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Dehydration of Alcohols to Olefins Catalyzed by ZrAPSO-34 Molecular Sieve

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Abstract

The lower olefins (Ethylene, propylene, and butylene) are considered the key to the polymeric and petrochemical industries. Dehydration of alcohols to produce light olefins (Methanol-to-olefins reaction) over SAPO-34 molecular sieve has attractedintoigh attention. Modified SAPO-34 zeolite catalyst with Zr metal was successfully prepared under microwave irradiation using morpholine as a structure direct agent. The microwave energy power used was 800 w and the crystallization time was 200 min. The catalyst sample was characterized by XRD, SEM, EDX, BET, FTIR, and TGA analysis. XRD analysis exhibited a typical chabazite structure with high crystallinity. The analysis showed macrocrystalline particles with moderate distribution of silica in the framework structure and a low surface area of 77 m^2/g. The vibration peaks of the prepared catalyst showed agreement with the SAPO-34 CHA structure. Catalyst performance towards methanol-to-olefins conversion was performed in a trickle bed reactor with temperatures of 350, 400, 450, and 500 ^oC at a weight hourly space velocity of 7.7 h^{-1}. The results also reveal at a temperature of 400 ^oC , that the best olefins selectivity was obtained, reaching 70%, with a longer lifetime of 500 min. methanol conversion was almost 100% at all reaction temperatures. In addition, the effect of methanol concentration was investigated and the results showed that increasing of water content plays a role in increasing catalyst lifetime and preventing coke depositions in pores.

Keywords: SAPO-34 zeolite catalyst; Zr metal incorporation; microwave irradiation; MTO, selectivity.

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1- Introduction

The crude oil domination in reserves has swayed sustainable research towards finding another source for energy and industrial raw materials [1, 2]. In recent years, light olefins have great attention in the industrial fields, especially for polymers such as fibers, plastics, and cosmetics [3, 4]. Light olefins (ethylene, propylene, and butylene) are produced largely from the thermal cracking of hydrocarbons with high temperatures (about 850 ^oC) [5]. In order to obtain high amounts of light olefins with low consumption of raw materials and energy, it must choose a suitable catalyst, operating conditions, and feedstock [6]. Zeolite catalyst is used widely in the industrial and wastewater fields [7-9]. One of the most important factors in operation is light olefin selectivity, which depends on catalyst constituents, pores structure, and acidity. Silicoaluminophosphate zeolite (SAPOs) is an appropriate catalyst type used for this purpose [10, 11]. Among SAPO catalysts, SAPO-34 showed good selectivity (higher than 90%) for light olefins ($C2^=$- $C4^=$) production. SAPO-34 is owing to chabazite (CHA) structure topology with a narrow pore framework (0.38*0.38 nm). SAPO-34 was reported to be an excellent catalyst for methanol conversion to light olefins (MTO) [12-14]. The drawback of this type in industrial process is the quick deactivation during reaction because of the coke formation into pores which reduces the catalyst lifetime, and hence, reduces the products [14]. Recently, a modification of promoting SAPO-34 with metals was made for the MTO process. Adding metals to SAPO-34 improves the acidity, increasing the primary reaction and reducing the side reactions [15, 16]. The crystallization using the hydrothermal heating method is widely used for the synthesis of SAPO-34 molecular sieves, but it takes a very long time reach to more than 48 h and consumes energy. Microwave irradiation was applied for the crystallization process instead of the hydrothermal method since it takes less time (< 3 h) [17, 18]. The other facials of microwave heating are the controlling of particle morphology, high crystallinity, and high product yield [19]. The main drawbacks of microwave synthesis are the low uniformity and insufficient irradiation power or time, an impurity phase such as SAPO-5 may form [20]. Merza et al. [21] synthesized modified SAPO-34 by incorporating Fe, Ag, and K ions hydrothermally. They found that light olefin selectivity increased with adding metals and reached 80 %, and also, the lifetime was prolonged to 10 h. Eslami et al. [19] used hydrothermal and microwave heating methods for preparing MnAPSO-

