnSAPO-34	- highest ethylene selectivity was 45 for Co. - highest propylene selectivity was 39 for Co.	
FeAPSO-34	20 mol% MeOH, 425 °C, W/F=13g.h/mol.	[20]
NiAPSO-34	- Ce had the best stability for 17 h.	
CoAPSO-34	- Ni had best ethylene selectivity of 18.5.	
LaAPSO-34	- Ce had best propylene selectivity of 17.22.	
CeAPSO-34		
CoAPSO-34	425 °C, GHSV: 1000 h ⁻¹ MeOH 15 mol%	[21]
NiAPSO-34	- Co had the best stability for 5h.	
FeAPSO-34	- Ni had best ethylene selectivity of 80%. - Co had best propylene selectivity of 15%.	
NiAPSO-34	MeOH 15mol%, 400 °C and WHSV=8.7 h ⁻¹ .	[22]
MgAPSO-34	- Ni had 300 h stability. - Ethylene selectivity was 69 and 67 for Ni and Mg. - Propylene selectivity was 25 and 19 for Ni and Mg.	
ZrAPSO-34	GHSV=10.5 cm ³ /g. h, 400 °C, 30% MeOH, 0.4g cat. - Highest stability and ethylene selectivity was recorded for Zr/Si=0.05. - Above x=0.05, selectivity declined.	[23]
GaAPSO-34	GHSV of 500 h ⁻¹ and 425°C. - Pure and Al/Ga=20 SAPO-34 had 92 and 88 conversion and C ₂ -C ₄ selectivity of 70 and 40.	[24]

2.5 The post-modification of SAPO-34 catalyst

Parent SAPO-34 can be promoted catalytically by post modification either by metal or chemical treatment. The Metallic post-treatment includes impregnation and liquid and solid-state ion exchange as summarized in **Table 5**. The metal incorporation was achieved by adding the parent zeolite to the aq. solution of metal precursor under stirring and heating. The SAPO-34 catalyst was impregnated by K, Cs, Ag, Mo, and Ce metals to reduce methane formation of MTO reaction

which is related to deactivation [21]. It was observed that K, Cs, and Ag enhanced the conversion and C₂-C₄selectivity and prolonged catalyst lifetime. The Other metals showed no catalytic improvement compared to parent SAPO-34.

Tian et al developed a modified SAPO-34 catalyst for MTO reaction using impregnation and liquid phase ion exchange techniques. The Ceria was incorporated equally for both impregnated and ion-exchanged SAPO-34 catalysts. The impregnated Ce-SAPO-34 exhibited better catalytic performance in terms of selectivity and stability compared to the ion-exchanged catalyst. No obvious enhancement was observed for ion exchange technique which indicates the resistance of Ce incorporation into structure [35]. The characterization results of XRD, XRF, FTIR, N₂-BET, and NH₃-TPD supported the excellent reaction results of the impregnated Ce-SAPO-34 catalyst.

Yttrium and lanthanum were incorporated to SAPO-34 by Lu et al group using liquid and solid-state ion exchange. The characterization results proofed the successful incorporation of Y⁺³ and La⁺³ ions. The solid-state ion-exchanged catalysts had the highest conversion and light olefins selectivity. Also, the catalyst deactivation was minimized by the solid-state ion exchange. The Y-IE-SAPO-34 was better than La-IE-SAPO-34 in terms of selectivity and stability which showed no obvious improvement [36]. Gao et al synthesized liquid exchanged Cu-SAPO-34 catalyst using Morpholine and TEA as SDAs for NO_x reduction application. The ICP, NMR and EPR characterizations were utilized to confirm the copper presence in the SAPO-34 structure backbone [37].

Table 5. The metallic post modification of SAPO-34 catalyst

Catalyst	Catalyst performance for MTO	Ref
K/SAPO-34	0.5 g cat, 500 °C , WHSV=2 h ⁻¹ and TOS=4 h	[21]
Cs/SAPO-34	- Impregnation with K, Cs, and Ag had the best stability for 5 h	
Ag/SAPO-34	- Cs/SAPO-3 had the highest C ₂ -C ₄ yield of 85%	
Mo/SAPO-34 Ce/SAPO-34		
L-IE-CeSAPO-34	1 g cat, 400 °C, and WHSV=2.5 h ⁻¹	[35]
Ce/SAPO-34	- Ce/SAPO-34 had the best stability for 2 h - Ce/SAPO-34 had best the highest C ₂ -C ₄ selectivity of 85%	
L-IE-YSAPO-34	0.2 g cat,450 °C ,WHSV=2.1 h ⁻¹	[36]
L-IE-LaSAPO-34	- Solid state ion exchange had better stability and yield	
S-IE-YSAPO-34	- S-IE-YSAPO-34 had the best stability of 3 h	
S-IE-LaSAPO-34	- S-IE-YSAPO-34 had the highest C ₂ -C ₄ yield of 85%	

The SAPO-34 zeolite can be chemically post-treated by either acid to delaminate or alkali to desilicate for modification of its physicochemical properties for certain reaction. The MTO reaction requires medium acidity. But, the SAPO-34 is high acidity zeolite so there is need to remove some of its aluminum content by acid leaching. The SAPO-34 structure is mainly built of aluminum atoms so the delamination process must be limited. Otherwise, the whole framework will collapse by excessive aluminum removal. Based on this limitation, few works reported SAPO-34 dealumination and none of them were carried out in mild condition using weak or low concentration acids. Qiao et al post treated the SAPO-34 catalyst by acid and alkali etching to tune its acidity and textural properties to match different reaction requirements. HCl and TEAOH were selected to be the etching precursors. The chemical treatment produced hollow interior crystals for both cases [38]. The external surface of crystals was Si-O-Si and Si-O-Al rich for acid and alkaline

treatments respectively. The XRF, N₂-BET, and Si-NMR characterizations were used to identify chemical and pore structure change.

The catalytic performance of SAPO-34 for MTO reaction was improved by oxalic acid dealumination. The crystallinity was dropped after acid treatment as detected by XRD and SEM. The XRF, Si NMR and NH₃-TPD results revealed the slight reduction of external surface acidity. The acid concentration was varied up to 0.4 M to identify the relation of concentration and catalytic performance. The catalyst lifetime and ethylene selectivity were increased at 450 °C and WHSV=2 h⁻¹ by dealumination [39]. Fjermestad et al developed DFT model to simulate the hydrolysis of the SAPO-34 bonds by alkali desilication. The potential energy profile of desilicated SAPO-34 was plotted to understand the mechanism of bonds hydrolysis.

2.6 The hierarchal modification of SAPO-34 catalyst

The purpose of the hierarchal modification is to facilitate the diffusion by porosity tuning of the catalyst. This modification is achieved by adding specific materials during synthesis to inhibit crystallization or adding transport pores. The modified catalyst will have higher surface area and mesopore volume which shorten the diffusion bath of reactant molecules and increase the exposed area for reaction. The SAPO-34 catalyst is one of the small pore zeolites which promotes the coke formation so the hierarchal modification can help to solve this issue.

Schmidt et al developed high surface area SAPO-34 catalyst for MTO reaction by the introduction of carbon transport pores to its structure. The carbon nanoparticles and nanotubes were added in-situ to the gel solution with a similar ratio. The SAPO-34 catalyst modified with carbon nanotubes exhibited the best catalytic performance in terms of lifetime and selectivity for TOS=5 h at 400 °C. This remarkable result was justified by the better pore accessibility as proofed by SEM and N₂-BET compared to the catalyst modified by carbon nanoparticles [40]. The DPHAB surfactant was used to modify the textural properties of the SAPO-34 catalyst by particle size reduction. The XRD, SEM, and N₂-BET revealed that the surface area, mesopore volume, and crystallinity were enhanced by increasing the surfactant ratio [41]. As a result of this, the catalytic stability and C₂-C₄ selectivity were improved. Gong et al used rapeseed pollen extract as synthesis media for a hierarchical modified SAPO-34 catalyst for MTO reaction. First, 10 wt. % rapeseed pollen extract was prepared by grain dissolving in DI water under stirring and hydrothermally treated at 180 °C for 5 days. Then, the catalyst was prepared by crystallization of gel solution prepared by dissolving different precursors in rapeseed pollen extract followed by crystallization using the hydrothermal method. This modification increased the surface area and pore volume of SAPO-34 catalyst [42].

2.7 Operation parameters effect

Operating conditions, feed properties, and reactor design are critical parameters for efficient conversion of methanol to higher value products. There have been many molecular sieve catalysts examined for the MTO process. However, SAPO-34 was believed to be the best catalyst in terms of activity and selectivity to light olefins. So, research efforts were focused to study the products and stability fluctuation with the reaction conditions over the SAPO-34 catalyst.

Reaction conditions such as temperature, pressure, catalyst loading, space velocity and feed dilution have been studied for their impact on methanol conversion to olefins and catalyst deactivation as summarized in **Table 6** [43], [44]. Co-feeding of aromatics and olefins has a promotional effect on conversion and olefins selectivity as presented in **Table 7**. This enhancement was attributed to its support for reaction aromatic cycle which enhances methylation and dealkylation reactions [45].

Table 6. The effect of operation conditions on MTO reaction

Parameter	Catalyst and conditions	MeOH conversion and C ₂ -C ₄ selectivity	ref
Temperature	SAPO-34 W/F=10 g*h/mol P=1 bar	Highest and lowest conversion of 100% and 36% were recorded at 500 and 300 °C. Maximum C ₂ +C ₃ selectivity of 5.2% was recorded for 300 °C and decreasing as temperature raised.	[43]
WSHV	SAPO-34 T=400 °C TOS=2.66 h ⁻¹ P=1 bar	-100% conversion until reaching 0.33 h ⁻¹ then conversion declined to 66% for 0.5 h ⁻¹ . C ₂ -C ₄ , selectivity was increased for 0-0.083 h ⁻¹ reaching 88% then slightly declined to 82% at 0.5 h ⁻¹ .	[44]
Methanol dilution	SAPO-34 T=400 °C W/F=10 g*h/mol P=1 bar	-conversion stability and coking rate enhanced as methanol diluted by water reaching maximum stability at 20% mole and further dilution leading to opposite effect.	[44]

Table 7. The Co feeding effect on MTO reaction

Parameter	Catalyst and conditions	MeOH conversion and C2+=C3=selectivity	Ref
Aromatics Co feeding	ZSM-5 W/F=0.1 kg*min/mol T=450 °C P=1 bar	-4% Co-feeding of benzene, P-xylene, and toluene had a conversion of 96, 98 and 100 respectively compared to 90% for pure feed. -4% Co-feeding of benzene, P-xylene, and toluene had a selectivity of 40, 48 and 46 respectively compared to 30% for pure feed.	[45]
Olefins Co feeding	ZSM-5 W/F=.01kg*min/mol T=450 °C P=1 bar	-20% Co feeding of C ₃ , C ₄ , C ₅ , and C ₆ increased conversion by 1.9,4.1,1.5 and 13.9 respectively. -highest ethylene and propylene selectivity were recorded for C ₆ and C ₃ addition.	[45]

2.8 The MTO reaction mechanism

There are different MTO reaction mechanisms over SAPO-34 proposed by researchers. The reaction mechanism developed with time where at the beginning they were simplified with assumptions until the development of characterization instruments to become more complicated. Previously, there was a general agreement that olefins were produced by coupling buildup and dehydrogenation reactions. But, this mechanism was not reasonable due to lack of experimental evidence and high activation energy [46]. Song et al investigated the effect of feed purity on MTO reaction rate. It was observed that the reaction rate is mainly affected by organic impurities. So, the MTO reaction is believed to proceed through an indirect mechanism, wherein hydrocarbon species act as reaction centers for product formation [47]. Those reaction centers may be olefins, aromatics, or both alkenes and aromatics simultaneously.

2.8.1 Olefins based mechanism

Dessau and co-workers proposed the olefin methylation/cracking mechanism for the MTO reaction in 1982 as illustrated in **Fig. 6**. According to Dessau's proposal, methanol is converted initially to light olefins by coupling reaction. Then, these light olefins undergo repeated methylation to

form higher alkenes which in turn converted to either aromatics by further methylation or light olefins by cracking [48], [49].

2.8.2 Aromatic based mechanism

Dahl et al suggested reaction mechanism called hydrocarbon pool where methanol will convert to n -CH₂- molecules that will convert in parallel to olefins, paraffin, and aromatics. This mechanism was developed based on the organic reaction center concept. N-methyl-benzene molecules generated inside the SAPO-34 pores by both reaction and feed impurity or coking. The reaction starts when trapped N-methyl-benzene inside SAPO-34 pores undergoes methylation followed by dehydrogenation and cracking reactions so the more methyl substitution results in higher light olefins yield [50].

2.8.3 Dual cycle mechanism

Another mechanism was proposed by Olsbye et al that suggests two parallel cycles for methanol conversion to olefins as shown in **Fig. 7**. The first cycle is olefin-based where methylation occurred followed by cracking reaction of higher olefins to lighter olefins. While the second one called aromatic based cycle where methylation occurred to form alkylbenzene compounds followed by dealkylation reaction. This dual cycle mechanism had strong consensus among scientists and researchers in MTO reaction field [51], [52].

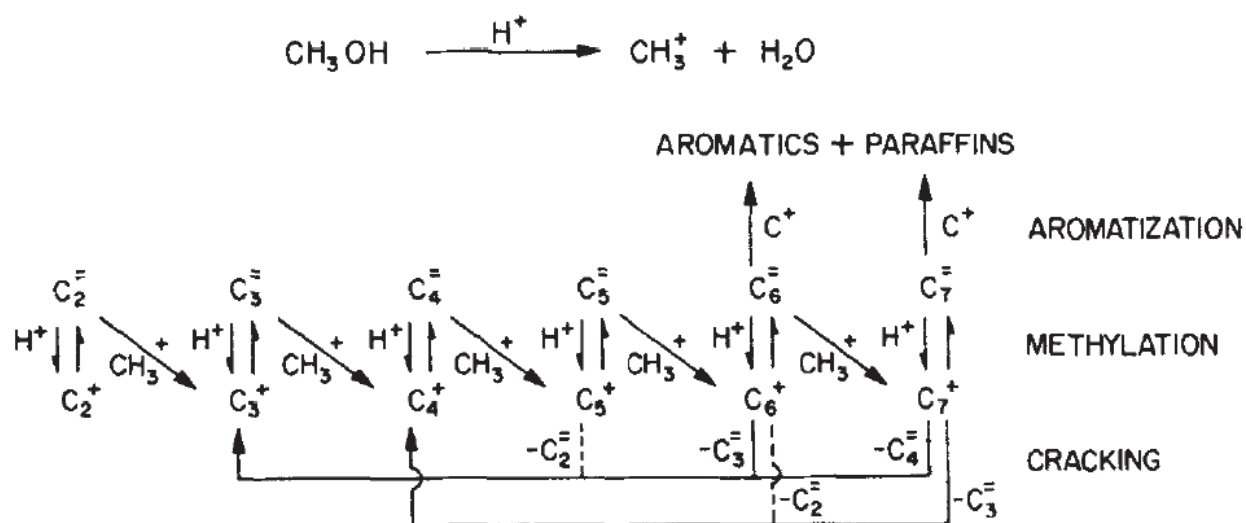


Fig. 6. The olefin based mechanism of MTO reaction. Adapted from [48]

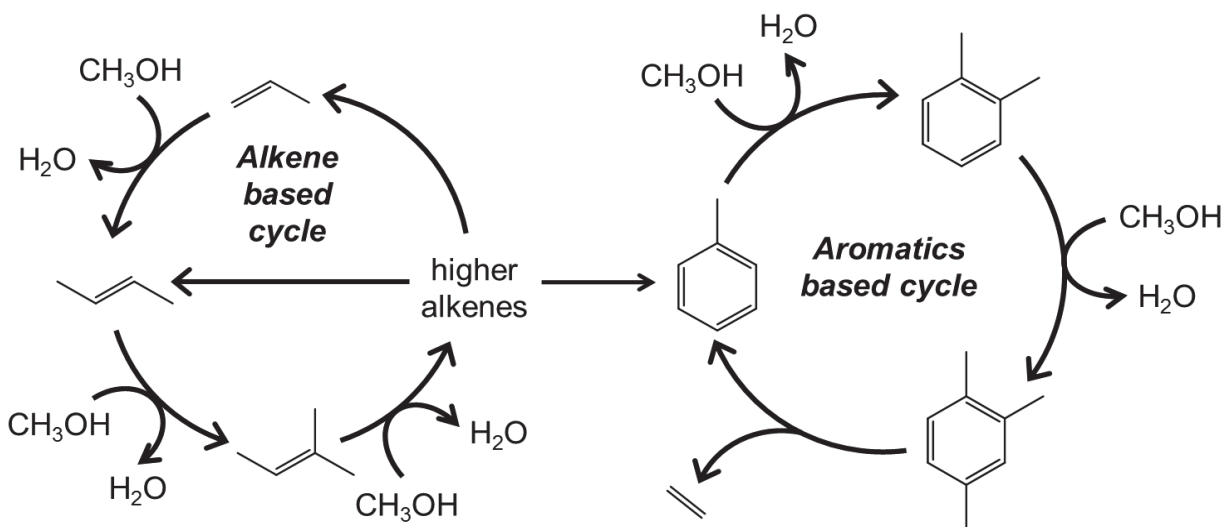


Fig. 7. The dual cycle mechanism of MTO reaction. Adapted from [51]

2.9 Diffusion, adsorption and desorption effect on MTO reaction

Generally, the methanol converted to olefins through adsorption, diffusion and reaction and desorption. Those steps of MTO reaction considered as resistances for methanol conversion to olefins. So, they had been studied to establish their effect on performance and develop model that simulate MTO reaction.

2.9.1 Coke formation effect

The effects of adsorption and diffusion of the reactants on methanol to olefins (MTO) and propene conversion over SAPO-34 have been studied by Chen et al [53]. The SAPO-34 was subjected to methanol and propene adsorption to establish its effect on MTO reaction. The adsorption data were plotted and fitted with Langmuir isotherm using **equation 2.1**. The adsorbed methanol was higher than propene at certain pressure. Also, the methanol adsorption affected more than propene adsorption by coke formation which indicates the secondary role of olefins reactions as compared to methanol reactions. The effect of coke formation was monitored for diffusion and reaction step where diffusivity of methanol and propene were calculated from **equations 2.2 and 2.3**. Then, it was substituted in **equation 2.4** of Weisz-Prater criterion to identify the reaction rate ($(r_A)_{obs}$). Also, Weisz number (W) was calculated using **equation 2.5** to identify the limiting the step of reaction. The methanol had higher Weisz number which indicates the significance of diffusion for methanol reactions as compared to secondary reactions of olefins. The coke formation affected the conversion more than adsorption which reflects the strong relation of conversion and diffusion. Moreover, the desorption rate of products maintained for period after the coke formation. This finding means that desorption is less sensitive to coke formation unlike adsorption. Finally, the rate limiting step for MTO reaction considering coke presence was found to be diffusion and reaction.

Chen et al developed a percolation model based on a realistic pore network, which also takes the site coverage effect into account, for describing the diffusion and deactivation due to coke deposition during the MTO reaction over SAPO-34 [54].

$$\frac{1}{q} = \frac{1}{q_s} + \frac{1}{b} \frac{1}{q_s} * \frac{1}{p} \quad 2.1$$

$$\frac{mt}{me} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \exp\left[-\frac{\pi^2 * t * D_c (2n+1)^2}{4L^2}\right] \quad 2.2$$

$$D_{ss} = \frac{D_c * C_{\infty}}{C_0} \quad 2.3$$

$$W = \eta * \phi^2 = \frac{(r_A)_{obs} * \rho_s * L^2}{D_{eA} * C_s} \quad 2.4$$

$$W = \frac{t_D}{t_R} = \frac{L^2}{k * D_{eA}} \quad 2.5$$

Chen et al developed a percolation model based on a realistic pore network, which also takes the site coverage effect into account, for describing the diffusion and deactivation due to coke deposition during the MTO reaction over SAPO-34 [54]. The material balance of each site was presented in equation 2.6. The diffusion length (Δ) was estimated using equation 2.7 based on the occupied volume fraction by deposited coke (q). It was observed that the occupied volume fraction is inversely proportional to the accessible sites fraction and diffusivity. This effect was reflected the reaction rate which declined rapidly as the occupied volume increased due to resistance for diffusion and reaction on active sites by deposited coke.

$$\frac{1}{\Delta^2} \left[\sum D(C_{nearest} - C_{i,j}) \right] - kC_{i,j} = 0 \quad 2.6$$

$$\Delta = \frac{q * L}{N} \quad 2.7$$

$$q = \frac{Coke}{V_p \rho_s (1 + X_{block})} = 1 - X_{block} - X_{access} \quad 2.8$$

2.9.2 Particle size and volume fraction Effect

Keil et al developed model based on Monte Carlo and Molecular dynamics calculations to estimate the diffusivity of each component [55]. Then, Spherical shell of catalyst pellet was considered and overall material balance and Taylor expansion were performed using equations 2.9 and 2.10 to estimate the overall effective diffusivity. Finally, the effectiveness was calculated as function of diffusivity using equations 2.11 and 2.12. Monte Carlo and Molecular dynamics calculations helped to plot diffusivity as function of concentration and temperature. Also, the model estimated the concentration of different components. The effectiveness of the catalyst was inversely proportional related to particle size and volume fraction due to lower mass transfer resistance and higher diffusivity.

$$j_t = (1 - \zeta) * j_m + \zeta * j_a \quad 2.9$$

$$R_t = (1 - \zeta) * R_m + \zeta * R_a \quad 2.10$$

$$\varphi^a = \frac{3}{\phi_a} \left[\frac{1}{\tanh(\phi_a)} - \frac{1}{\phi_a} \right] \quad 2.11$$

$$\phi_a = r_0 \sqrt{\frac{k_a}{D^a}} \quad 2.12$$

2.9.3 Fluidization effect

Chang et al developed computational study for MTO reaction in fluidized bed using CFD and kinetic modelling [56]. The momentum, mass and heat transfer equations were used accompanied with kinetic model parameters adapted from (Chen et al., 2000, 2007; Zhuang et al., 2012). The model results revealed the non-uniformity of velocity profile, volume fraction and concentration

in the axial and radial directions of bed which resulted in the fluctuation of conversion and yield especially in the bottom of the bed. The conversion and light olefins yield were enhanced by increasing the pressure, temperature, methanol concentration and circulation speed of catalyst. The opposite effect was observed for the superficial gas velocity and coke amount.