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34. They found that irregular particles with amorphous phases were formed when using low microwave power. For the MTO conversion process, the catalyst synthesized by microwave irradiation showed low selectivity towards light olefins than that prepared with hydrothermal method. Huang et al. [22] used coating method to fabricate SAPO-34/t-ZrO_2. They reported an excellent conversion of methanol to olefins reaching 100% with 90% lower olefins selectivity. Also, the catalyst lifetime was enhanced which reached 1130 min with the increase of 770 min as compared to SAPO-34. Salah Aldeen et al. [23] found that ethylene and propylene yield enhanced by 21.78 wt% and 23.8 wt%, respectively, using 2% Zr and 2% Ce on SAPO-34 catalyst. The mechanical strength of zirconium and thermal resistance could enhance SAPO-34 thermal stability against coke formation, and hence, improve the catalyst lifetime [22]. In addition to metal incorporation, the most important conditions that affect SAPO-34 activity and lifetime during MTO reaction are the operation temperature and water content in the feed [24].

In this work, modified ZrAPSO-34 was prepared under microwave irradiation. Also, a novel material of aluminum chloride was used as an alumina source. TEOS was used as a silica source. The prepared catalyst was characterized using XRD, SEM, EDX, FT-IR, BET, and TGA analysis. The conversion of methanol to light olefins was investigated in a trickle bed reactor to show the performance of the catalyst in lifetime and selectivity.

2- Materials and Method

In the microwave synthesis, the materials used for $Zr_{0.1}$APSO-34 preparation are aluminum chloride hexahydrate ($AlCl_3.6H_2O$, Fluka, 99%), tetraethylorthosilicate (TEOS, Aldrich, 100%), phosphoric acid (H_3PO_4, Merck, 85%), zirconium oxynitrate hydrate (IV) ($ZrN_2O_7.xH_2O$, 30%, Himedea) used as Al, Si, P and Zr sources, respectively. Morpholine (MOR, 99%, Aldrich) was used as the template.

2.1. Preparation of ZrAPSO-34

$Zr_{0.1}$APSO-34 zeolite catalyst was prepared under microwave irradiation method for gel molar composition of AL_2O_3:P_2O_5:0.6SiO_2:4MOR:0.1Zr:60H_2O. At first, 9 g of aluminum chloride was mixed with 16.5 ml of demineralized water and stirred for 30 min. The phosphoric acid solution was mixed in dropwise with the mixture. In this step, PH reduced near one. Then, TEOS was added to the mixture with stirring for 30 min, PH reached less than one. After that, zirconyl nitrate (IV) was added and mixed for 20 min. Afterward, morpholine as a template was slowly added to the mixture at room temperature. The final solution was stirred for 2 h. The precursor was transferred to a Teflon-stainless steel autoclave with a capacity of 100 ml. the, it was placed in a microwave apparatus with irradiation energy of 800 w for 200 min without stirring. After crystallization, the product gel was cooled at room temperature and centrifuged in 2200 rpm for 30 min to collect the solid crystal product, washed three times with distilled water and filtered. The sample dried at 120 °C overnight and then calcined at 560 °C for 5 h to remove template molecules. The synthesized crystal was sampled to analyze it. Then, it was tableted to small particles with 2-3 mm diameter to use in methanol to light olefins conversion.

2.2. Sample characterization

The zeolite catalyst ZrAPSO-34 was characterized with XRD (X-ray diffraction), SEM (scanning electron microscopy), EDX (energy-dispersive X-ray spectroscopy), BET (Brunauer-Emmett-Teller), FT-IR (Fourier transforms infrared spectroscopy) and TGA-DTG (Thermogravimetric analyses) analyzing techniques. The XRD pattern was composed of a Bruker D8 CuKα diffractmeter radiation, = 1.5406 °A in the range of 2θ equal to 5–80. The particle morphology and size were conducted using SEM photos with a Philips XL30 instrument. BET surface area was measured by analyses of N_2 isotherm with ASAP 2010 micrometrics device. FTIR spectra were composed with palletized diluted KBr using Bruker Tensor-27 spectroscopy. TGA–DTG data were obtained in N_2 gas at 20 °C/min and flow of 20 ml/min using the Shimadzu DTG-60 model. The characterizations were performed at Ondokuz Mayıs University in Turkey.