2.10 Kinetic modeling of MTO reaction

2.10.1 Kinetic model based on coke formation

Yuan et al conducted a comparative study on MTO kinetics in fixed and fluidized bed reactors. The model was developed Based on experimental data and simulating the both reactor configurations [57]. The coke formation was found responsible for the variation of product selectivity for both configurations. The distribution of the coke deposition was independent of catalyst position and bed height and changed with TOS for the fluidized bed reactor. On the other hand, the coke deposition shows a distribution along the bed height in a fixed bed reactor. The fixed bed and fluidized bed reactors were considered as ideal mixed (FBR) and plug flow reactors (PBR), respectively. A relation between fixed bed and fluidized bed reactors was established through coke deposition using the proposed model. As illustrated by both experimental data and model, the water content had positive effect on stability. While, the light olefins yield and coke amount were decreased with dilution. Moreover, the stability and yield were declined with increasing WHSV and oppositely for coke formation. The reactor divided to three zones as shown in Figure 2.6, the first one called deactivation zone where most of methanol converted to methane rather than olefins. The second zone called methanol conversion where the olefins produced in this section. The last zone is product section where the olefins by-reacted to produce aromatics and paraffin. The catalyst position in the bed is a parameter that affects the performance of PBR. The stability and yield enhanced by placing the catalyst away from the top section. The kinetic model

predicted the performance of MTO reaction over SAPO-34 catalyst in fluidized bed reactor with experimental data obtained in fixed bed reactor, or verse vice.

Reactor model

$$\text{For FBD} \quad \frac{d\rho_j}{dt} = k_f(\rho_j^{in} - \rho_j) + R_j \quad 2.13$$

$$\text{For PBD} \quad \frac{d\rho_{i,j}}{dt} = k_f(\rho_{i-1,j} - \rho_{i,j}) + R_{i,j} \quad 2.14$$

Kinetic model

$$\text{Coking model} \quad \frac{dC_c}{dt} = k * \rho_{in}^m * WHSV * \alpha * (C_c^{max} - C_c) \quad 2.15$$

Reaction rates

$$R_{MeOH} = -\frac{W_{cat}}{V_g} * [k_{s,1}(C_c^{max} - C_c) + k_{c,1}C_c] * \rho_{MeOH} * \emptyset \quad 2.16$$

$$R_{C_2=} = -\frac{W_{cat}}{V_g} * \{ [k_{s,2}(C_c^{max} - C_c) + k_{c,2}C_c] \rho_{MeOH} \emptyset + k_{c,5}C_c \rho_{C_4} \emptyset - k_{s,5}(C_c^{max} - C_c) \rho_{C_2=} \emptyset \} \quad 2.17$$

$$R_{C_3=} = \frac{W_{cat}}{V_g} * [k_{s,3}(C_c^{max} - C_c) + k_{c,3}C_c] * \rho_{MeOH} * \emptyset \quad 2.18$$

$$R_{C_4=} = \frac{W_{cat}}{V_g} * \{ [k_{s,4}(C_c^{max} - C_c) + k_{c,4}C_c] \rho_{MeOH} \emptyset - k_{c,5}C_c \rho_{C_4} \emptyset - k_{s,5}(C_c^{max} - C_c) \rho_{C_2=} \emptyset \} \quad 2.19$$

$$\emptyset = \frac{\exp(-k_d \frac{C_c^{max} - C_c^{cri}}{C_c^{max} - C_c})^p}{\exp(-k_d \frac{C_c^{max} - C_c^{cri}}{C_c^{max}})^p} \quad 2.20$$

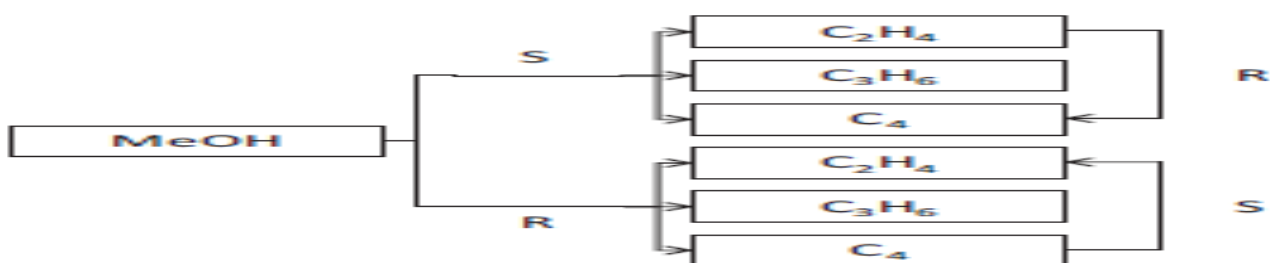


Fig. 8. MTO Reactions network where S and R represent the olefin and aromatics based cycles

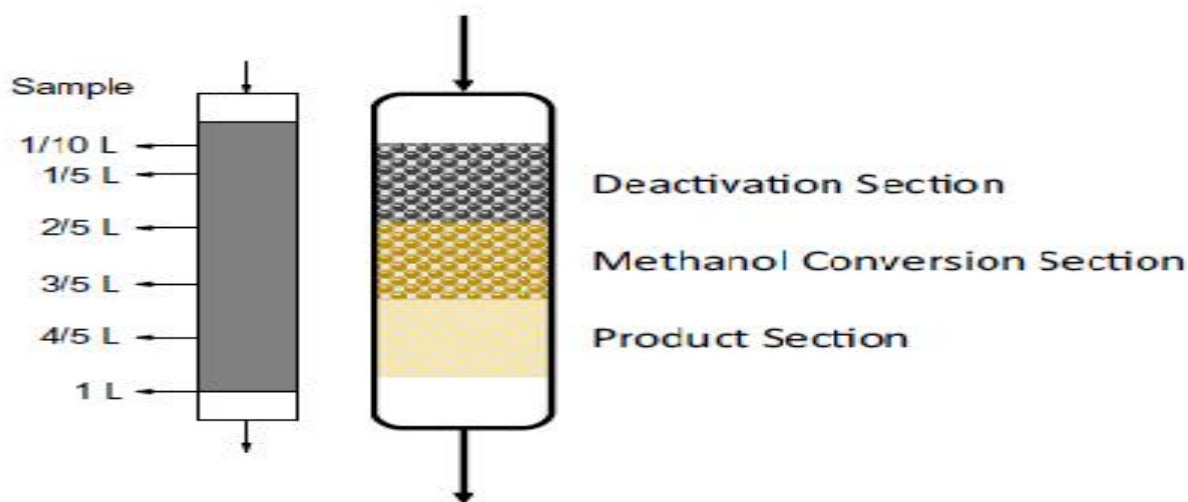


Fig. 9. MTO reactor divisions

2.10.2 Seven lumped kinetic model

Ying et al developed a lumped kinetic model for the MTO process over a commercial SAPO-34 catalyst [58]. The kinetic model takes into account seven lumps, i.e. methane, ethylene, propylene, propane, C_4 , C_5+ and coke. Also, the model simulates the deactivation to evaluate the changes of product selectivity and activity during reaction. The kinetic model was developed with varying the temperature, feed content and WHSV for the fluidized bed reactor as compared to experimental data from fixed bed reactor. The kinetic parameters were calculated using a nonlinear least square method and the axial coke distribution was considered. The stability improved after dilution as indicated by the delay of methanol breakthrough as shown in figure 2.8. While, increasing of

WHSV had opposite effect on stability. Also, it was found that neither stability nor light olefins were affected by temperature. The variation range of temperature, feed content and WHSV was small which resulted in the light olefins yield did not change.

Reactor model

$$\text{For FBD} \quad \frac{dX}{dW/F_{MeOH}} = k_t(1 - X)^n \quad 2.21$$

Kinetic model

Reaction rates

$$R_{CH_4} = k_1 * \theta_W * C_{MeOH} * Mw_{CH_4} \quad 2.21$$

$$R_{C_2H_4} = 1/2 * k_2 * \theta_W * C_{MeOH} * Mw_{C_2H_4} \quad 2.22$$

$$R_{C_3H_6} = 1/3 * k_3 * \theta_W * C_{MeOH} * Mw_{C_3H_6} \quad 2.23$$

$$R_{C_3H_8} = 1/3 * k_4 * \theta_W * C_{MeOH} * Mw_{C_3H_8} \quad 2.24$$

$$R_{C_4} = 1/4 * k_5 * \theta_W * C_{MeOH} * Mw_{C_4} \quad 2.25$$

$$R_{C_5^+} = 1/5 * k_6 * \theta_W * C_{MeOH} * Mw_{C_5^+} \quad 2.26$$

$$\text{Coking model} \quad R_i = v_i * k_i * \theta_W * C_{MeOH} * \varphi_i * Mw_i, \quad i = 1 - 7 \quad 2.27$$

$$\varphi = \frac{A + 1}{A + \exp(BC_c)} \quad 2.28$$

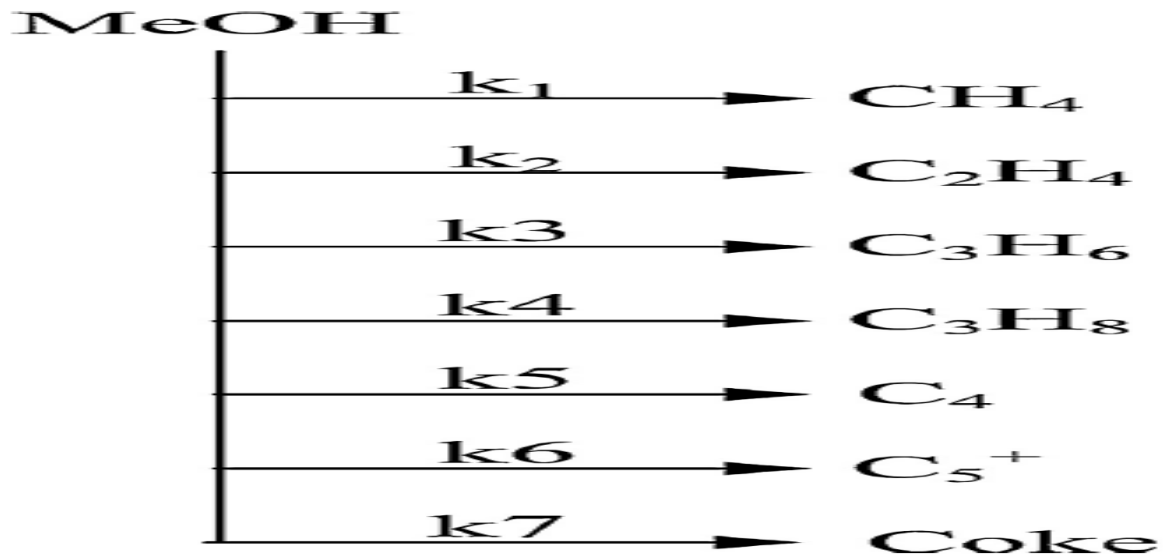


Fig. 10. Reaction network for seven-lumped model

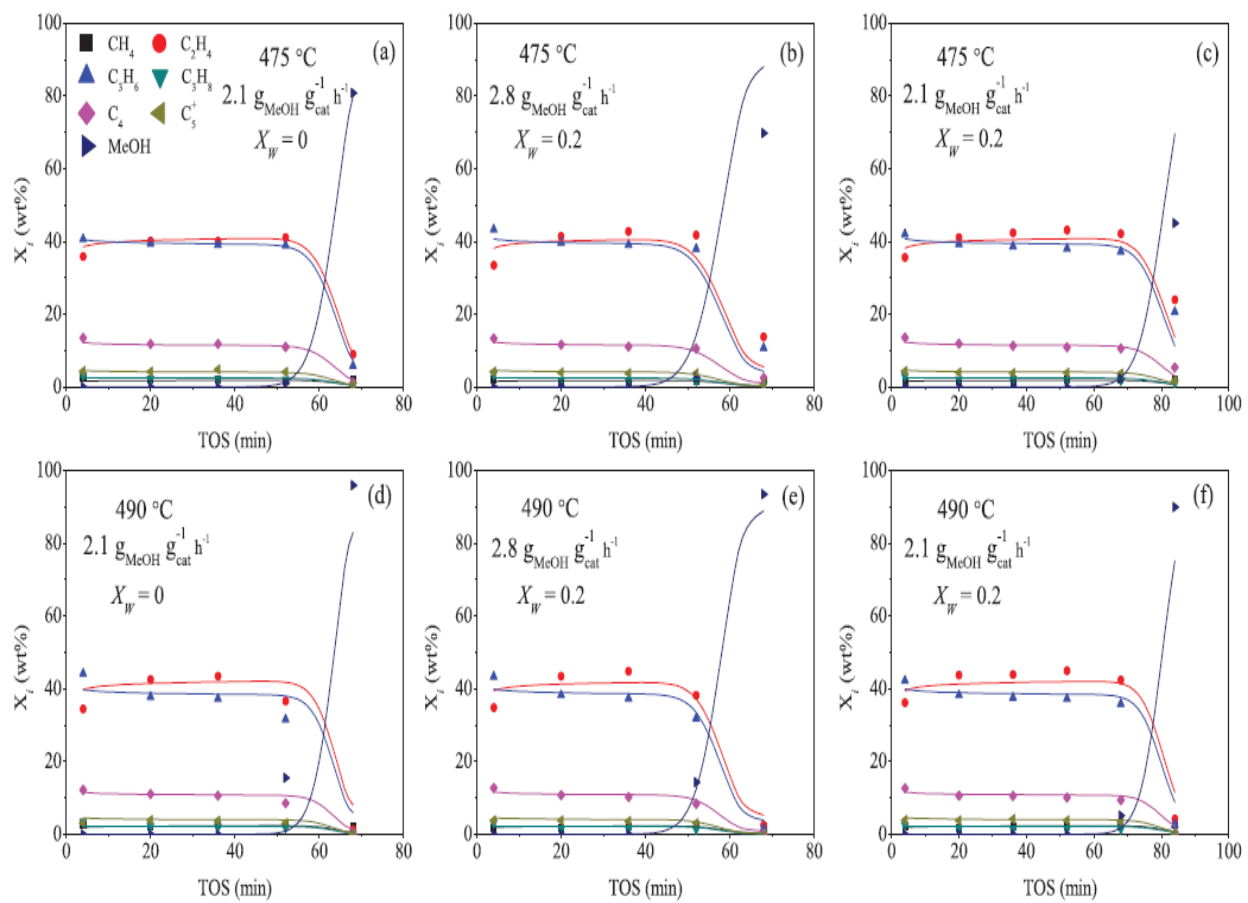


Fig. 11. Concentration profile of the seven-lumped model

2.10.3 Kinetic model based on the consecutive reaction steps

Gayubo et al proposed a kinetic model to simulate the MTO reaction over SAPO-18 catalyst using fluidized bed reactor in a wide range of operating conditions [59]. The model predicts the evolution of reaction products with time on stream, which follows three consecutive periods: initiation, maximization of olefin production and declining period. The kinetic scheme takes into account these three steps of formation of active intermediate compounds, an step where olefins are formed by reaction of oxygenates (methanol/DME) with these intermediates and deactivation of intermediates by degradation to coke. The water content in the reaction medium reduces the reaction rate of these steps. The kinetic equations and parameters were identified by solving the mass conservation equations of each component with the kinetic equation for deactivation with considering the water content on the kinetics of each step. The olefin yield was improved with increasing the dilution and WHSV. While, the temperature had opposite effect. As shown in figure 2.10, the dilution enhanced both of activity and reaction rate. But, it inhibited the intermediates formation. Also, temperature increase exhibited similar effect. Moreover, the increase of WHSV did not affect both of activity and intermediates formation. While, the reaction became slower.

$$\text{Disappearance of oxygenates} \quad -r_A = \frac{dX_A}{d\left(\frac{W}{F_0}\right)} = -k_O X_A Y_R \theta_a - k_{CH_4} X_A Y_R \theta \quad 2.29$$

$$\text{Formation of olefins} \quad r_O = \frac{dX_O}{d(W/F_0)} = k_O X_A Y_R \theta_a \quad 2.30$$

$$\text{Formation of methane} \quad r_{CH_4} = \frac{dX_{CH_4}}{d\left(\frac{W}{F_0}\right)} = k_{CH_4} X_A Y_R \theta \quad 2.31$$

$$\theta = \frac{1}{1 + K_W (X_W)^n} \quad 2.32$$

$$\text{Formation of intermediates} \quad r_R = \frac{dY_R}{d\left(\frac{W}{F_0}\right)} = (k_2 X_A + k_3 X_A Y_R) \theta_a \quad 2.33$$

$$\text{Coking model} \quad r_d = -\frac{da}{dt} = k_d (X_A + X_O) \theta_a a^d \quad 2.34$$

$$\theta_d = \frac{1}{1 + K_{Wd} (X_W)^{n_d}} \quad 2.35$$

$$a = \frac{r_o}{(r_o)_f} = \frac{\left(\frac{dX_O}{d(W/F_0)}\right)}{\left(\frac{dX_O}{d(W/F_0)}\right)_f} \quad 2.36$$

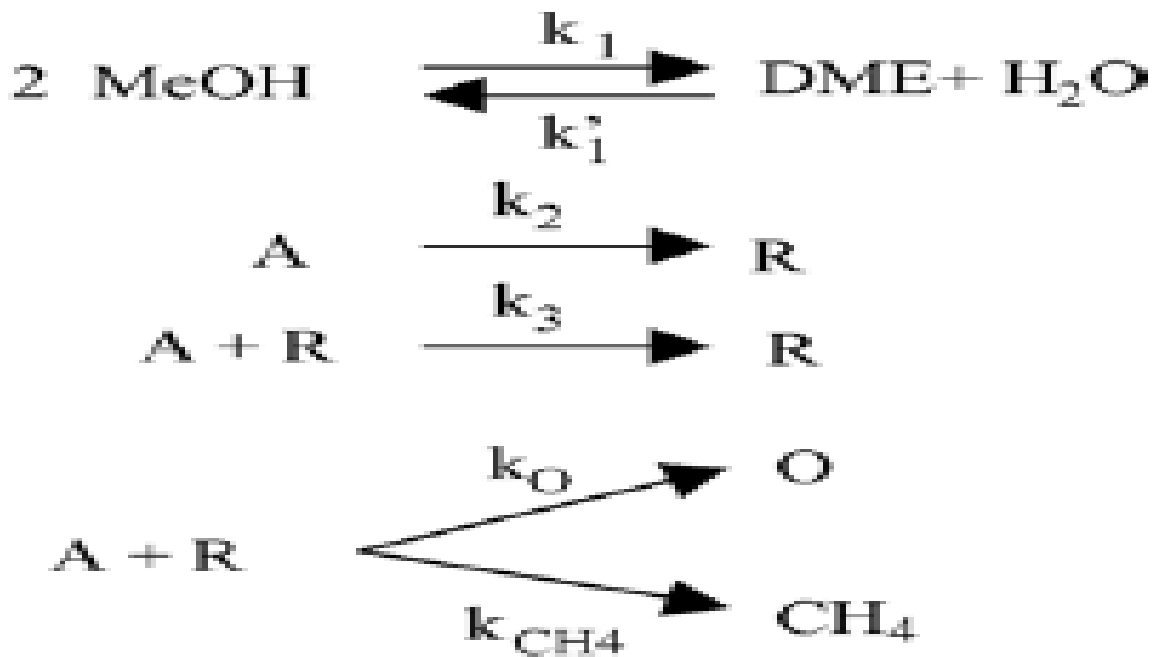


Fig. 12. The reaction network of MTO

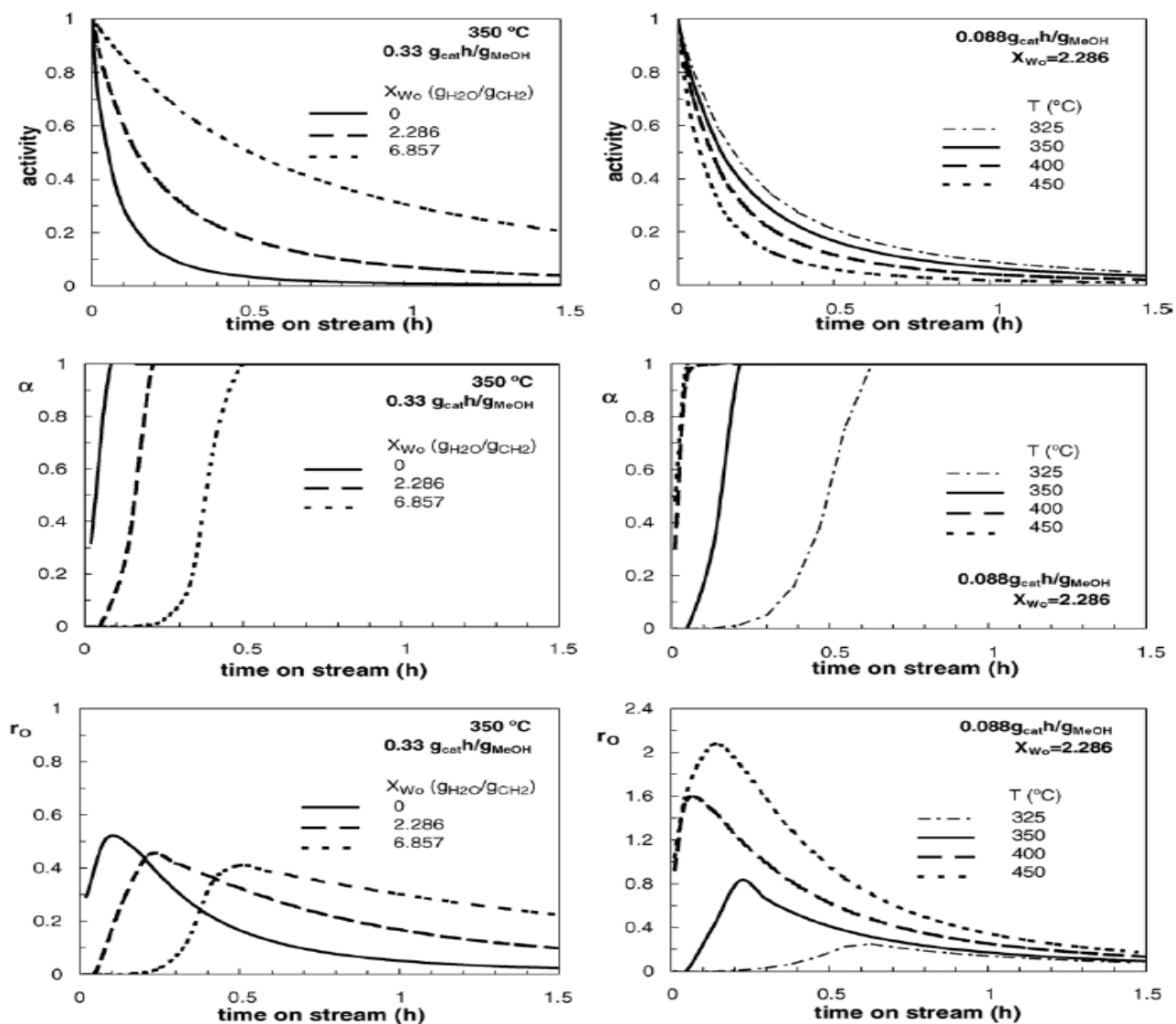


Fig. 13. The effect of operating conditions on the activity, rate, and intermediate percentage

Chapter 3

Experimental work

3.1 Synthesis

3.1.1 Materials: aluminum isopropoxide ($\text{Al}(\text{O-i-Pr})_3$), Aluminum hydroxide (Merck, 98%), 40 wt.% tetra ethyl ammonium hydroxide (TEAOH), 40 wt.% colloidal silica (HS sigma Aldrich or snowtex), Tetraethyl orthosilicate (TEOS, 99.99 wt.%), ludox HS colloidal silica (30 wt.%), 85wt.% ortho phosphoric acid, copper nitrate tri hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$), calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), tungsten carbide (WC), magnesium nitrate hexahydrate, calcium nitrate hexahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), barium nitrate ($\text{Ba}(\text{NO}_3)_2$), iron nitrate nonahydrate, cobalt nitrate hexahydrate, nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), Boric acid from Sigma Aldrich (99.5 wt.%), sodium hydroxide (Sigma Aldrich, pellets) and DI water.

3.1.2 Parent SAPO-34 synthesis

SAPO-34 zeolite was prepared by in-situ crystallization of gel solution prepared by dissolution of aluminum isopropoxide in deionized water then orthophosphoric acid was added to the solution and aged for 1 h to allow AlPO_4 to form. Later, snowtex 40 wt. % colloidal silica was added to the solution. Finally, TEAOH solution was added as structure directing agent. Then Gel solution was aged for 3 h under stirring. The molar composition of the synthesis gel was $1 \text{ Al}_2\text{O}_3 : 1.15 \text{ P}_2\text{O}_5 : 0.55 \text{ SiO}_2 : 2 \text{ TEAOH} : 110 \text{ H}_2\text{O}$. Aged gel solution was transferred to teflon and covered to be placed in the autoclave. Crystallization process was carried out inside the hydrothermal oven at a temperature of 180°C for 72h. Then, Autoclave was cooled by rinsing in cold water. The SAPO-34 powder was separated from the solution by high-speed centrifuge and washed with deionized

water to neutralize powder pH. The wet powder was dried in an oven at 110 °C for overnight. The impurities and template were removed by calcination in an automatic furnace at 600 °C and ramping rate of 10 °C/min for 5h. Finally, the catalyst powder was formed in pellet shape by mechanical pressing and then crushed and sieved to particles with a diameter of 0.5-1 mm.

3.1.3 In-situ modified SAPO-34 synthesis

Firstly, metal modified SAPO-34 zeolite was prepared by in-situ crystallization of gel solution prepared by dissolution of aluminum isopropoxide in deionized water after which orthophosphoric acid was added to the solution and aged for 1 h. Later, snowtex 40 wt.% colloidal silica was added to the solution then metal precursor was added to the solution. Finally, TEAOH solution was added as structure directing agent. Then, gel solution was aged for 3 h under stirring. The molar composition of the synthesis gel was 1 Al₂O₃:1.15 P₂O₅:0.55 SiO₂:2 TEAOH: 110 H₂O:0.007 MeO_x. On the other hand, boron silica-alumina phosphate molecular sieve was synthesized by in-situ crystallization of gel solution prepared by mixing of boric acid and sodium hydroxide with stoichiometric ratios in deionized water until being fully dissolved to have neutralized aq. Solution. Then, TEAOH Solution was added and stirred with the mixture for a while followed by Aluminum isopropoxide addition to the solution and stirred for 1 h until dissolution. Finally, Tetraethylorthosilicate and orthophosphoric acid were added dropwise to the solution and cloudy color of the gel was observed. Then, Gel solution was aged for 3 h under stirring. The molar composition of the synthesis gel was 1 Al(O-*i*pr)₃:2 H₃PO₄:0.3 SiO₂:2 TEAOH:30 H₂O which is taken from Zhibin li et al work [60]. Aged gel solution was transferred to Teflon and covered to be placed in the autoclave. The crystallization process was carried out inside the hydrothermal oven at a temperature of 180 °C for 72h. Then, Autoclave was cooled by rinsing in cold water. Catalyst powder was separated from the solution by high-speed centrifuge and washed with

deionized water to neutralize powder pH. The wet powder was dried in an oven at 110 °C for overnight. The impurities and template were removed by calcination in an automatic furnace at 600 °C and ramping rate of 10 °C/min for 5h. Ion exchange with ammonium nitrate ((NH₄)₂NO₃) followed by 2nd calcination step was performed for boron-containing samples to remove sodium. Finally, the catalyst powder was formed in a pellet shape by mechanical pressing and then crushed and sieved to particles with a diameter of 0.5-1 mm.

3.1.4 Post modified SAPO-34 synthesis

After parent SAPO-34 catalyst was produced, post-modification can be performed to improve its catalytic properties either by metallic or chemicals addition. The metallic post modifications that have been used here for Parent SAPO-34 were liquid phase ion exchange and impregnation. The liquid phase ion exchange was carried out by mixing 1 g of zeolite in 0.4 M aq. solution of alkaline earth metals (Mg, Ca and, Ba). The ion exchange was achieved by stirring and heating at 70 °C for a half-hour to incorporate Me⁺² ions into the structure. The transition metals (Ni, Fe and, Co) were selected to be impregnated into SAPO-34 by mixing 1 g of zeolite in 5 wt.% metal aq. Solution. The impregnation was performed under stirring and heating at 70 °C for a half-hour. Moreover, Bi metallic post modification was tried for a catalyst for better evaluation of both transition and earth alkaline metals effect. Then the impregnated zeolite solution was stirred overnight to evaporate excess water and the wet powder was dried completely in an oven at 110 °C.

The chemical post modifications include alkaline (desilication) and acid (dealumination) treatments of zeolite. In the present work acid dealumination rather than desilication was carried out for SAPO-34 because of its low Si/Al ratio which causes high acidity affecting its catalytic lifetime. Therefore, dealumination treatment was investigated using several weak and strong acids.

First 1 g of zeolite was mixed in x M ($x=0-1$) acid aq. solution under stirring at 75 °C for a half-hour. Then, the solution was filtered by high-speed centrifuge and the collected powder was washed 3 times with DI water to maintain neutral pH and dried in an oven at 110 °C overnight. Finally, the catalyst powder was calcined at 550 °C for 5 h under air flow and formed in a pellet shape by mechanical pressing and then crushed and sieved to particles with a diameter of 0.5-1 mm.

3.2 Characterization

3.2.1 X-ray diffraction (XRD)

After drying the prepared samples, XRD characterization was performed in order to identify the crystallinity of the powdered catalysts and their phases. This was also performed after calcination in order to determine the crystallite size changes before and after calcination. A Rigaku Miniflex II Desktop X-ray diffractometer at Imaging Laboratory CENT (Center for Excellence in Nanotechnology, KFUPM) was used for this analysis. The powdered samples were analyzed using a start angle of 5 ° and stop angle of 40 °, sampling step size of 0.03, the scan speed of 3.00, 30 kV and 15 mA.

3.2.2 Field Emission Scanning Electron Microscopy (FE-SEM)

Imaging analysis of the prepared samples was performed using Scanning Electron Microscope (Oxford Instrument, X-Max) fitted with (Oxford Instruments, EDX) energy dispersive X-ray spectrometry to view the crystalline appearance and shapes of the samples in nanoscale magnification and identify the chemical composition. The SEM images were taken at a magnification of 200 kx with a high voltage of 20 kV at a scaling of 10 µm.

3.2.3 Brunauer–Emmett–Teller (BET) analysis

Nitrogen adsorption was measured by a Micromeritics ASAP 2020 porosimeter equipped with liquefied N₂ adsorption at −196 °C. it was used to identify the textural properties such as pore volume and size distribution and BET surface area. Firstly, 0.2 g sample was degassed at 350 °C for 12 h then N₂-adsorption was performed for a downtime of 24 h at a temperature of 180 °C.

3.2.4 Temperature Programmed Desorption (TPD)

The NH₃-TPD was performed to investigate and evaluate the presence and strength of acid sites on the prepared samples of modified SAPO-34. This was carried out using Chemisorb 2750 Micrometrics Chemisorption Analyzer. For NH₃-TPD analysis, 0.1 g of each sample was used for the experimental characterization. These samples were heated to 600 °C at a rate of 30 °C/min for initial treatment, under a constant flow of helium gas at a flow rate of 25 mL/min for a half-hour. Subsequently, the samples were cooled to 45 °C and 100 °C for adsorption of NH₃ (10 %) at 28 mL/min. The adsorption was carried out for a half-hour, followed by injection of helium gas for 1 h to flush the physisorbed gases from the surface of the sample specimens. Afterwards, the setup was heated to 900 °C at a rate of 10 °C/min. The quantity of desorbed gas was measured and recorded using a TCD detector at 0.5 s interval.

3.2.5 Fourier Transform Infrared Radiation (FT-IR)

Functional group identification was performed on the parent and the modified SAPO-34 catalyst via Thermo Scientific Nicolet 6700 spectrometer. The thin translucent wafer was prepared by mixing KBr and catalyst powder in 95:5 wt. ratio and shaped as a wafer by mechanical pressing. Subsequently, spectra reading was obtained at a scanning range of 200 – 4000 cm⁻¹.

3.2.6 Diffuse Reflectance UV-Vis analysis

UV-vis diffuse reflectance spectra of the samples were analyzed to identify chemical composition. The Cary 5000 UV-VIS NIR spectrophotometer was used for this purpose equipped with PbSmart detector which enhances its photometric performance to reach high wavelength up to 3300 nm.

3.3 Experimental setup for catalytic evaluation

Catalytic testing was carried out in a stainless steel tubular fixed bed reactor at atmospheric pressure. First, the pelletized catalyst was packed in the middle of the bed in between two quartz wool pieces. The catalyst was pretreated prior to testing at 500 °C for 1 h under helium gas flow. The feed to methanol-to-olefins (MTO) reactor consisted of 5 mole% of methanol and 95 mole% He, which was used as a carrier gas to facilitate the flow of the reactants and products. The activity of synthesized catalysts was examined at 350 °C for energy saving and better evaluation of their activity at harsh conditions. Methanol conversion and product selectivity were evaluated for synthesized catalysts with varying time of stream (TOS). The reaction experiment was run at a constant weight hourly space velocity (WHSV) of 4.85 h⁻¹. Reaction products were analyzed by on-line Shimadzu gas chromatography equipped with a capillary column HP-PLOT (30 m × 0.53 mm, 6 µm film thickness) and a flame ionization detector (FID).

Carbon balance was used to calculate methanol conversions and product selectivity (i.e. carbon mole amounts in product per total number of carbon moles in overall product mixture without unconverted feed) according to the equations below.

$$\text{Methanol Conversion} = \left(\frac{MeOH_{in} - MeOH_{out}}{MeOH_{in}} \right) \times 100\% \quad 3.1$$

$$\text{Product Selectivity} = \left(\frac{n_i C_i}{\sum n_i C_i} \right) \times 100\% \quad 3.2$$

$$\text{Yield} = \text{Conversion} \times \text{Selectivity} \quad 3.3$$

Chapter 4

Results and discussion

4.1 The characterization

4.1.1 Catalyst crystallinity:

The XRD patterns of the synthesized catalysts were shown in figures below. It is clear that no extra peaks belong to impurities and all peaks represent chabazite structure of the synthesized catalysts. Also, the XRD pattern of post Metallic modified catalysts was identical to parent SAPO-34 because of low concentration and its peaks are overlapped with zeolite phase. This can be considered as evidence for the presence of metal heteroatoms in gel solution results in good crystallinity product. The parent SAPO-34 exhibited the highest crystallinity of synthesized samples. In contrast, metal modified samples had lower crystallinity due to crystal size reduction and partial distortion of crystal structure by metal atoms. Also, it is observed that peaks in **Fig. 14** shifted slightly to left due to metals isomorphous substitution into the SAPO-34 structure and the lattice parameters and interplanar spacing change [61]. As shown in **Fig. 15**, the crystallinity dropped as indicated by a characteristic peak at 20.7° for dealumination by acids. The crystallinity drop was higher for strong acids and reduced as acid strength lowered. In addition, the bi metallic catalysts exhibited lower crystallinity as compared to parent SAPO-34 as shown in **Fig. 16** due to the formation irregular and rough surface particles. In contrast to the metal effect. Boron exhibited enhancement of crystallinity as B/Si increased as shown in **Fig. 17**.