2.3. Experimental setup for MTO

The MTO conversion tests were performed in a laboratory trickle bed reactor. The experimental setup scheme is depicted in Fig. 1. It consists of a gas and liquid feed section, primary heater, trickle-bed reactor, furnace, and analytical section. The process was done in continuous flow at atmospheric pressure. For the MTO process, 2.5 g of ZrAPSO-34 was overloaded into the tubular reactor (d=1.2 cm and L=48 cm). Quartz balls were used to fix the catalyst inside the reactor. 90 ml/min of N_2 carrier flow gas at opened onto the catalyst at 650 °C for 1 h, and then, it cooled to reaction temperature. A feed solution of 30% wt/wt of methanol to water ratio was pumped and the primary heater raised the feed temperature to about 250 °C. The feed vaporized and entered the reactor. The reaction temperature was set up to 350, 400, 450, and 500 °C with a weight hourly space velocity (WHSV) of 7.7 h^{-1}. Methanol conversion, light olefins selectivity, and catalyst lifetime were performed at all reaction temperatures. Methanol to water weight ratio of 30 and 70% was also investigated at 400 °C and 7.7 h^{-1}.

Gas chromatograph BS-GC7820, BIOBASE, China, which was equipped with a Plot-U column and FID (flame-ionization detector) was used for analyzing the product. The structural property of synthesized $Zr_{0.1}$SAPO-34 using microwave irradiation is demonstrated in Table 1.

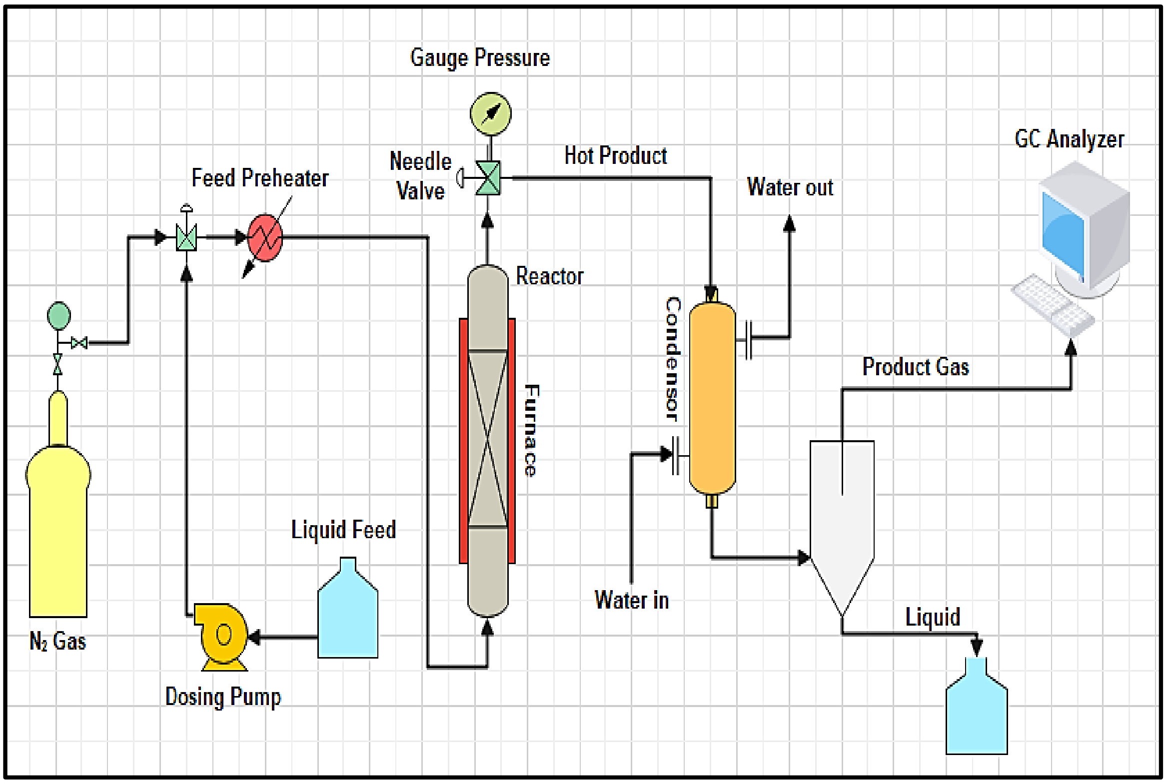

Fig. 1. The Experimental Setup of the MTO Conversion Process

Table 1. Structural Property of Prepared Zrapso-34 with Microwave Irradiation

Sample	Template	Metal incorporated	Heating method	Power (w)	time (min)	BET (m^2/g)	Pore volume (cm^3/g)
SAPO-34	Morpholine	Zr	MW	800	200	77.57	0.22