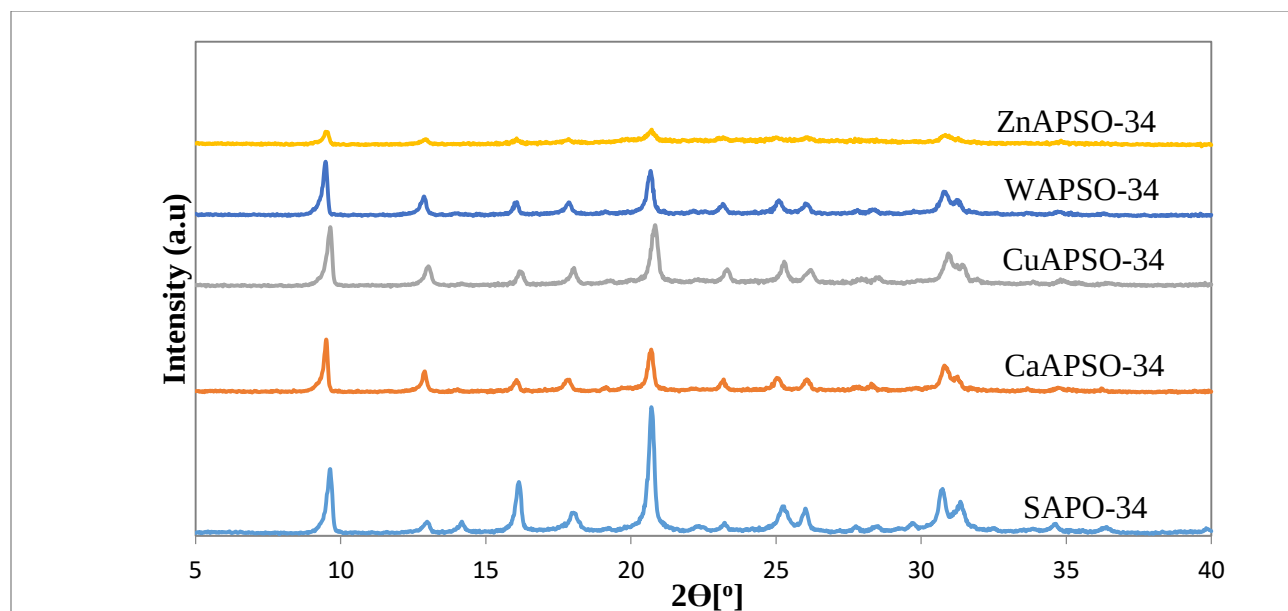


Fig. 14. XRD of metal in-situ incorporated catalysts

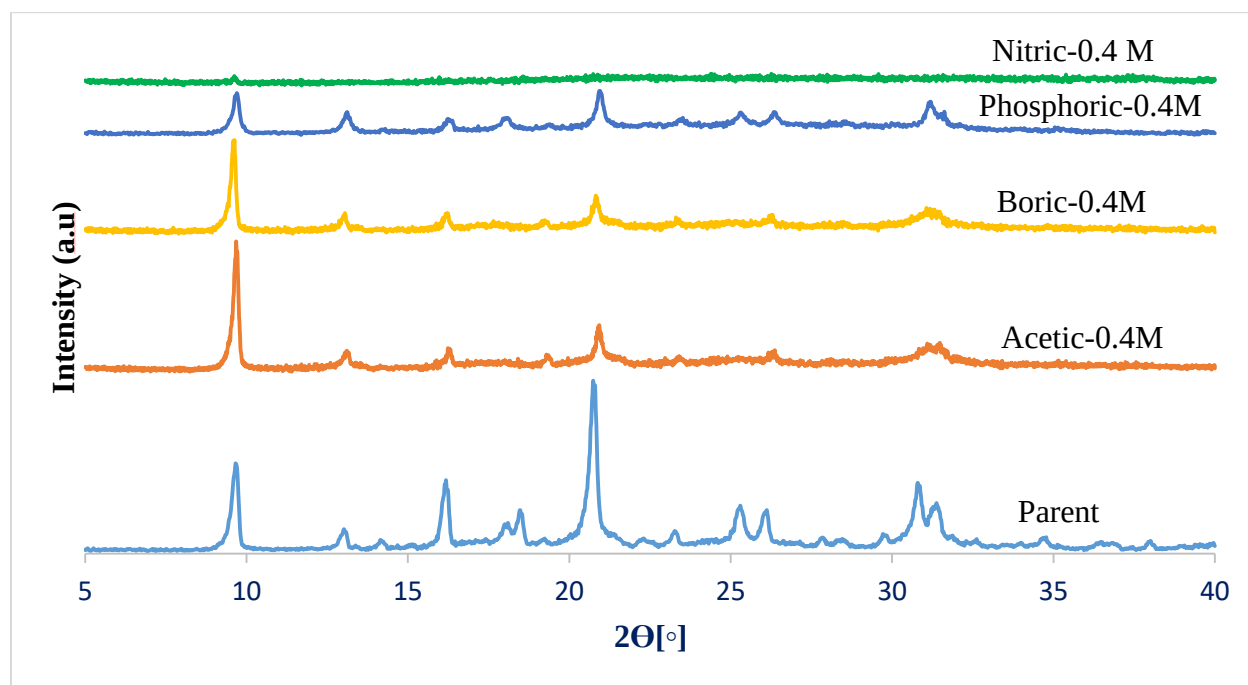


Fig. 15. XRD patterns of Dealuminated SAPO-34 catalysts

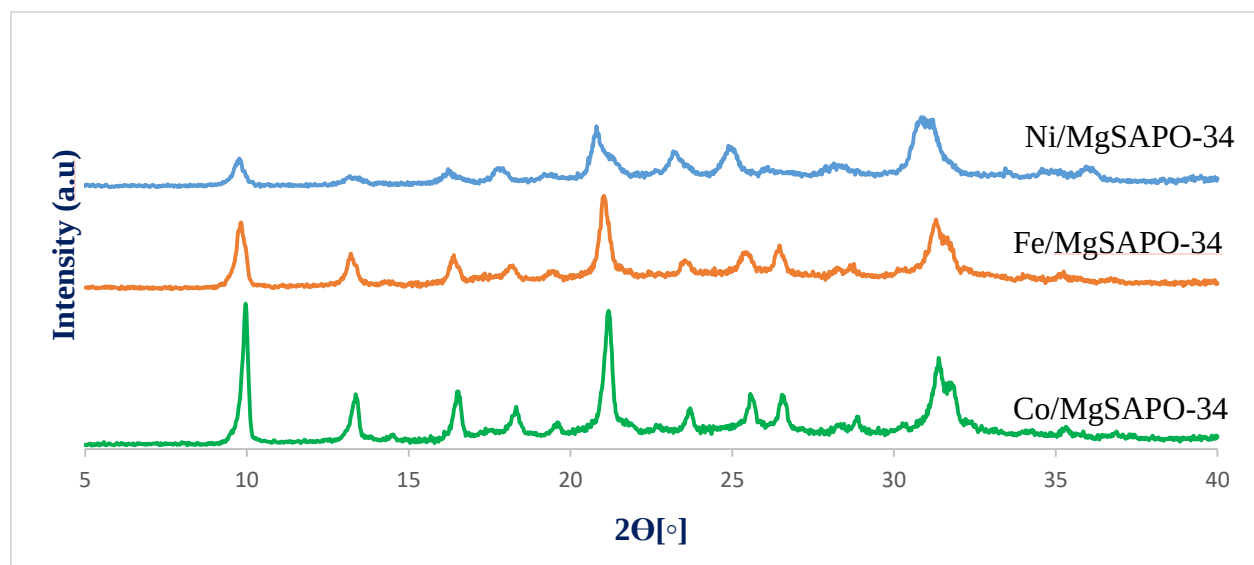


Fig. 16. XRD patterns of Bi-metallic post modification of SAPO-34

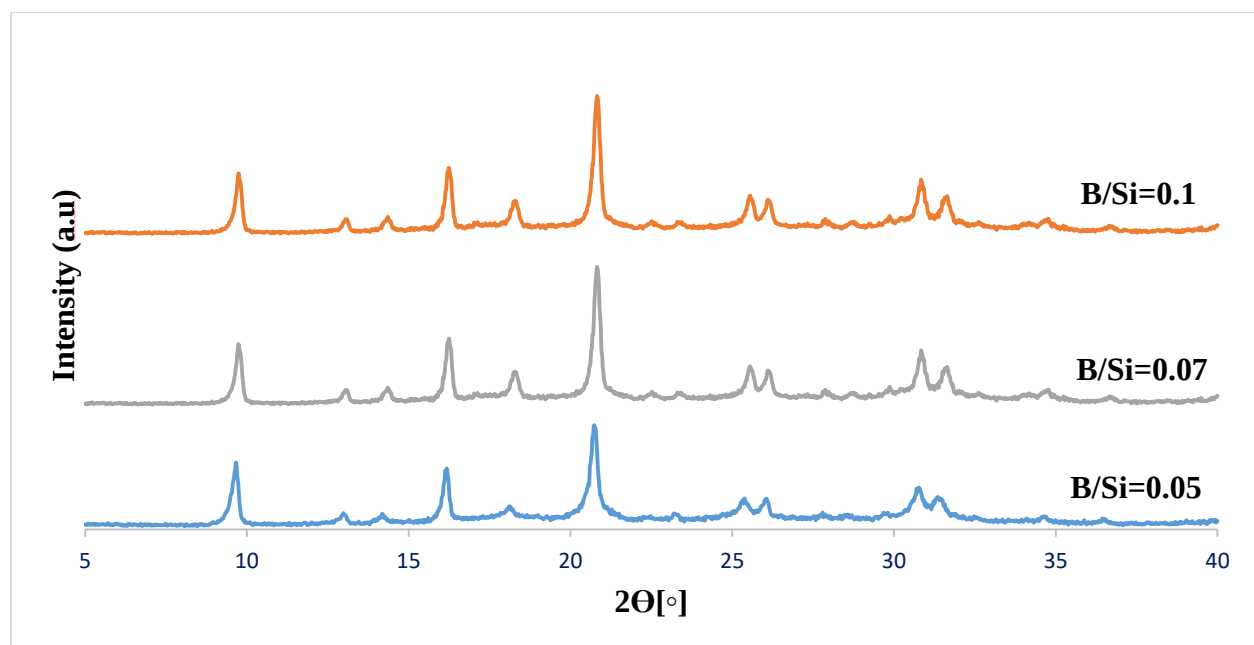


Fig. 17. XRD patterns of boron-SAPO-34 catalysts

4.1.2 Catalyst morphology:

FESEM images of synthesized samples shown on figures below revealed cubic morphology which is common for CHA phase of zeolite and specifically SAPO-34. It was observed that MEAPSO-34 samples have more uniform cubes compared to SAPO-34 cubes associated with extra irregular shape particles and aggregation. As shown on SEM images shown in **Fig. 18** and **Fig. 19**, CaPASO-34 and CuPASO-34 catalysts tend to have a rectangular surface, unlike WPASO-34 and parent samples which had square surface. Also, FESEM images showed that MePASO-34 samples have a rough surface which supports XRD finding of crystallinity drop. Moreover, the particle size of SAPO-34 samples reduced after metal incorporation due to slower crystallization. Generally, Particle size distribution of samples is medium and Parent SAPO-34 had the largest particle size. Calcium and copper addition lowered size by 50%. The SEM images of BSAPSO-34 catalysts revealed the particle growth effect due to boron presence during synthesis. Also, it was observed that the boron supports the formation of sheet-like shape particles but they are agglomerated over each other as layers to form cube as shown in **Fig. 20**. The impregnated samples had a larger particle size and rough surface as shown in **Fig. 21**, which explain the XRD result of crystallinity drop. The particle size was reduced after the ion exchange with alkaline metals as shown on **Fig. 22**. Moreover, the surface had higher porosity compared to parent SAPO-34 which reflects the proportional effect of textural properties. As shown in **Fig. 23**, The Ni/MgSAPO-34 had elliptic particle shapes which can be justified by the nickel was saturated in the outer shell and higher size of Ni particles compared to iron and cobalt.

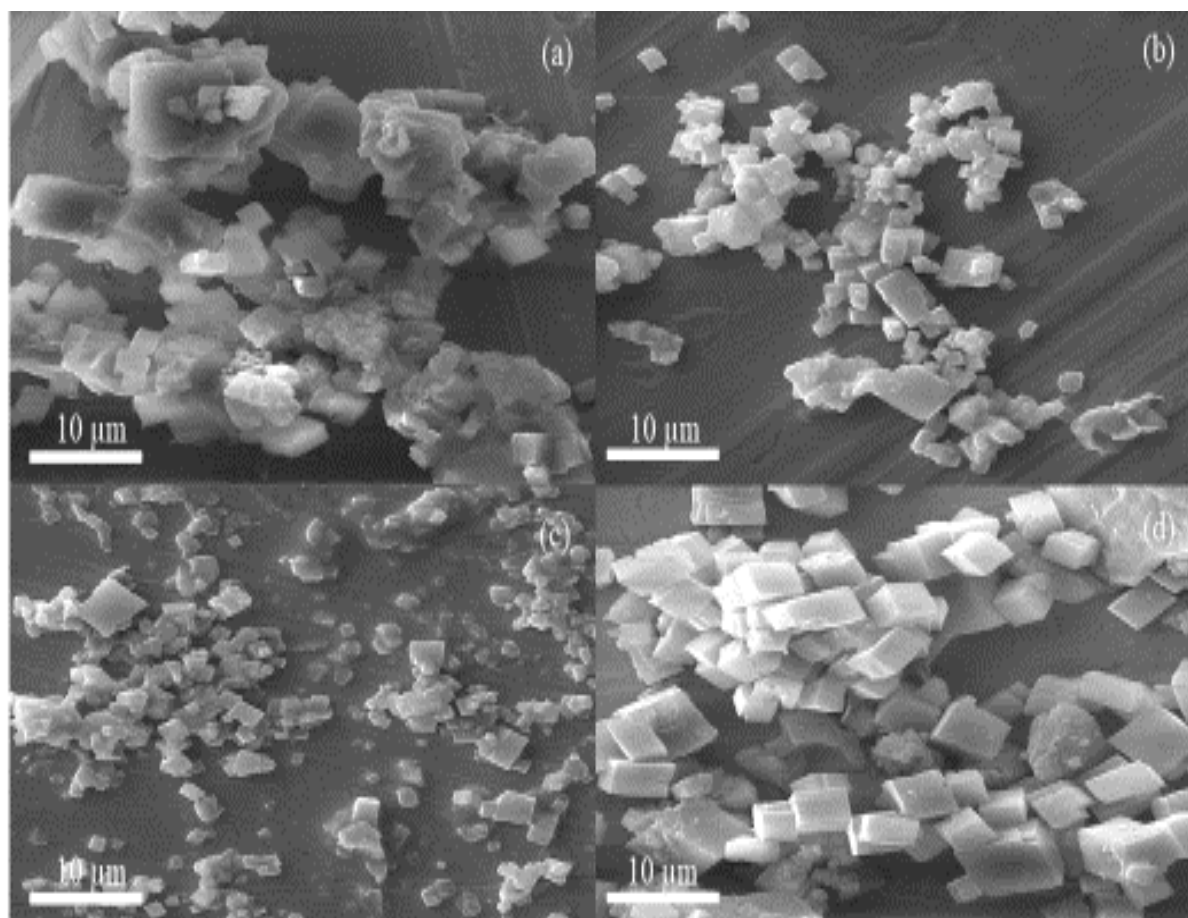


Fig. 18. SEM images of parent and modified SAPO-34 catalysts where [a]: SAPO-34, [b]: CaPAO-34, [c]: CuPASO-34 and [d]: WPASO-34

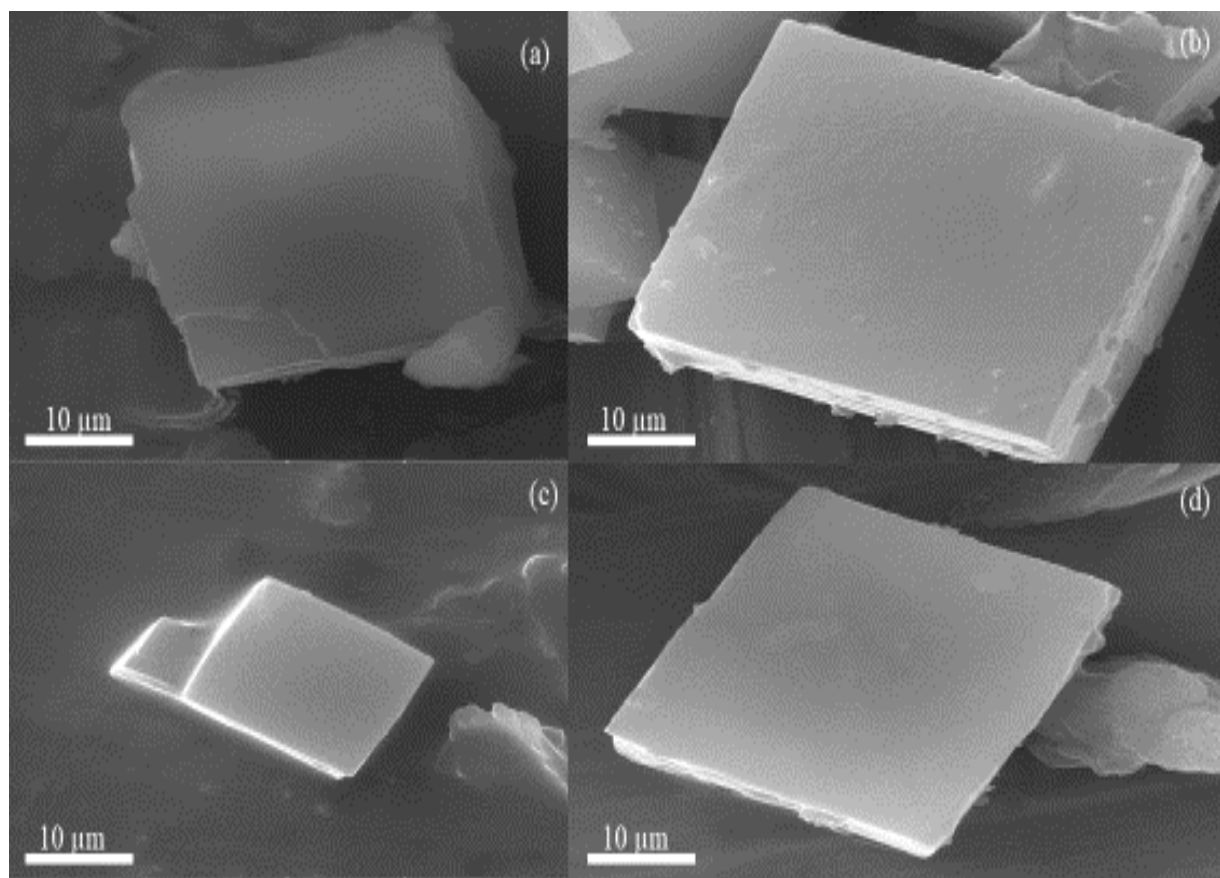


Fig. 19. SEM images of single particles of MePASO-34 catalysts where (a) SAPO-34, (b) CaPAO-34, (c) CuPASO-34 and (d) WPASO-34

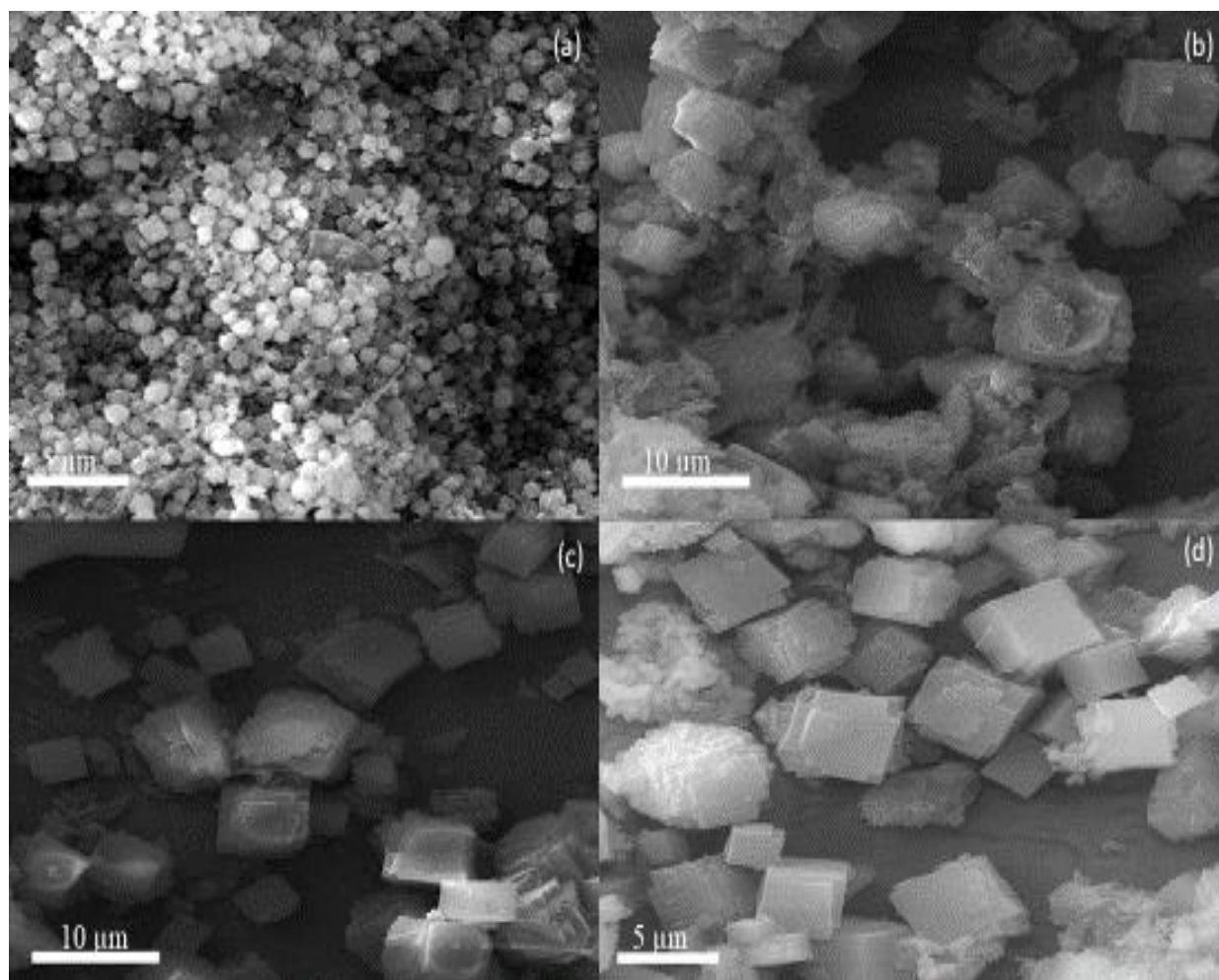


Fig. 20. The images of the BSAP0-34 catalysts where: (a) SAPO-34, (b) $B/Si=0.05$, (c) $B/Si=0.07$ and (d) $B/Si=0.1$

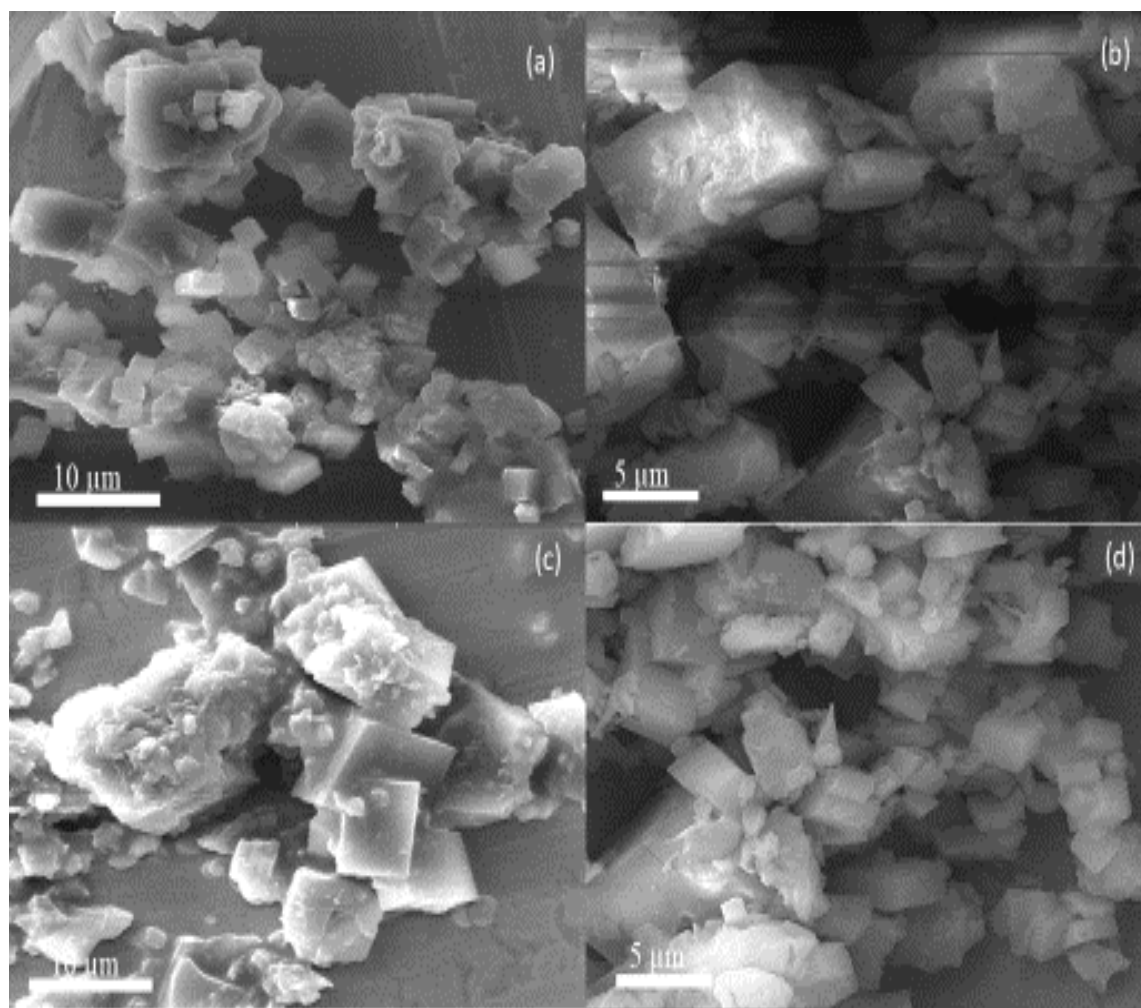


Fig. 21. The images of the impregnated SAPO-34 catalysts where: (a) SAPO-34 ,(b)Ni/SAPO-34 ,(c)Fe/SAPO-34 and (d)Co/SAPO-34