3- Results and Discussion

3.1. Catalyst Characterization

3.1.1. XRD Analysis

The XRD diffraction pattern of ZrAPSO-34 is shown in Fig. 2. The standard peaks of SAPO-34 are at 2θ = 9.5, 12.8, 15.5, 17.7, 20.5, 26, and 30.5 [25]. The pattern of the prepared catalyst consists of SAPO-34 chabazite phase structure (JCPDS 01087-1527, Rhombohedra) [21]. The observed peaks indicate high catalyst purity as reported in [22, 24]. The modified SAPO-34 zeolite catalyst with the incorporation of Zr metal obviously has a CHA structure with successful fabrication using the microwave irradiation method. This indicates that using aluminum chloride as an aluminum source with, TEOS as a silica source with a MOR template can form a pure SAPO-34 catalyst under microwave irradiation with the existence of Zr metal ions in the framework. It is depicted that metal ions have a positive effect in increasing nucleation rate, and hence, increasing the crystal growth. The metal ions work like a seed and help to form a highly pure phase [26]. It can be noted that XRD analysis showed no peaks of Zr appeared. That is for the perfect Zr diffusion into the surface of the catalyst [23].

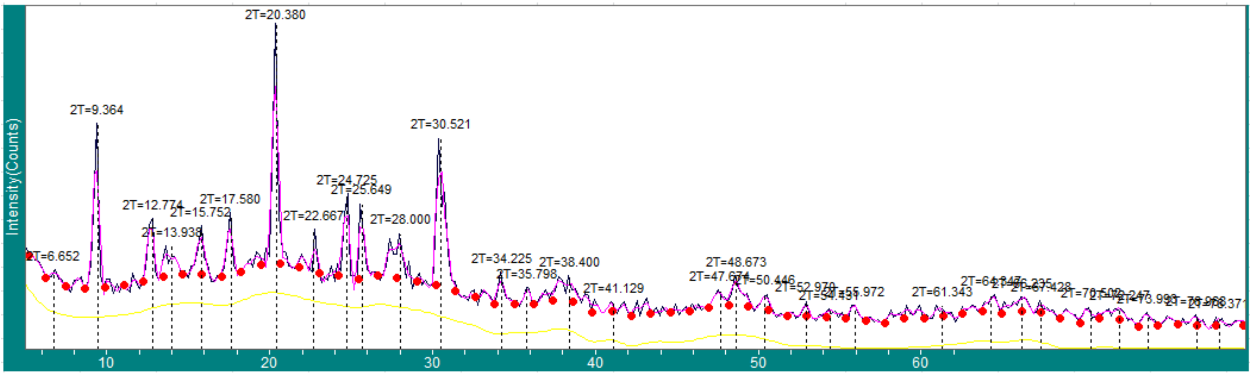

Fig. 2. XRD Patterns Analysis for ZrAPSO-34 Sample

3.1.2. SEM Analysis

Fig. 3 illustrates the scanning electron microscopy images of ZrAPSO-34. The catalyst particles show cubic-like irregular morphology which is similar to CHA structure. The ununiformed cubic type indicates to physical coating of Zr on the catalyst surface during preparation. It is clear that incorporating Zr to catalyst leads to producing cubic structural morphology instead of spherical particles which is almost observed when using microwave heating in the crystallization process. On the other hand, the aggregation caused by microwave crystallization affects the catalyst morphology due to the fast nucleation compared to the hydrothermal method [27]. There is a variation in the morphology of the catalyst. This difference may be attributed to the double effect of using TEOS with a morpholine template. The interaction between morpholine and silica is the major factor that affects the rate of nucleation and crystallization. Using TEOS leads to form a Mono-Si structure unit which causes rapid crystallization. This can make changes in particle morphology [28].

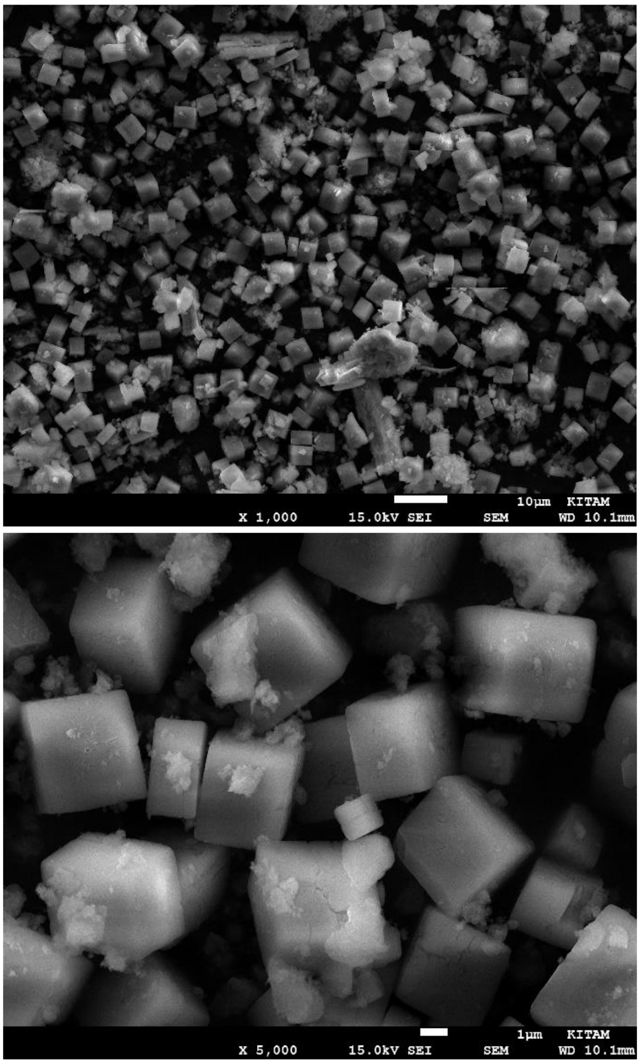

Fig. 3. SEM Images of ZrAPSO-34 Sample

3.1.3. EDX Analysis

The molar ratio of obtained $Zr_{0.1}$APSO-34 catalyst n(Al): n(Si): n(P) is 1.89: 0.17: 0.34. The moderate ratio of Si indicates proper distribution and incorporation of silicon in the catalyst. Fig. 4 shows the EDX dot-mapping analysis of the ZrAPSO-34 sample. The dot-mapping image shows Si has good distribution and density in the catalyst. The proper distribution gives it an important role in framework structure, acidity, and activity in reactions. In other hand, there is a big difference in the molar ratio of Al and P elements [10]. The presence of Zr proves the successful synthesis of modified SAPO-34 with metal incorporation. This variation may be explained to that Zr metal had a crucial effect on silicoaluminophosphate crystal at the nucleation stage which affects the Si coordination structure and the acid intensity of the prepared molecular sieve. For whole synthesized catalyst samples, it seems that the application of high-intensity microwave power with long crystallization time has a great influence on the distribution of elements and metal ions in SAPO-34 synthesis [22].