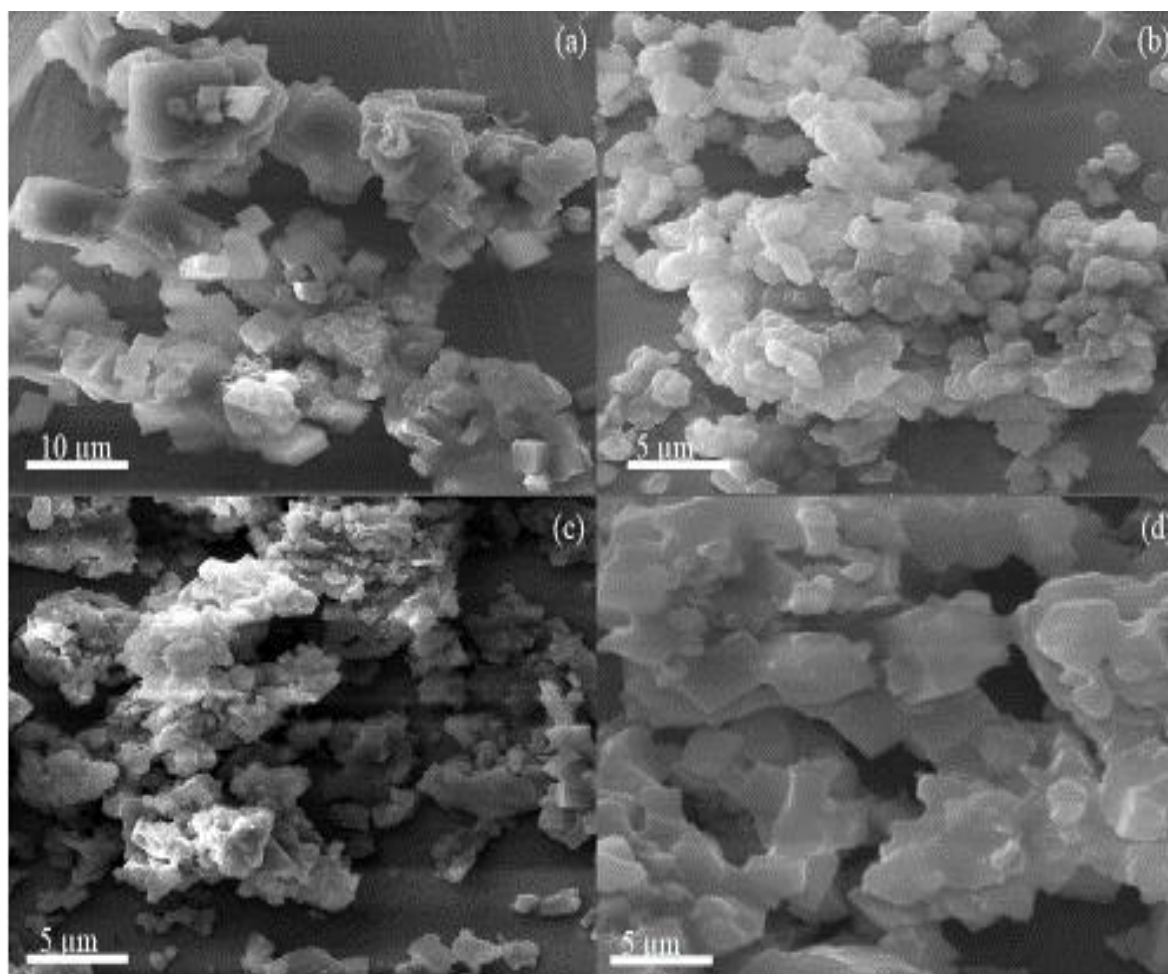


Fig. 22. The images of Bi metallic post modification of SAPO-34 where: (a)SAPO-34 , (b)Ni/MgSAPO-34, (c)Fe/MgSA-34 and (d)Co/MgSapo-34

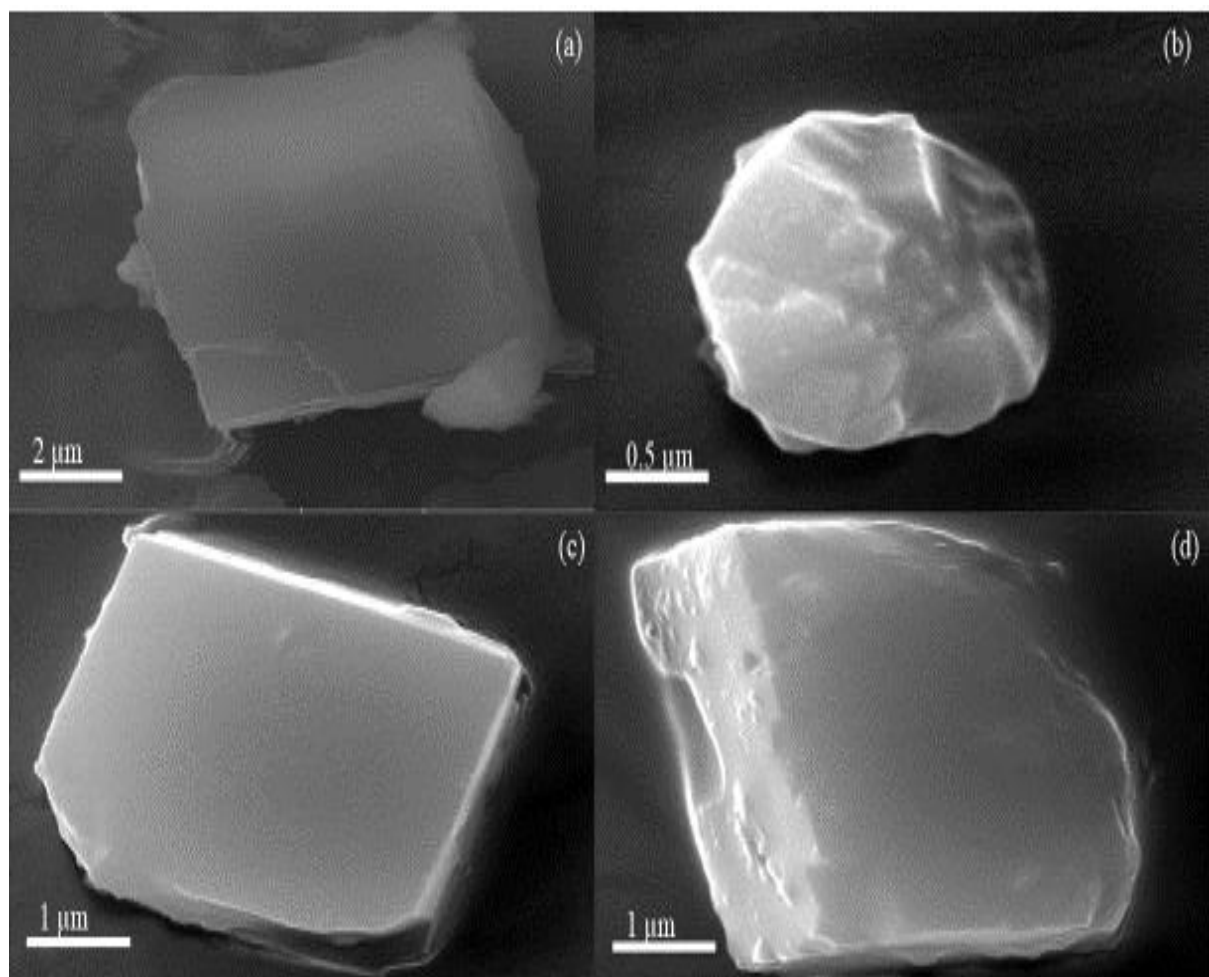


Fig. 23. The single particle images of Bi metallic post modification of SAPO-34 where: (a)SAPO-34 ,(b)Ni/MgSAPO-34,(c)Fe/MgSAPO-34 and (d)Co/MgSapo-34

4.1.3 Elemental composition:

EDX analysis of modified samples was presented in **Table 8**. It indicates metals in the gel solution are attached to the framework and/or stuck on particle surface as an amorphous phase. The Successful incorporation into SAPO-34 framework was confirmed by XRD and FESEM analysis which revealed that there is no extra amorphous phase. Also, it was observed that metals did not have the same percentage which means every metal had a different impact on silicon incorporation. The boron presence was confirmed with the almost same composition of gel. Moreover, the EDX detected slight aluminum removal by acetic acid which supports the successful dealumination.

Table 8. Elemental analysis of various catalysts using EDX

Catalyst	Si (%)	Al (%)	P (%)	Me (%)							B (%)
				Ca	Cu	W	Mg	Ni	Fe	Co	
SAPO-34	16.70	47.61	35.69	-	-	-	-	-	-	-	-
CaAPSO-34	18.90	45.34	35.08	0.68	-	-	-	-	-	-	-
CuAPSO-34	18.14	46.31	34.93	-	0.62	-	-	-	-	-	-
WAPSO-34	17.20	47.21	35.1	-	-	0.49	-	-	-	-	-
Ni/MgSAPO-34	18.10	45.11	30.96	-	-	-	1.13	4.7	-	-	-
Fe/MgSAPO-34	18.65	44.97	30.57	-	-	-	1.16	-	4.65	-	-
Co/MgSAPO-34	18.59	45.02	30.45	-	-	-	1.21	-	-	4.73	-
Acetic-0.4M-S	17.54	46.79	35.71	-	-	-	-	-	-	-	-
B-SAPO-34 (B/Si=0.1)	18.34	45.96	34.17	-	-	-	-	-	-	-	1.53

4.1.4 Textural properties:

The BET surface area of in-situ modified catalysts were presented in **Table 9** and **Table 10**. The highest surface area was recorded for the SAPO-34 sample ($555 \text{ m}^2/\text{g}$), then it declines with metal and boron incorporation because of their lower crystallinity and surface smoothness which is consistent with XRD and FESEM characterization results. On the other hand, metal and boron modification enhanced diffusion properties of the SAPO-34 catalyst due to mesopores that preferentially formed instead of micropores by aluminum isomorphous substitution. Calcium modified catalyst had the highest mesopore volume which indicates its better aluminum substitution as compared to other metals. The pore volume was proportional to B/Si ratio of BSAPO-34 catalysts which means the higher boron added, the better incorporation occurred. On the other hand, metallic post modification improved surface area and porosity of catalyst as shown in **Table 11**. The metallic post modified SAPO-34 had excellent textural properties due to porosity promoting by isomorphous substitution which was proofed by SEM results in **Fig. 21**. The IE-MgSAPO-34 catalyst had the highest surface area and pore volume. Then, the surface area and pore volume were reduced due to metal partial blockage of pores after impregnation.

Table 9. Textural properties of metal in-situ modified SAPO-34 catalysts

Catalyst	S_{BET}	S_{micro}	S_{ext}	V_{TOT}	V_{micro}	V_{meso}
	(m²/g)	(m²/g)	(m²/g)	(cm³/g)	(cm³/g)	(cm³/g)
SAPO-34	555	520	35	0.25	0.20	0.05
CaAPSO-34	497	469	28	0.28	0.20	0.08
CuAPSO-34	483	455	28	0.27	0.20	0.07
WAPSO-34	422	394	28	0.24	0.20	0.04

Table 10. Textural properties of boron in-situ incorporated SAPO-34 catalysts

Catalyst	S_{BET}	S_{micro}	S_{ext}	V_{TOT}	V_{micro}	V_{meso}
	(m²/g)	(m²/g)	(m²/g)	(cm³/g)	(cm³/g)	(cm³/g)
SAPO-34	463	353	110	0.31	0.18	0.13
B-SAPO-34 (B/Si=0.05)	401	367	34	0.22	0.16	0.06
B-SAPO-34 (B/Si=0.07)	392	356	36	0.23	0.16	0.07
B-SAPO-34 (B/Si=0.10)	367	330	37	0.24	0.16	0.08

Table 11. Textural properties of post metallic modified SAPO-34 catalysts

Catalyst	S_{BET}	S_{micro}	S_{ext}	V_{TOT}	V_{micro}	V_{meso}
	(m²/g)	(m²/g)	(m²/g)	(cm³/g)	(cm³/g)	(cm³/g)
SAPO-34	555	520	35	0.25	0.20	0.05
IE-MgSAPO-34	641	605	36	0.28	0.21	0.07
IE-CaSAPO-34	594	557	37	0.27	0.20	0.07
IE-BaSAPO-34	637	604	33	0.27	0.21	0.06
Fe/MgSAPO-34	531	498	33	0.26	0.21	0.05
Co/MgSAPO-34	533	510	23	0.26	0.21	0.05
Ni/MgSAPO-34	529	497	32	0.25	0.21	0.04

4.1.5 Catalyst acidity:

Acidity is a crucial parameter that affects the catalytic properties of acid zeolites. The strength and amount of acid sites of the prepared samples were evaluated by The NH_3 -TPD. TPD profiles of parent and in-situ metal modified SAPO-34 are shown in **Fig. 24**. It was observed for all samples that there are two peaks centered around 150–300 and 450–600 °C. The weak and strong acidity are related to low and high temperature desorption peaks respectively. Quantitative evaluation of catalyst acidity is presented in **Table 12**. The acidity reduction was achieved by metal incorporation into the SAPO-34 framework as shown in **Fig. 24** and **Table 12**. CaAPSO-34 had the lowest number of acid sites compared to other samples. This can be attributed to higher silica incorporation and silica islands formation due to the metal substitution of aluminum which is the main ingredient of SAPO-34 backbone. Strong acidity decreased in the order of WAPSO-34>CaAPSO-34>CuAPSO-34>SAPO-34. It was agreed that weak acid sites are favorable for DME and water formation. While, strong acid sites are important to convert DME to light olefins which is the main industrial target for MTO reaction so based on this finding better catalytic performance was expected for MeAPSO-34 catalysts [62], [63].

The acidity of post modified SAPO-34 was evaluated by NH_3 -TPD. It was revealed that post modification changed the acidity as shown in **Fig. 25** and **Fig. 26**. The weak and strong acidity were represented desorption peaks located around 100–250 and 300–450 °C respectively. Then, the acid sites intensity was converted to desorption capacity to evaluate the catalyst acidity quantitatively as presented in **Table 13** and **Table 14**. It was observed that the ion exchange decreased the weak acidity and increased strong acidity due to metal incorporation as shown in **Fig. 25**. While the impregnation of IE-MgSAPO-34 increased both weak and strong acid acidity as shown in **Fig. 26**. The Fe/MgSAPO-34 had the highest number of strong acid sites compared to

other catalysts. The strong acidity increased in the order of SAPO-34<Co/MgSAPO-34<Ni/MgSAPO-34<Fe/MgSAPO-34. The strong acidity was reported to be a promoter of olefins formation by DME dehydration in bridging hydroxyl acid sites (Si-OH-Al). As a result of this finding, the post modified SAPO-34 is expected to has better catalytic performance in terms of methanol conversion and olefins selectivity as compared to parent SAPO-34.

Table 12. Acid sites distribution of in-situ SAPO-34 catalysts

Sample	Acidity(NH ₃ desorption(mmol/g))	
	Weak 150-300 °C	Strong 450-600 °C
SAPO-34	1.21	0.45
CuAPSO-34	0.86	0.69
CaAPSO-34	0.77	0.76
WAPSO-34	0.65	0.61

Table 13. Acid sites distribution of ion exchanged SAPO-34 catalysts

Sample	Acidity(NH ₃ desorption(mmol/g))	
	Weak 100-250 °C	Strong 300-450 °C
SAPO-34	1.21	0.45
IE-MgSAPO-34	0.62	0.85
IE-CaSAPO-34	0.73	0.81
IE-BaSAPO-34	0.78	0.75

Table 14. Acid sites distribution of Bi metallic modified SAPO-34 catalysts

Sample	Acidity(NH ₃ desorption(mmol/g))	
	Weak 100-250 °C	Strong 300-450 °C
SAPO-34	1.21	0.45
Fe/MgSAPO-34	0.74	0.92
Co/MgSAPO-34	0.76	0.88
Ni/MgSAPO-34	0.79	0.86