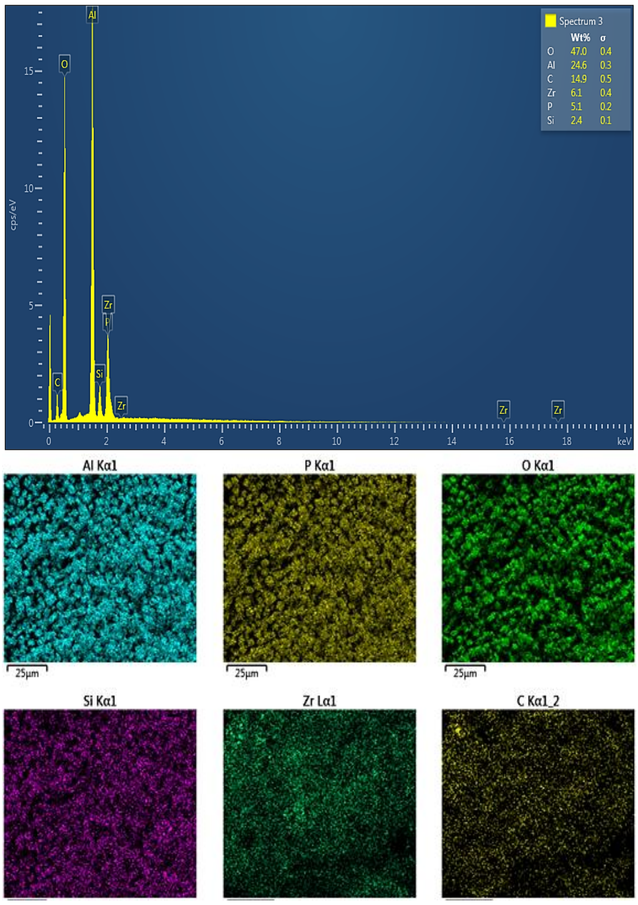

Fig. 4. EDX-Dot-Mapping Analysis of ZrAPSO-34 Sample

3.1.4. BET Analysis

The surface area of the ZrAPSO-34 catalyst was calculated by the BET method of N_2 adsorption/desorption manner as reported in Table 1. The sample remark macroporous structure with a low surface area of 77.57 m^2/g and total pore volume of 0.22 cm^3/g. The average pore radius is 5.6 ^{o}A. The surface area and micropore volume are less than that observed without adding Zr metal as reported in [22-24]. It indicates that the dispersed metal ions of zirconium in the channels and over the particles can reduce the surface area and pore volume [24]. This dispersion causes a reverse effect on reactant diffusion in pores, and hence, may reduce the catalyst activity [29, 30]. The possible explanation for the decreasing surface area is due to the permeation of ZrO_2 oxides into catalyst cavities [23]. Another reason that may be taken into account is that low growth of crystalline surface at short synthesis time with microwave irradiation leads to the production of large particle sizes with small surface area [19].

3.1.5. FT-IR Analysis

The ZrAPSO-34 prepared catalyst which corresponds to the CHA framework structure was characterized by FTIR analysis as shown in Fig. 5. The infrared spectra were in the range of 400-4000 cm^{-1} which gives a wide frequency to get more accuracy in functional groups. The reported vibrations consist of the chabazite SAPO-34 framework. The vibration peaks of spectra of 3420 and 3387 cm^{-1} are of bride hydroxyl groups such as Si-OH and P-OH, respectively. The hydroxyl groups play active site roles in the conversion of methanol to olefins [19]. The peaks of about 2450, 2400, and 2100 cm^{-1} can indicate CO_2 absorption from the atmosphere [21]. The vibration peaks of about 1640 cm^{-1} can be assigned to physical water adsorption. The stretching vibrations of 1330 and 1097 cm^{-1} correspond to O-P-O asymmetric stretching vibration. The peaks of about 711, 634, and 420 cm^{-1} indicate symmetric stretching P-O (or Al-O) vibration, a double six-membered ring of chabazite characteristic of SAPO-34 and T-O bending stretch vibration of SiO_2, respectively [19, 31].

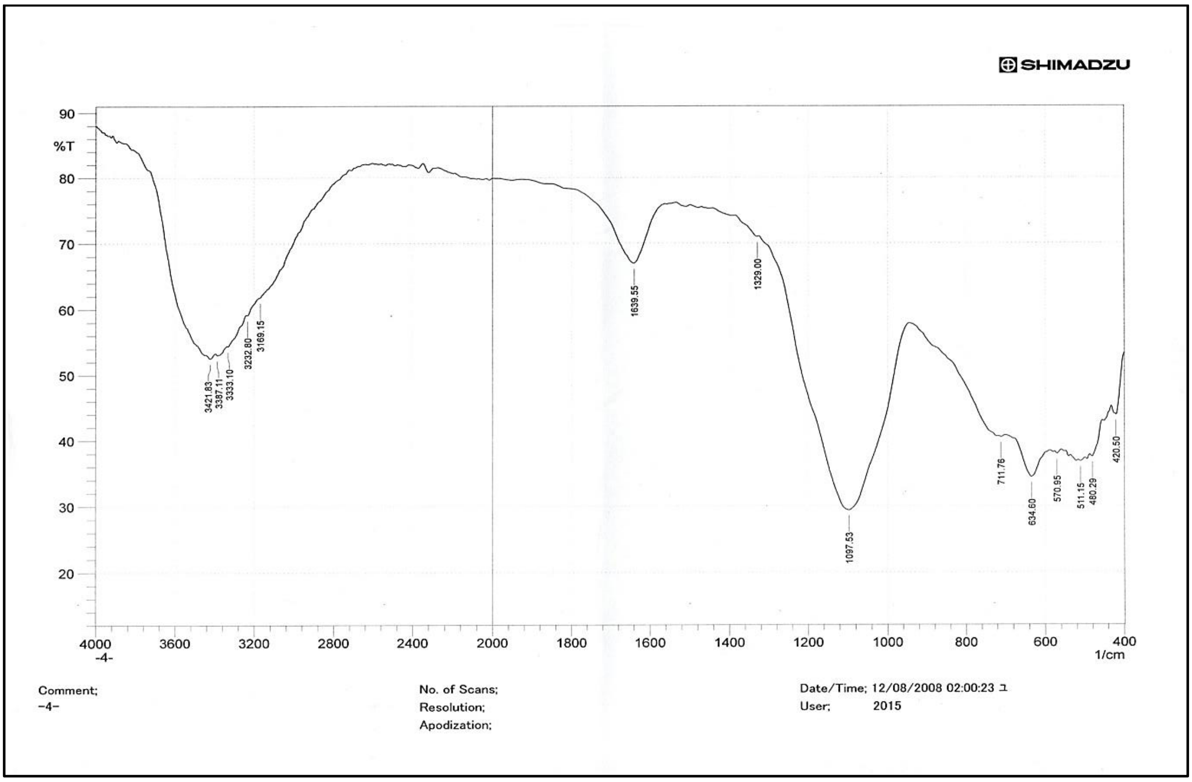

Fig. 5. FTIR Spectra for ZrAPSO-34 Sample

3.1.6. TGA-DTG Analysis

Thermogravimetric TG and differential temperature analysis of the ZrAPSO-34 sample are demonstrated in Fig. 6. The test was conducted at a very high temperature reaching 1100 ^{o}C. The sample showed high stability against coke formation which does not exceed 19% of the initial sample weight. The DTG analysis shows three steps of weight loss. The first region is at 160-190 ^{o}C, which indicates endothermic desorption of water. The second step occurred in the temperature range of 420 to 480 ^{o}C, which is attributed to the exothermic effect associated with the calcination of coke formed [18]. The third is in small effect of losing weight at a temperature of about 900 ^{o}C. The ratio of weight-losing calcination region (region II) is about 3.34%. The DTG shows a drop manner of losing weight decreased in the following order: region I> region II> region III [27]. It can be seen from the results that the ZrAPSO-34 catalyst will show high lifetime performance and moderate mass transfer resistance with high product purity.

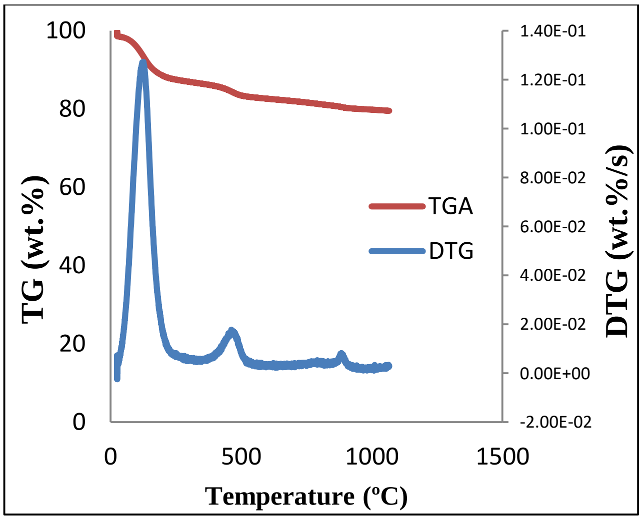

Fig. 6. TGA and DTG Analysis of ZrAPSO-34 Catalyst

3.2. Catalyst Performance

ZrAPSO-34 catalyst performance towards MTO conversion was performed in a trickle bed reactor. The temperature of 350, 400, 450, and 500 °C was investigated for conversion, selectivity, and lifetime with a space velocity of 7.7 h^{-1}. Moreover, the effect of methanol concentration in the feed on the olefin products was also studied.