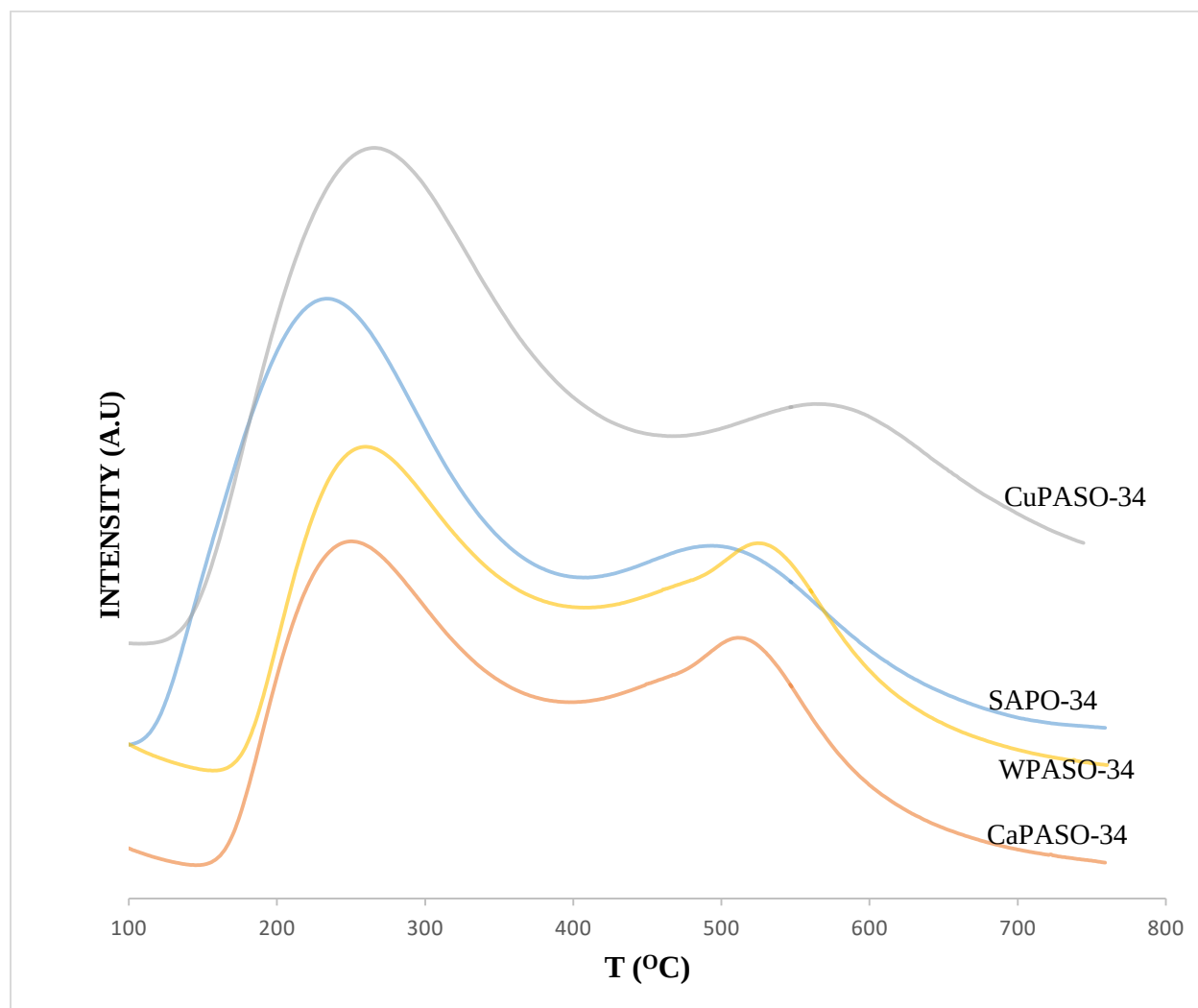


Fig. 24. *NH₃-TPD pattern for MeAPSO-34 catalysts*

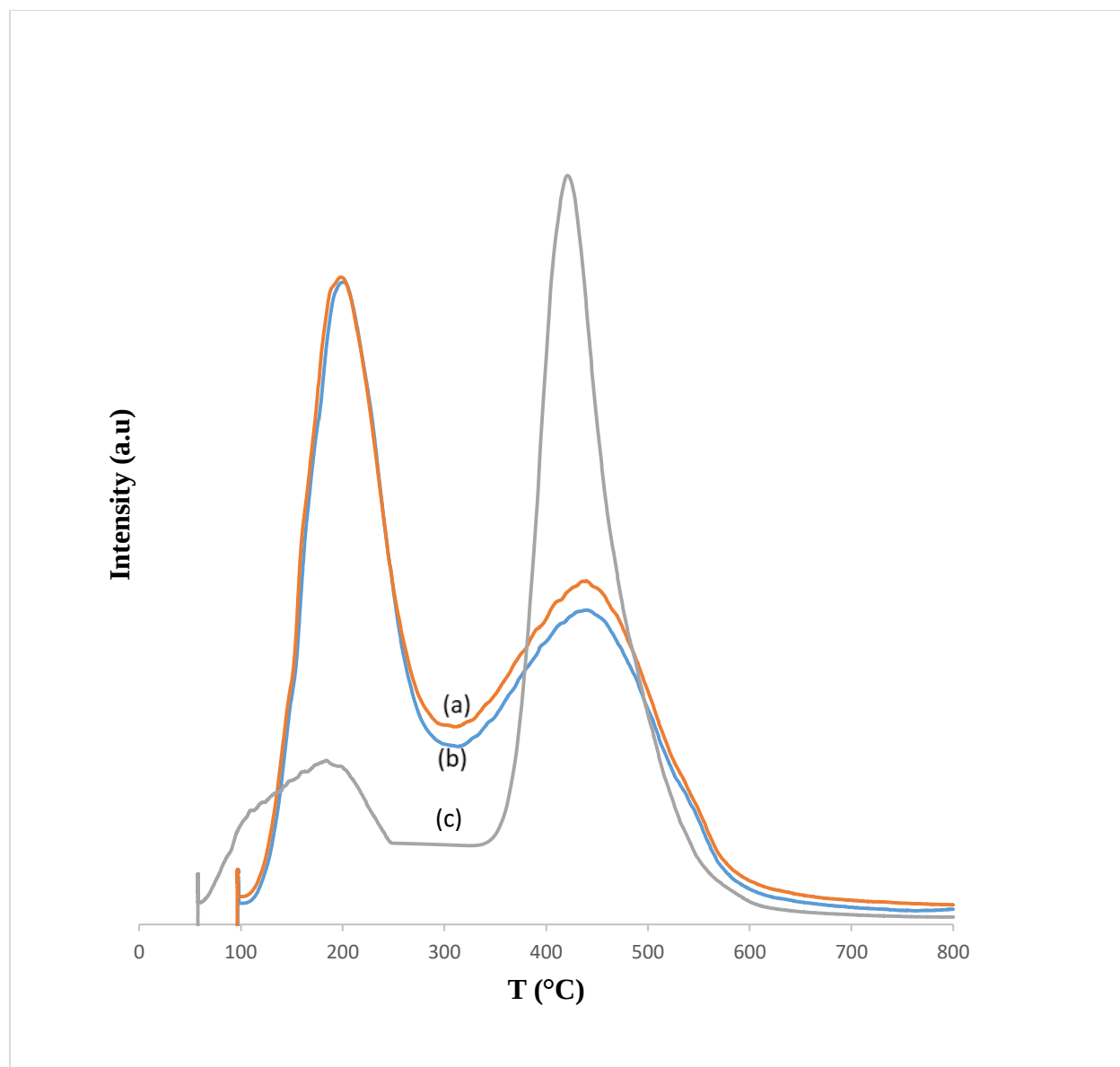


Fig. 25. NH₃-TPD profile of ion-exchanged SAPO-34 catalysts where (a) IE-CaSAPO-34, (b) IE-BaSAPO-34 and (c) IE-MgSAPO-34

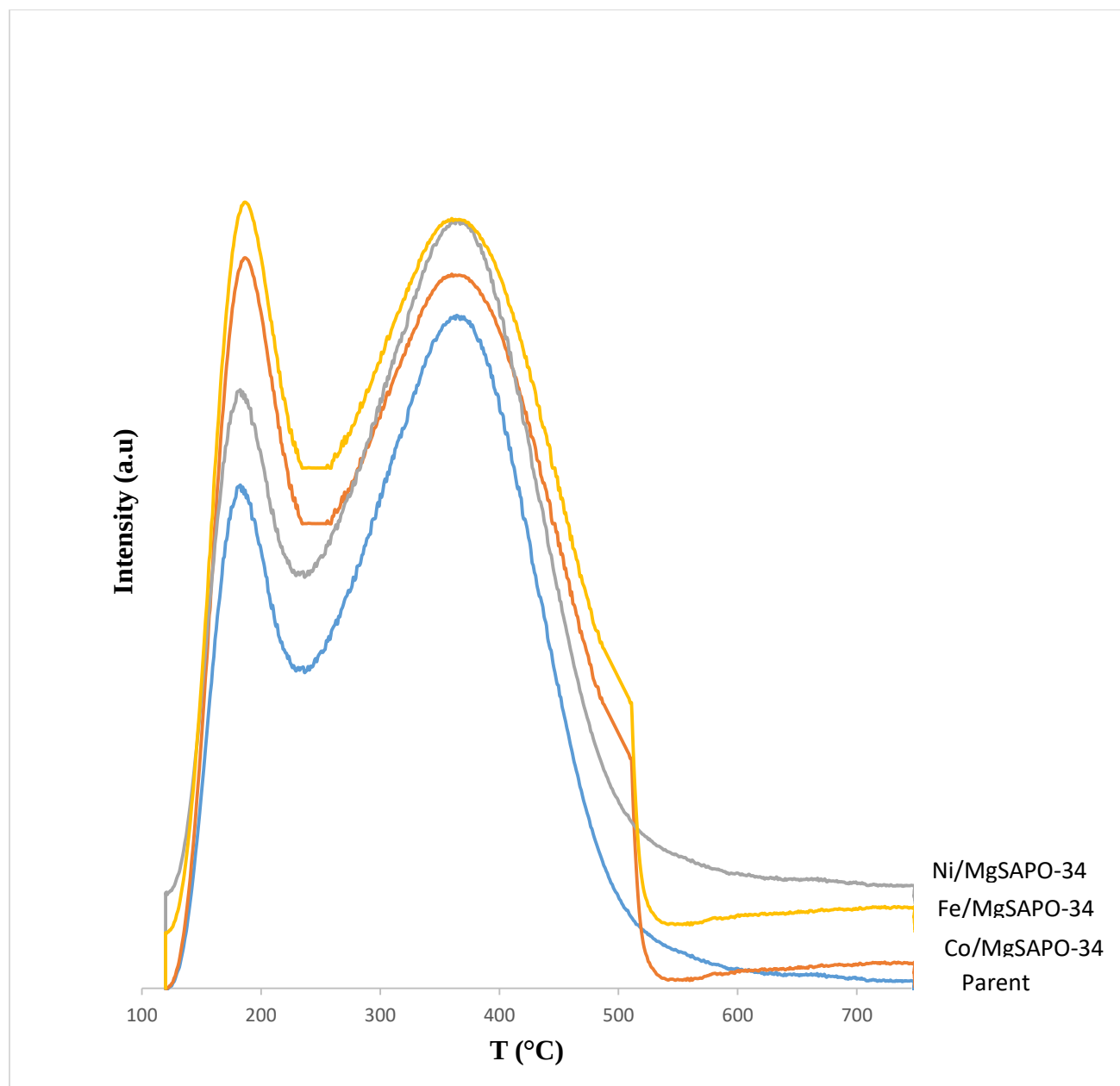


Fig. 26. The NH₃-TPD profiles of the Bimetallic SAPO-34

4.1.6 Fourier Transform Infrared Spectroscopy (FTIR):

Fourier Transform Infrared Spectroscopy (FTIR) was used for framework vibrations measurement by getting peaks at certain wavenumbers to identify silicon incorporation, CHA structure formation, Phosphorus location, physical adsorption and Bronsted acidity. The framework vibrations of synthesized catalysts are identical to CHA phase as shown in **Fig. 27**. The peak at a wavenumber of 420 cm^{-1} is attributed to M-O which support previous characterizations finding of successful metal incorporation [64]. Also, it was observed that silicon was incorporated as SiO_4 form inside the SAPO-34 structure based on bending at 490 cm^{-1} . XRD finding of SAPO-34 phase for all samples was confirmed by a peak at 640 cm^{-1} which belongs to D-6 ring formation of CHA. The peaks at a wavenumber of 710 , 1110 and 1650 cm^{-1} wavenumber are attributed to asymmetric and symmetric O-T-O stretches and physical H_2O adsorption respectively. Metal addition to SAPO-34 framework enhanced the adsorption properties of the catalyst because of 1650 cm^{-1} peak growth with metal presence. The presence of bridging and tetrahedral hydroxyl groups (Si-OH-Al, T-OH) was confirmed by peaks at a wavenumber of 3450 and 3590 cm^{-1} [27]. The intensity of Si-OH-Al peak was increased after metal modification indicating higher Bronsted acidity which is favorable for MTO reaction. Moreover, the peak of T-OH was almost eliminated after modification which means less extra frameworks of Si-OH, Al-OH and P-OH supporting the good crystallinity of modified samples from SEM and XRD characterizations. But all these findings of acidity change need to be verified by Pyridine FTIR which is not feasible for SAPO-34 due to its small pores that will not allow pyridine molecules to diffuse so NH_3 -TPD was used to support our claims.

Also, Fourier Transform Infrared Spectroscopy (FTIR) was carried out for BSAPO-34 catalysts to identify the surface functional groups. The FTIR spectra was helpful to evaluate silicon incorporation, CHA structure formation, Phosphorus location, physical adsorption and Bronsted acidity. The framework vibrations of synthesized catalysts are identical to CHA phase as shown in **Fig. 28**. It was observed that silicon was incorporated as SiO_4 form inside the SAPO-34 structure based on bending at 490 cm^{-1} . XRD finding of SAPO-34 phase for all samples was confirmed by a peak at 640 cm^{-1} which belongs to D-6 ring formation of CHA phase. Also, the asymmetric and symmetric O-T-O stretches were detected by peaks at a wavenumber of 710 and 1110 cm^{-1} respectively. The peak at a wavenumber of 1650 cm^{-1} is attributed to physical H_2O adsorption. Boron presence into the framework of SAPO-34 was identified by peaks at a wavelength of 670 and 920 cm^{-1} which attributed to B-O-Si stretch. Moreover, the peak at a wavelength of 1400 cm^{-1} appeared after ion exchange with NH_4NO_3 to remove sodium attributed to B-OH stretch. The peaks at a wavenumber of 3450 and 3590 cm^{-1} are attributed to bridging hydroxyl group of Si-OH-Al which have a share of Bronsted acid sites and hydroxyl group associated with the tetrahedral atom (T-OH)[27]. It is clear the positive effect of boron for acidity where the peak intensified after boron added indicating higher Bronsted acidity which is favorable for light olefins formation.

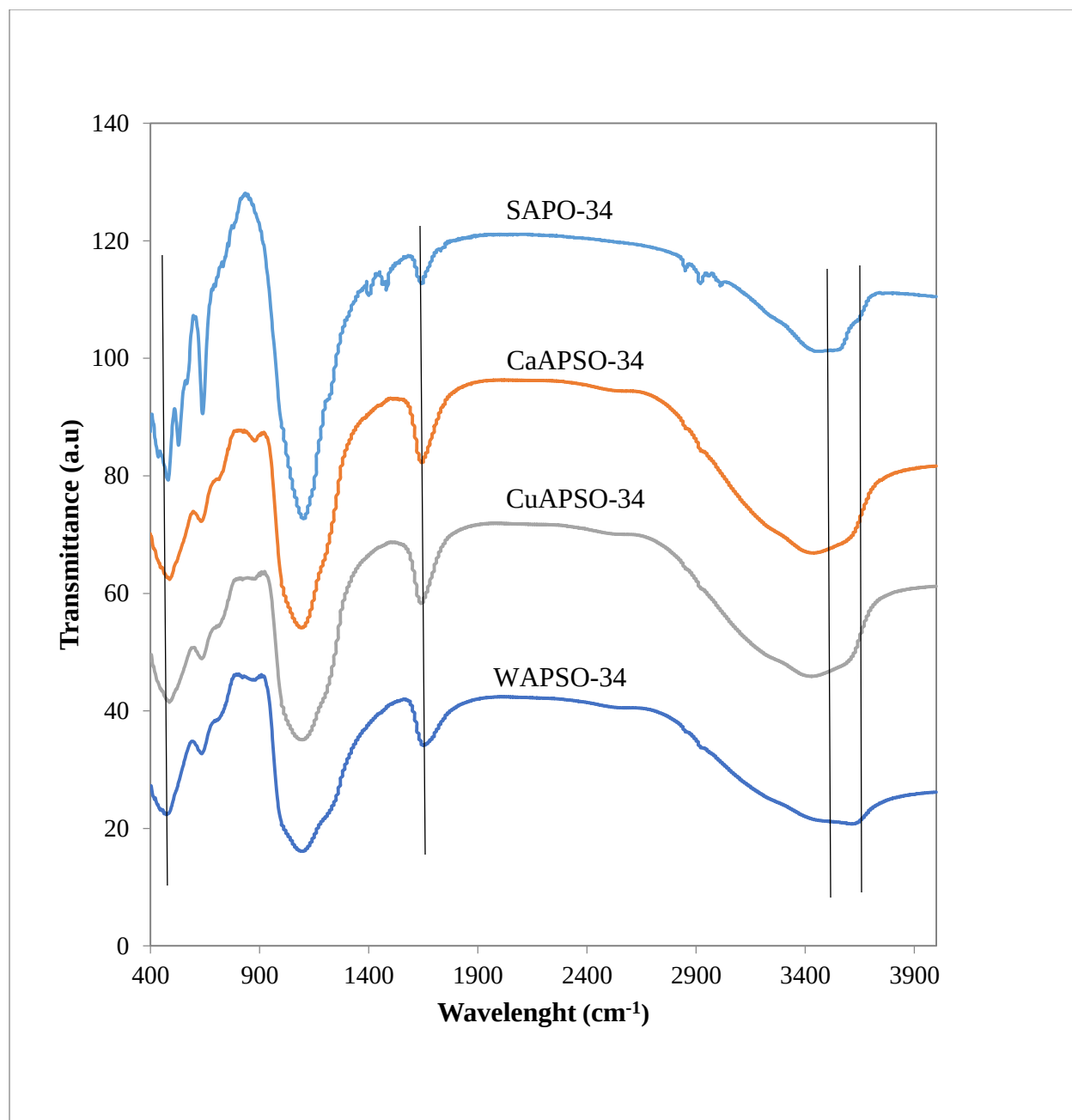


Fig. 27. FTIR analysis for metal in-situ incorporated SAPO-34

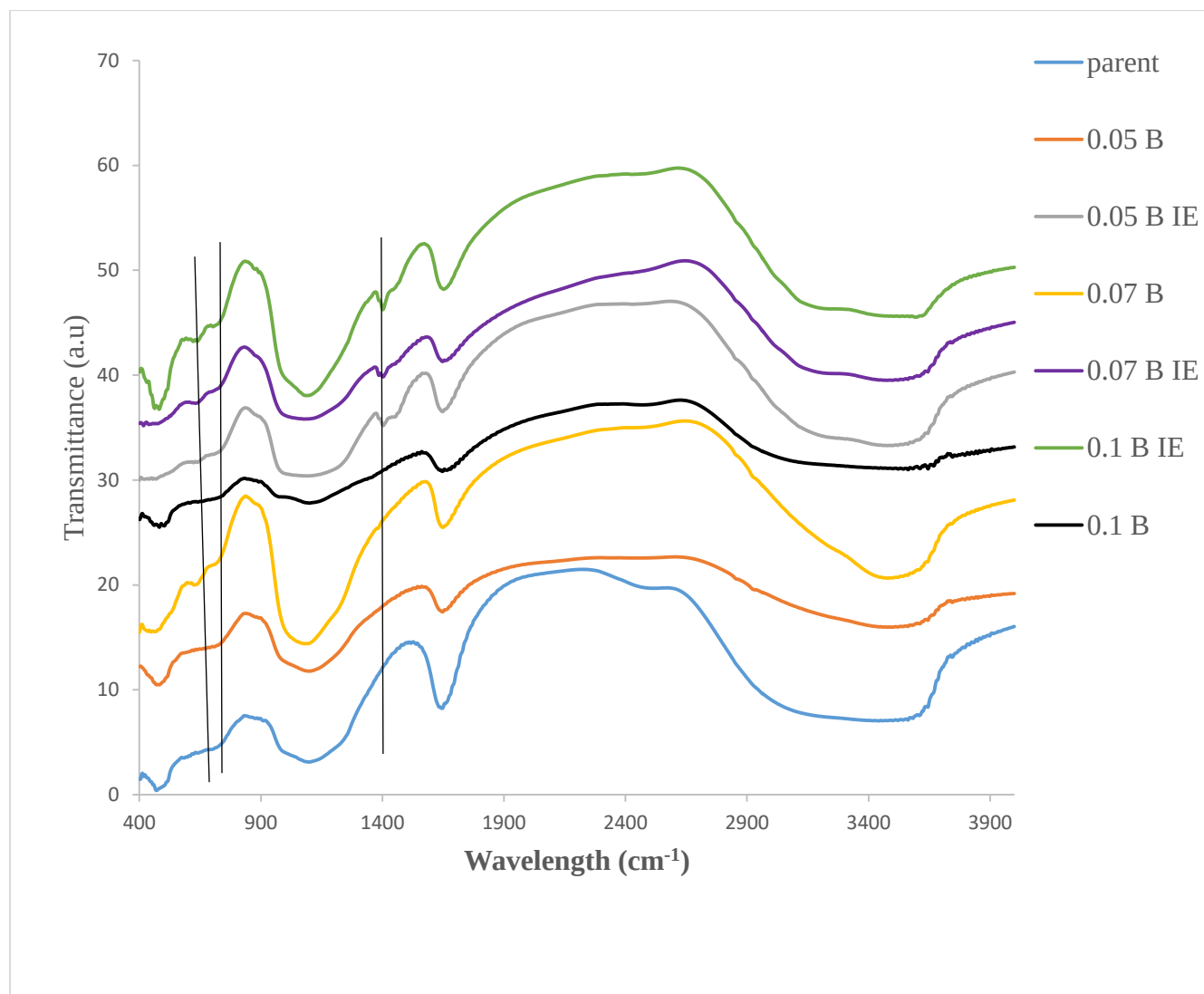


Fig. 28. FTIR spectra for B-SAPO-34 catalysts before and after ion exchange

4.1.7 Diffuse Reflectance Ultraviolet-Visible Spectroscopy (Dr UV-VIS):

The diffuse reflectance (DR) UV-Vis spectra of synthesized samples are shown in **Fig. 29**. The Metal location in the SAPO-34 framework was investigated by Dr UV-VIS technique. It was observed that no absorption bands for both parent and MePASO-34 samples. The broad band was detected in the wavelength of 220-260 nm for both parent and MePASO-34 samples. This broad band is attributed to Al-O charge transfer transitions of Aluminum tetrahedral species in or outside framework [65]. There are small bands overlapped with this broad band in low and high wavelength attributed to tetrahedral and octahedral metal species respectively [61], [66]. Weak bands were observed as shown in **Fig. 30** in the wavelength of 260-350 nm which indicates the metal presence in tetrahedral form MeO_4 . On the other hand, the octahedral metal species were not formed due to bands absence in the wavelength of 660-730 nm. Also, there is a shift to the left of broad band location for modified samples due to the metal substitution of aluminum into the framework. Moreover, there are no aluminum extra frameworks for both parent and MePASO-34 samples where no weak bands observed at 850-950 nm wavelength [27].

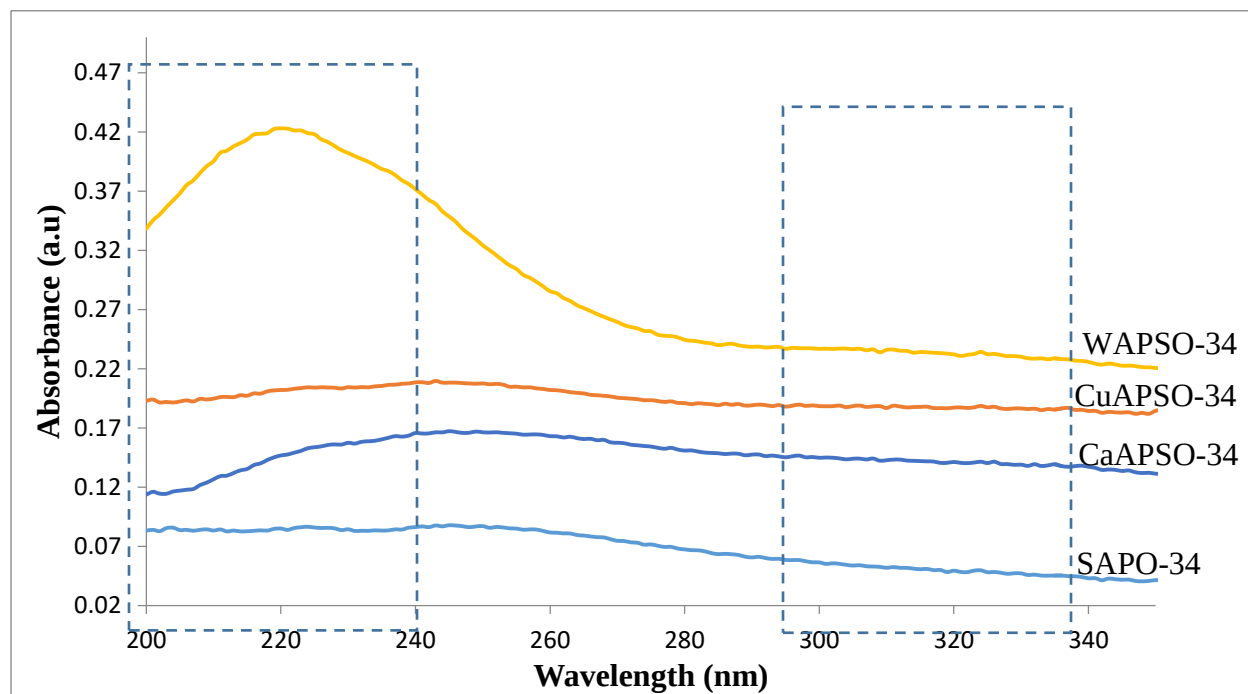


Fig. 29. The UV-VIS spectra of synthesized MeAPSO-34 samples

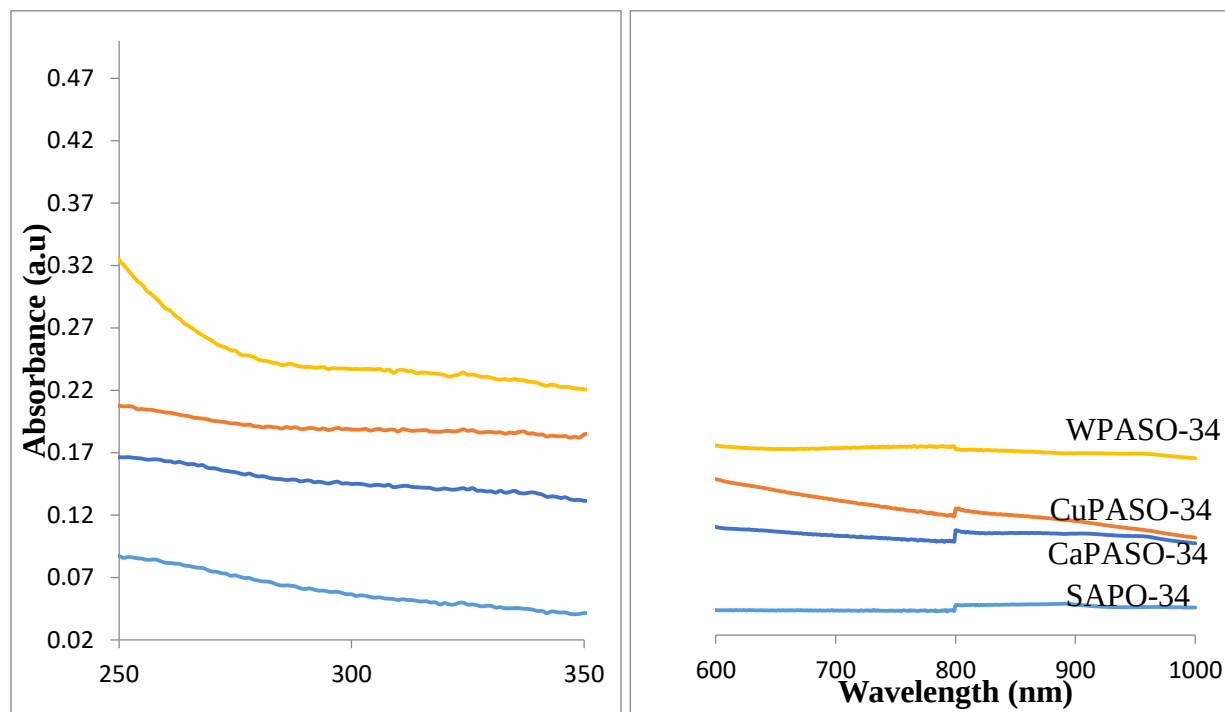


Fig. 30. Dr UV-VIS spectra of metal in-situ modified SAPO-34 catalysts

4.2 Catalytic testing Set-up

The modified SAPO-34 catalysts were evaluated using a tubular fixed bed reactor made of stainless steel at atmospheric pressure as shown in **Fig. 31**. First, the pelletized catalyst was packed in the middle of the bed in between two quartz wool pieces. Then, the pretreatment of catalyst was performed prior to testing by heating to 500 °C for 1 h under helium gas flow to remove the moisture. The reaction feed consisted of 5 mole% of methanol and 95 mole% He, which was used as a carrier gas to facilitate the diffusion. The activity of synthesized catalysts was examined at 350 °C to reduce energy consumption and evaluation at harsh conditions. The Methanol conversion and product selectivity were evaluated with varying time of stream (TOS). The weight hourly space velocity (WHSV) was kept constant at 4.85 h⁻¹ during the reaction. Reaction products were analyzed by on-line Shimadzu gas chromatography equipped with a flame ionization detector (FID) and capillary column HP-PLOT (30 m × 0.53 mm, 6 μm film thickness).

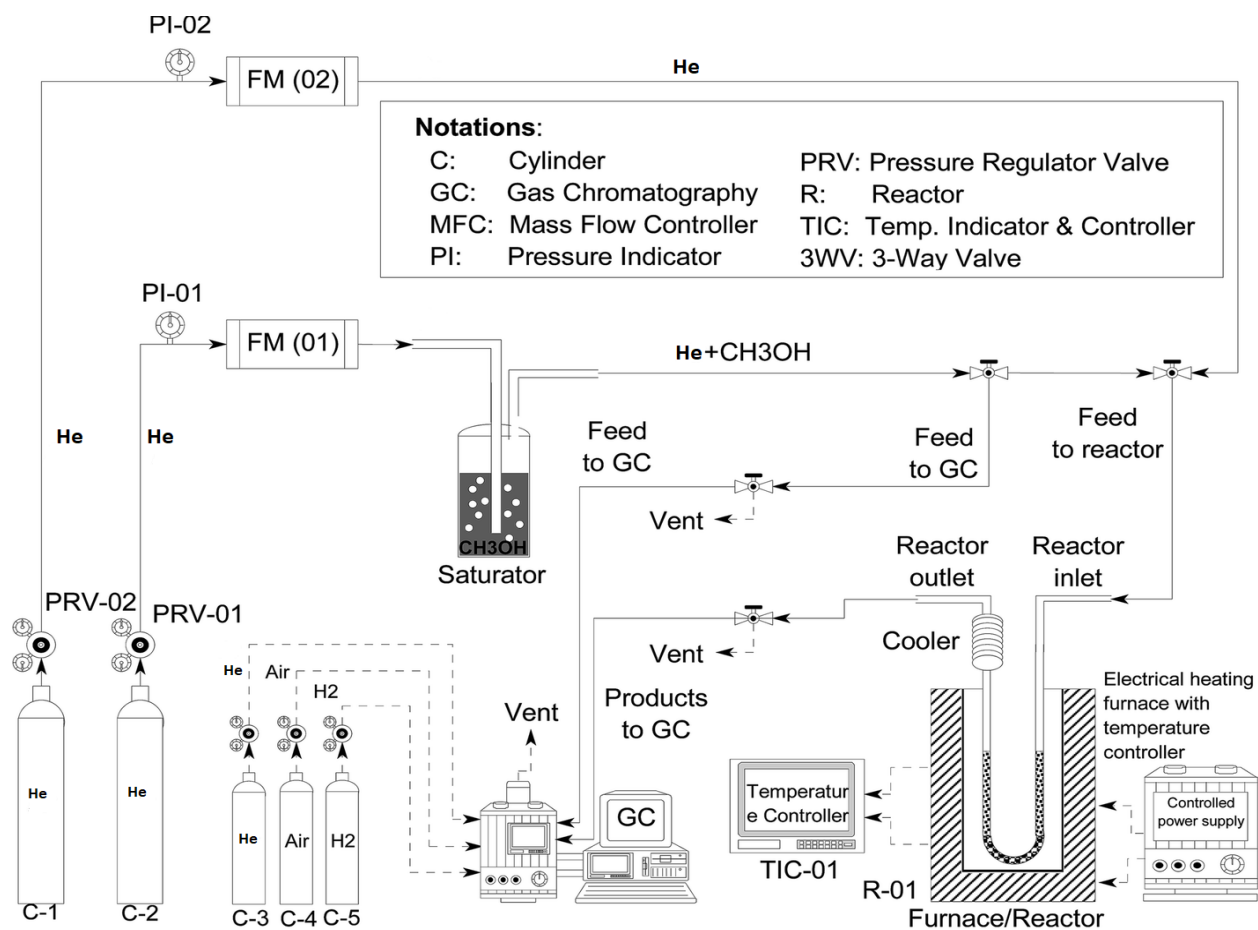


Fig. 31. Fixed bed reactor used for MTO catalytic evaluation

4.3 Catalytic performance of the synthesized catalysts

The catalytic performance is reported in below figures where methanol conversion and light olefins yield were calculated for different catalysts with time on stream. The catalytic testing of synthesized samples was carried out at 350 °C, 1 atm and space-time of 6.6 g_{cat} h/mole. All synthesized catalysts showed high selectivity towards olefins at the startup time which can be justified by the acidity and special pore structure of parent and modified samples. Generally, the light olefins yield was declined for all catalysts due to deactivation by coking. But, propylene and butene were influenced more than ethylene because of favorable suppression of higher weight intermediates which produce higher olefins. Also, the methanol conversion was decreased with time on stream due to blockage of methanol molecules to access active sites by accumulated coke. MeAPSO-34 catalysts exhibited better catalytic stability during reaction compared to unmodified parent catalyst by cause of the acid active sites decrease which inhibits the formation of heavy aromatic products of coke. Moreover, light olefins formation was enhanced by metal presence inside the SAPO-34 structure which created more active sites that favor olefins rather than paraffin formation.

The Textural properties are considered as an important parameter that affects the catalytic performance. Metal in-situ addition changed the textural properties of synthesized catalysts as presented in **Table 9** of N₂-BET results. Metal in-situ incorporation enhanced diffusion efficiency by creating mesopores that facilitate the flow of methanol and olefins molecules. As a result of this, unwanted hydrogen transfer reactions will be minimized which improved conversion and yield as shown in **Fig. 32** and **Fig. 33**. Moreover, the MeAPSO-34 catalysts showed better adsorption properties as shown in FTIR spectra **Fig. 21** where adsorption peak at a wavelength of

1650 cm^{-1} had grown when metal introduced to the framework. These modifications of textural properties were reflected on conversion stability and selectivity of the MeAPSO-34 catalyst.

As presented in **Table 15**, the metal incorporation into SAPO-34 lowered deactivation rate but their major achievement is favorable olefins production. The characterization results revealed enhancement in morphological, textural and acidity properties for a MeAPSO-34 catalyst which led to this superior catalytic performance. As shown in **Fig. 32**, poor catalytic stability was observed for parent SAPO-34 catalyst where it is deactivated instantaneously. In contrast, the CaAPSO-34 and CuAPSO-34 catalysts maintained a conversion of 95% for an hour of methanol injection. The reasoning for this boost is a reduction of strong acid sites that favors cyclization reactions of aromatics that form coke which blocks diffusion of methanol molecules to produce light olefins.

Light olefins yield of 80% was achieved by parent catalyst at the beginning of the reaction but it reduced momentarily accompanied with DME formation which indicates deactivation. On the other hand, the modified catalysts maintained higher yield for almost 1 h of time on stream. Methanol conversion to olefins passes through two steps where methanol is dehydrated first to DME followed by further dehydration to olefins. The first reaction that produces DME requires the defect structural OH groups (including Si-OH, Al-OH, and P-OH) which considered as weak acid sites and the second step requires strong acid sites of bridging hydroxyl groups (Si-OH-Al) [27]. So, MeAPSO-34 catalysts had preferential selectivity towards light olefins due to its lower acidity proved by NH_3 -TPD and FTIR where Si-OH-Al groups had grown as shown in **Fig. 27** by metal incorporation leading to the higher conversion rate of DME to olefins. Calcium incorporation seems to have a tendency to produce propylene as presented in **Table 15**. While, copper favors ethylene rather than propylene formation. This favorable catalytic activity towards

specific olefin could be justified by the difference in active sites of dealkylation reactions which produce light olefins. The synthesized catalysts showed good catalytic activity in terms of methanol conversion and selectivity where MeAPSO-34 catalysts specifically CaAPSO-34 had light olefins selectivity of almost 60% which is higher than other MeAPSO-34 that tested under similar conditions for MTO reaction. Though the methanol flowrate was double and not diluted as in another work case, our MeAPSO-34 catalyst had a better outcome which proves its effective catalytic performance [23].

On the other hand, WAPSO-34 catalyst showed almost equal selectivity of ethylene and propylene which indicates the small gap between weak and strong acid sites as confirmed by NH₃-TPD. Light olefins yield for different catalyst reduced in the order of CaAPSO-34>CuAPSO-34>WAPSO-34>SAPO-34 as shown in **Fig. 33**. These results reveal the superior enhancement of MTO reaction by earth alkaline metals compared to transition metals in terms of conversion, selectivity, yield and catalytic lifetime. According to above results, the MeAPSO-34 catalyst represents an attractive alternative of a pure SAPO-34 catalyst to convert methanol to olefins.

The post-metal modification enhanced the acidity by adding more acid sites for reactant methanol molecules as proofed by NH₃-TPD results in **Fig. 25**. It was observed that the transition metals such as Fe, Co, and Ni increased the strong acid sites number which enhanced the DME conversion to olefins. Subsequently, the weak acid sites were increased which enhanced the methanol conversion to DME. Moreover, the alkaline metals were ion exchanged to incorporate into the structure which will prolong lifetime. It can be concluded that the Bi metallic post modification improved the catalytic performance of the SAPO-34 catalyst.

The surface area and pore volume of the SAPO-34 catalyst were increased by metal post modification. This effect facilitated the diffusion of reactants and products and minimized the mass transfer resistance which is reflected in the catalytic performance. The Fe/MgSAPO-34 catalyst had the highest conversion and light olefins yield due to its superior textural properties as presented in **Table 11**. So, the strong connection between textural properties and catalytic performance that had been observed for in-situ modified catalysts was confirmed.

As shown in **Fig. 34**, poor catalytic stability was observed for pure SAPO-34 catalyst where it deactivated instantaneously, in contrast, the ion-exchanged catalysts had a conversion of 100% maintained for more than an hour of methanol injection. The reasoning for this boost is a reduction of strong acid sites that favors cyclization reactions of aromatics that form coke which blocks diffusion of methanol molecules to produce light olefins. The IE-MgSAPO-34 catalyst exhibited the best catalytic stability where it maintained 100% conversion for 2 h. The catalyst lifetime reduced by coking in the order of IE-MgSAPO-34 > IE-CaSAPO-34 > IE-BaSAPO-34 > SAPO-34. The impregnation by Fe, Co and Ni reduced the lifetime of the IE-MgSAPO-34 catalyst by the half due to the partial blockage of pores which enhances the cyclization reactions.

Light olefins yield of 85 % was achieved by parent catalyst at the beginning of the reaction, but it reduced momentarily accompanied with DME formation which indicates that deactivation. On the other hand, the ion-exchanged catalysts by alkaline metals maintained 90% yield for 1 h as shown in **Fig. 35** due to lower acidity which helps to resist olefins dehydrogenation. The impregnation of IE-MgSAPO-34 catalyst increased the light olefins yield as shown in **Fig. 37** by adding more acid sites to boost the 2 steps process of methanol conversion to olefins. This acidity promotion effect was indicated by NH₃-TPD profile shown in **Fig. 25** and **Fig. 26**.

The iron-containing catalyst showed the highest acidity which supported its catalytic performance to reach 92.2% C₂-C₄= yield at TOS of 1 h. The enhancement by post modification of SAPO-34 was obvious in **Table 16** where average conversion was elevated from 72 up to 90%. Also, the ethylene and propylene were increased by post modification. The highest conversion was achieved by the IE-MgSAPO-34 catalyst. While the Fe/MgSAPO-34 catalyst had the highest ethylene and propylene selectivity of 25.8 and 23.6% respectively. The IE-MgSAPO-34 formed the minimum DME among other catalysts which supports its excellent stability that observed in **Fig. 34**.

Table 15. The conversion and product selectivity of in-situ modified catalysts at 350⁰ C, 1atm, 5 mole% MeOH and W/F=6.6 g_{cat}*h/mole

Catalyst	Conversion (%)	C2= (%)	C3= (%)	Paraffin (%)	DME (%)
Parent	72.3	16.9	13.1	11.5	55.4
CaAPSO-34	90.7	24.9	33.8	8.0	30.9
CuAPSO-34	87.7	26.3	22.7	7.9	35.1
WAPSO-34	74.0	19.8	21.1	10.2	41.8

Table 16. The conversion and product selectivity of post modified catalysts at 350 °C, 1atm, 5 mole% MeOH and W/F=6.6 g_{cat}*h/mole

Catalyst	Conversion (%)	C2= (%)	C3= (%)	Paraffin (%)	DME (%)
Parent	72.3	16.9	13.1	11.5	55.4
IE-MgSAPO-34	93.7	24.1	22.3	6.5	40.4
IE-CaSAPO-34	91.9	22.7	20.8	8.7	42.5
IE-BaSAPO-34	90.1	23.5	21.9	8.3	43.2
Fe/MgSAPO-34	91.9	25.8	23.6	7.6	42.6
Co/MgSAPO-34	91.2	24.8	22.9	7.9	43.4
Ni/MgSAPO-34	90.6	24.3	22.5	8.2	43.9

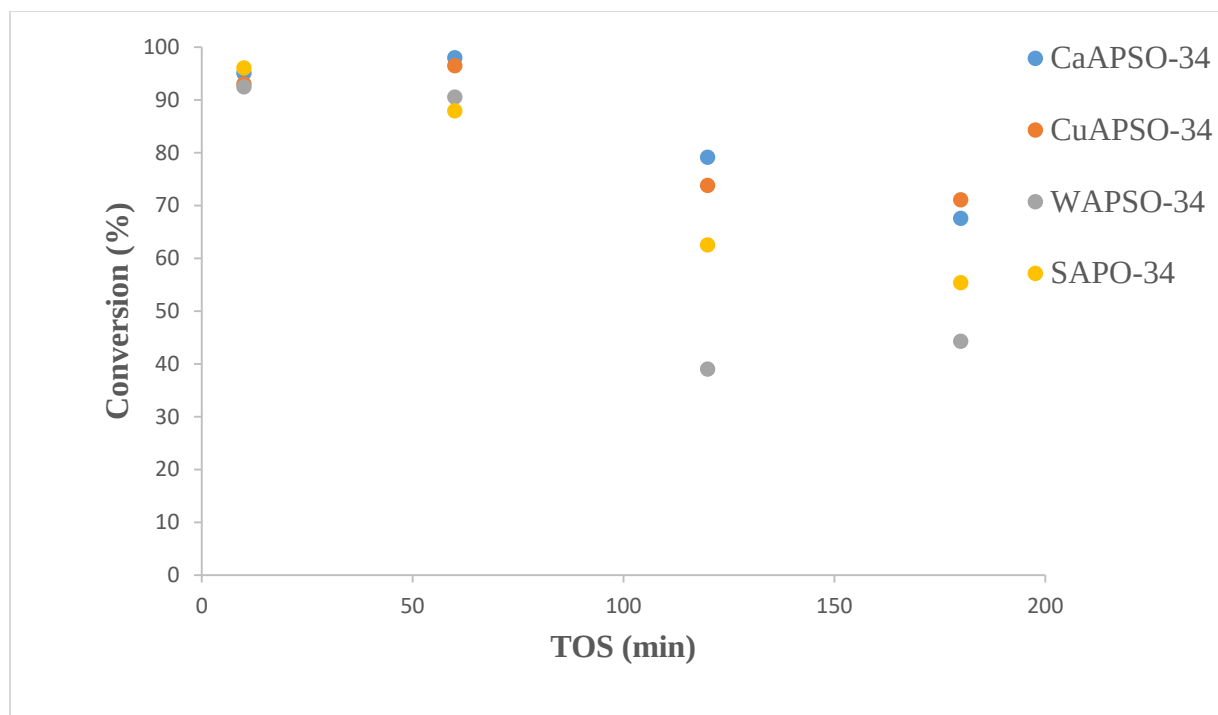


Fig. 32. The methanol conversion using in-situ metal modified SAPO-34 catalysts

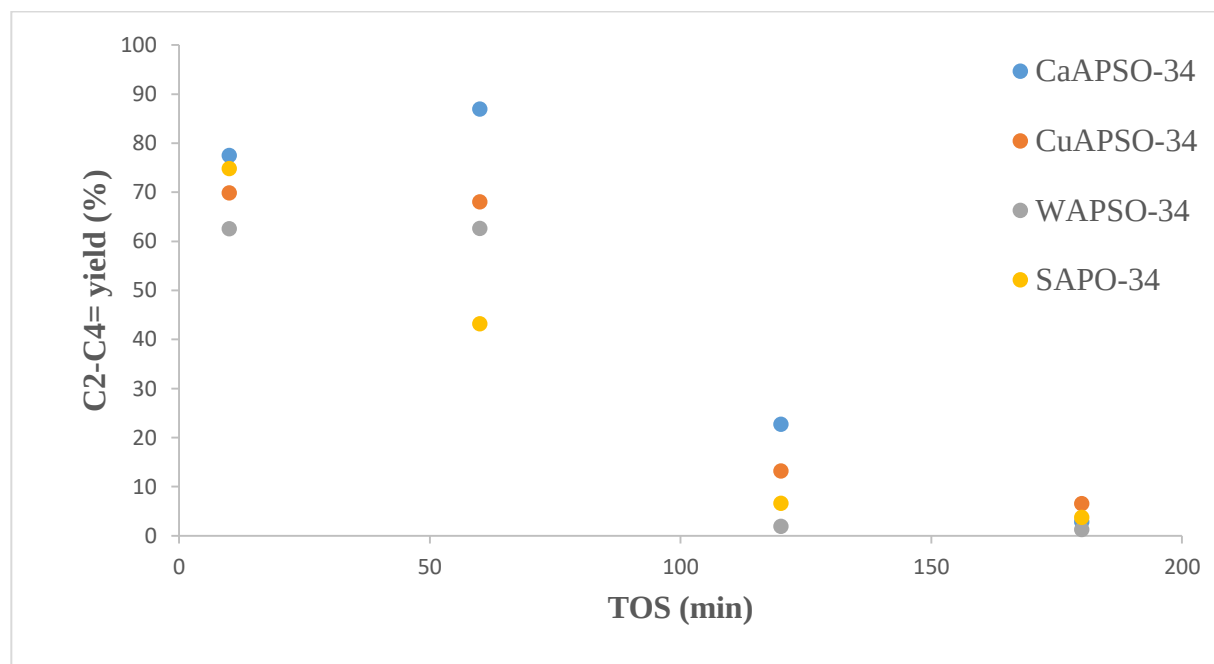


Fig. 33. The C2-C4= yield using in-situ metal modified SAPO-34 catalysts

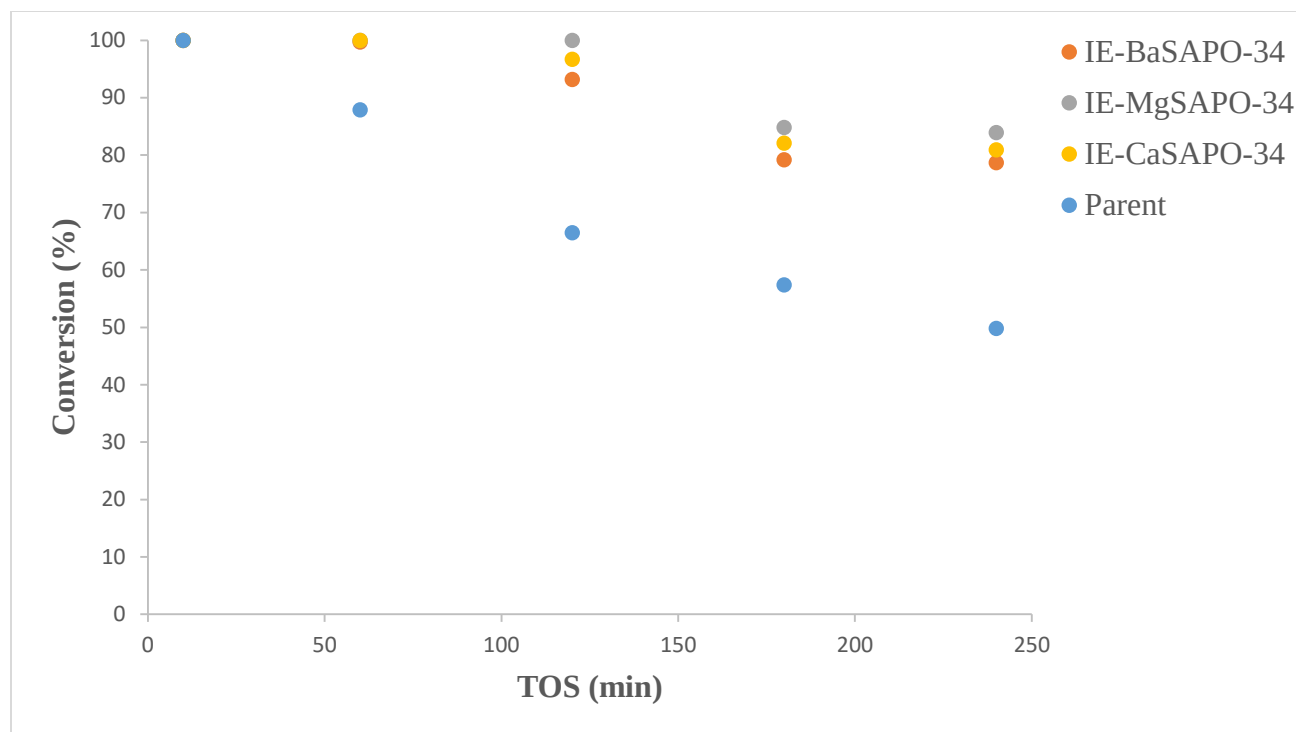


Fig. 34. The methanol conversion of ion-exchanged SAPO-34

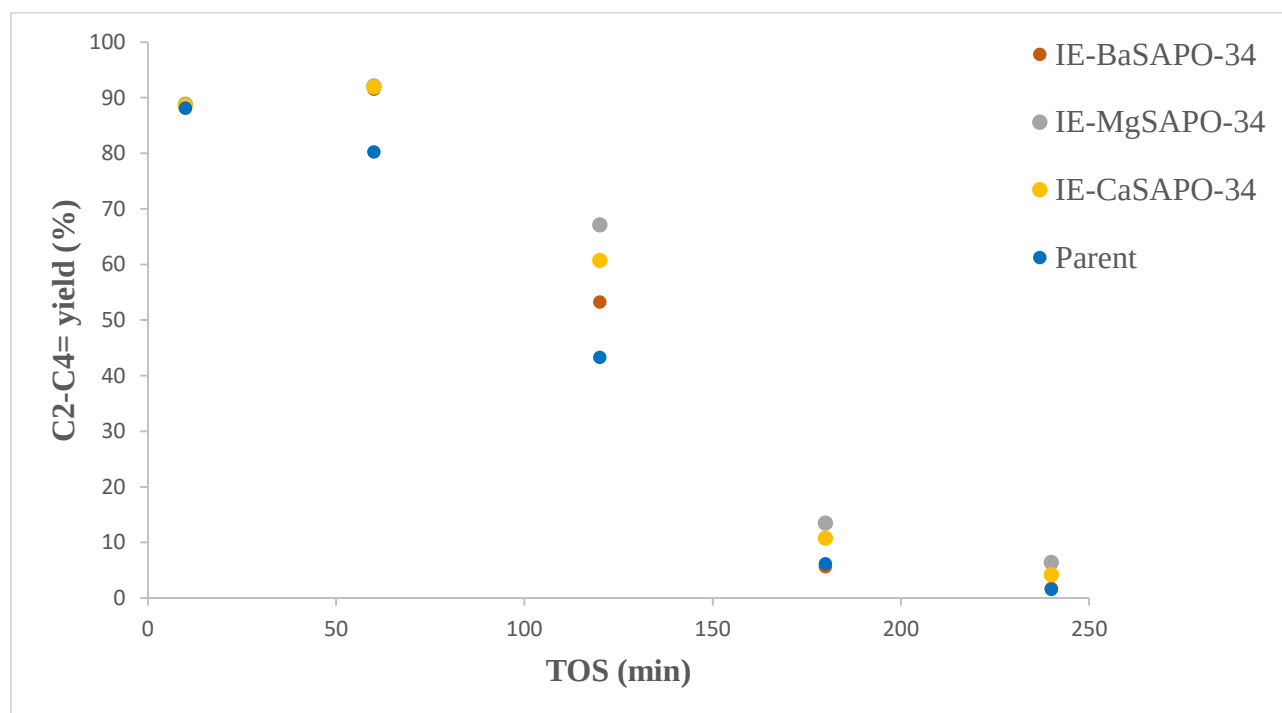


Fig. 35. The C2-C4 yield of ion-exchanged SAPO-34

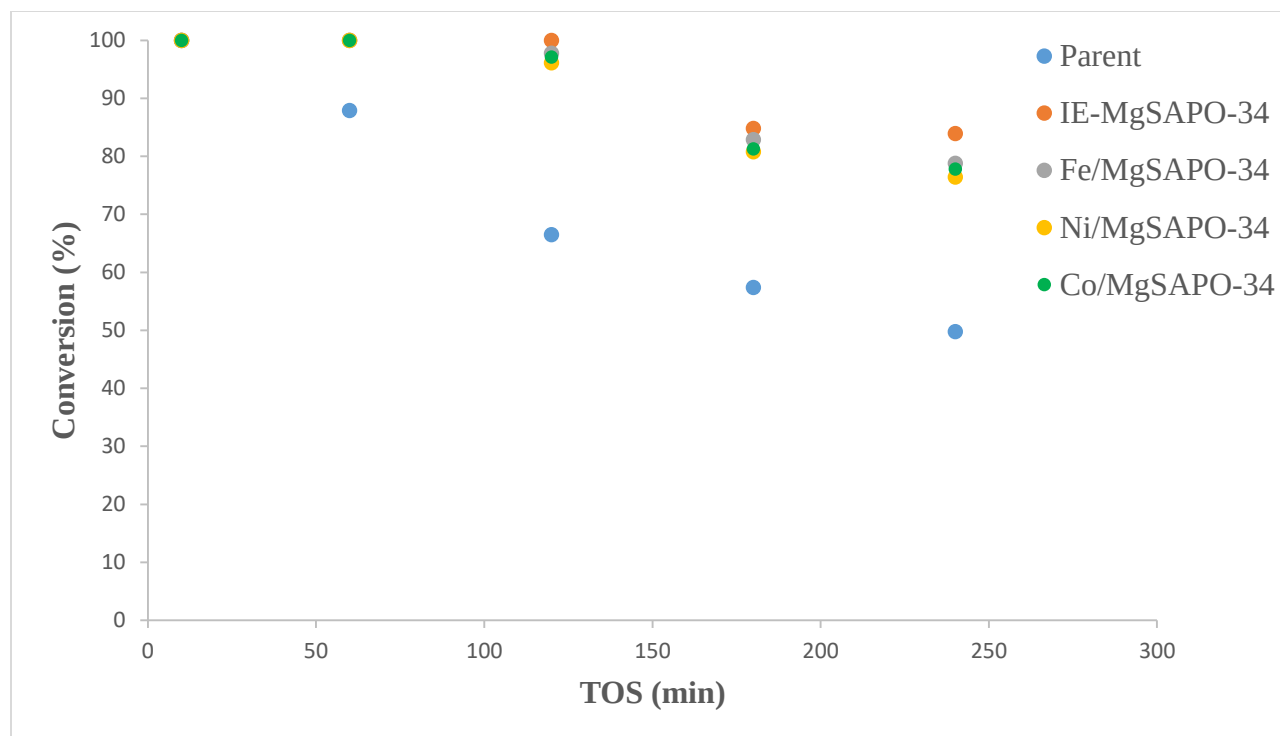


Fig. 36. The methanol conversion of Bi metallic modified SAPO-34

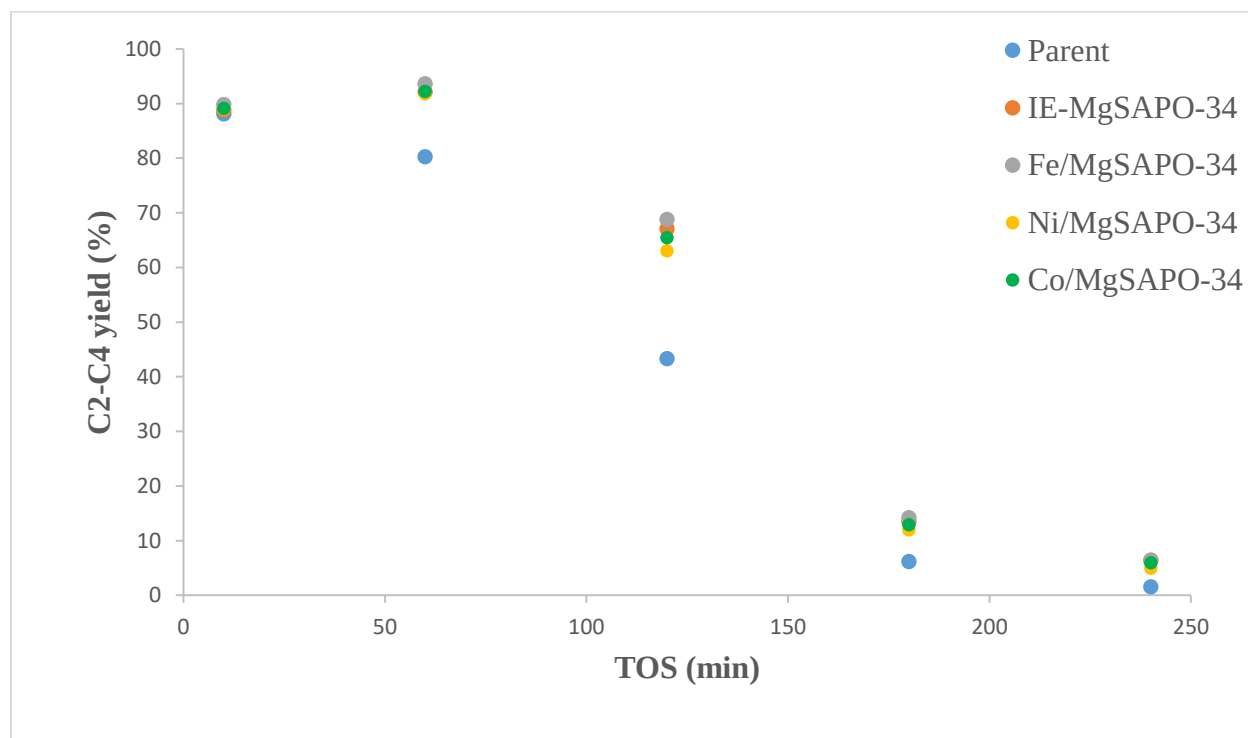


Fig. 37. The C2-C4 yield of bi metallic modified SAPO-34

Chapter 5

Conclusion and recommendations

5.1 Conclusion

The SAPO-34 catalyst was prepared by a hydrothermal method using TEAOH as a template. The catalytic performance of parent catalyst was not stable. So, it was modified to improve catalytic performance by in-situ and post modifications. The in-situ modification divides into metallic and nonmetallic where alkaline or transition metals and boron were incorporated into the framework of SAPO-34. Copper, calcium, tungsten, and boron were selected for in-situ modification of SAPO-34 catalyst. Smaller particles were produced by in-situ modification with narrower size distribution. Also, in-situ modification enhanced textural properties by creating more mesopores. The activity of synthesized catalysts was examined for MTO application. The in-situ Incorporation into framework reduced both intensity and strength of the acid sites as proofed in NH_3 -TPD profile. On the other hand, the post-modification of SAPO-34 was performed either by metallic addition or chemical treatment. Subsequently, the physicochemical properties were improved as proofed by excellent morphological, textural and acidity characteristics as observed in FESEM, N_2 -BET and NH_3 -TPD characterizations.

Different catalysts had been tested at harsh conditions to evaluate their activity and they showed promising results. The in-situ and post metallic incorporation improved catalyst lifetime and light olefins selectivity. It was observed that in-situ modified catalysts supported propylene production over ethylene due to their higher strong acid sites intensity. While, the post modified catalysts exhibited the opposite preference. The light olefins yield was reduced in the order of $\text{CaAPSO-34} > \text{CuAPSO-34} > \text{WAPSO-34} > \text{SAPO-34}$. The CaAPSO-34 showed the best catalytic performance

among other in-situ modified catalysts due to its better acidity tuning. Furthermore, the metallic post modification enhanced the lifetime and selectivity towards olefins. The ion exchange by alkaline metals prolonged the lifetime to reach 2 h for the IE-MgSAPO-34 catalyst. After, it was impregnated by nickel, cobalt, and iron. The light olefins formation was improved as a result of the growth of strong acid sites as confirmed by NH_3 -TPD results. Finally, it can be summarized that the post modification is more attractive option to enhance the SAPO-34 catalyst for MTO reaction because of higher incorporation percentage and better acidity adjustment compared to the in-situ modification.

5.2 Recommendations

This study can be improved by further research work to optimize the synthesis and reaction conditions, to obtain better catalytic performance in terms of stability and products distribution.

The following recommendations are highlighted for future work:

- Further work on the dealumination either by acids or steam to establish efficient method to adjust catalyst acidity after the synthesis based on the reaction results.
- Better accessibility for N₂-BET, NH₃-TPD and NMR characterizations to monitor the change of physicochemical properties by various modifications.
- The reaction mechanism and network need to be studied deeply for a better understanding of the actual enhancement needed.

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Languages

- **Arabic:** mother tongue
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Objective

- I have the desire to contribute to an established company and improve my skills and knowledge holding paramount the safety, health, and welfare of the public.

Education

- August, 2015-december, 2017: King Fahd University of Petroleum and Minerals, Dharhan ,Saudi Arabia
 - M.Sc. (Honor Degree, First Class) in Chemical engineering.
- 2008 – 2013: University of Khartoum, Khartoum, Sudan
 - B.Sc. (Honor Degree, First Class) in Chemical engineering.
- 2005 – 2008: African council Secondary School, portsudan, Sudan
 - High School Certificate – Scientific Branch.

Publication

- Catalytic enhancement of SAPO-34 for Methanol conversion to light olefins using in-situ metal incorporation (under review).

Conferences

- 4th Saudi International Nanotechnology Conference (Oct, 2016)
- Workshop of Nanomaterials development for petro-catalytic applications (Oct, 2016)
- 26th and 27th Annual Saudi-Japan Symposiums (Nov, 2016 and 2017)
Theme: “Catalysts in Petroleum Refining and Petrochemicals”

Work Experience

January. 2014 –June.2014:

- **Part time Teaching Assistant at University of Khartoum:** Computer Applications
- course includes the following contents:
 - EZ Solver.
 - HYSYS.
 - Super Pro Designer Software.
- **Part time Teaching Assistant at University of Science and Technology:** For following courses:
 - Fluid mechanics lab.
 - Corrosion engineering lab.
 - Heat transfer lab.
 - Chemical engineering principles tutorial.

June .2014-september .2014

- **Production engineer at almohandis paints factory:**
- Ensuring availability of raw materials, skilled and trained labor, utilities and appropriate state of equipment to run.
- Supervision of production processes for high quality and safe product.

September.2014-august.2015

- **Production supervisor at henelie spray dried gum factory , Elie holding group:**
- Make sure all production units are ready to run and availability of production inputs.
- Operation of various equipment and ancillaries manually or using control unit.
- Supervision of production processes and monitoring FSMS ISO-22000 application for high quality and safe product.
- Plan and organize resources to get maximum productivity.

September .2016-december .2017

- **Part time teaching assistant at King Fahd University of petroleum and minerals:**
- Grading home works and quizzes of CHE425 and CHE306 courses.

June .2016-december .2017

- **Part time Research engineer at CENT KFUPM RI under the CENT2206 project**
- Development of methanol conversion to olefins
- Catalysis and reaction kinetics research
- Scientific publications and patents