3.2.1. Methanol Conversion

The conversion activity trend of methanol to light olefins over ZrAPSO-34 zeolite catalyst at various temperatures with WHSV of 7.7 h^{-1} is shown in Fig. 7. The conversion was very high and almost completed for all reaction temperatures. It was 100% for more than 500 min and then decreased by only 3% at time of 600 min. These results indicate to that the optimum temperature for methanol conversion is at ranging from 400 to 450 °C [21]. Also, it can be seen that modified SAPO-34 with incorporated Zr metal offers high thermal stability with a long lifetime in reactions. The obtained results are approaching that reported in [16, 22]. The methanol conversion trend was largely reduced below 90% at a time of 600 min. During this stage, the activity of ZrSAPO-34 decreases which can be ascribed to the coke formation. The inactive coke blocks the pores and channels and prevents the reactants reach the active sites [24]. The catalyst activity depending on reaction temperature shows a coincident trend at 400, 450, and 500 °C. It indicates to very stable catalyst with stable conversion at high temperatures. This is due to the excellent mechanical strength of zirconium metal which provides more catalyst thermal stability [23]. On the opposite side, the conversion of methanol was low at a temperature of 350 °C. this may ascribed to insufficient temperature to complete the conversion inside the pores [13, 27].

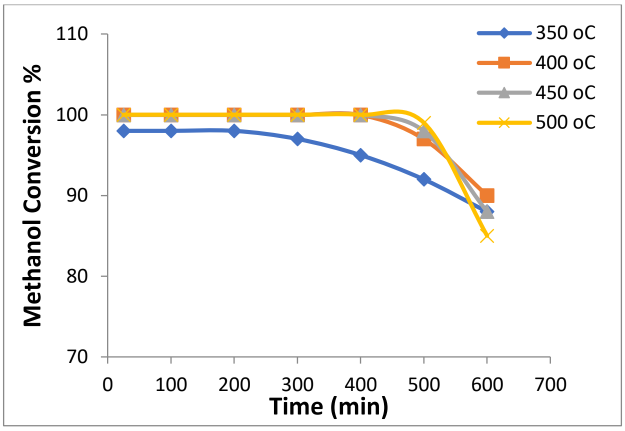

Fig. 7. Methanol Conversion to Light Olefins Over ZrAPSO-34 Sample at Different Temperatures with 7.7 h^{-1} under Atmospheric Pressure

3.2.2. Product Selectivity

The effect of temperature on light olefins selectivity over modified Zr$_{0.1}$APSO-34 is illustrated in Fig. 8. The results showed enhancement of lifetime of catalyst against coke deposition and reduction in light olefins production. By increasing the reaction temperature from 350 to 400 °C, the selectivity of light olefins increased from about 60% for 400 min to 70% for 500 min, respectively. As increasing temperature to 450 and 500 °C, the selectivity reduced to 66% for 400 min and 47% for 300 min, respectively. In general manner, the stability was good before occurring catalyst deactivation, and in the same time, the lower olefin selectivity decreased with high temperature. The best catalyst performance was at 400 °C which had completed conversion with 70% light olefins selectivity and longer lifetime reached to 500 min. According to results, it can be noted that ZrAPSO-34 has a little impact on selective lower olefins of ethylene, propylene and butylene, but it postures a significant effect on conversion and stability. It seems to produce methane and alkanes. The high activity of ZrSAPO-34 toward producing light olefins can be ascribed to the change in the catalytic acidity. The addition of Zr enhances the acidity and strengthens the weak acid [23]. As a result, the efficiency of the catalyst increases. In contrast, the increasing of the surface acidity speeds up the secondary reactions, and hence, reduces the catalytic activity due to coke formation [13, 23]. During microwave crystallization of modified SAPO-34 with Zr metal, the compositing constructed structure of chemical interphase is regulated Si distribution on the SAPO-34 surface, and as a result, modified acid density [13, 16, 19]. The macropore's particle morphology and modified acid density reduce the carbon formation that deposits around the external surface and effectively utilize many active sites within the SAPO-34 framework which reduces the deactivation rate. That leads to enhancing the catalyst's lifetime during reaction [22, 23].

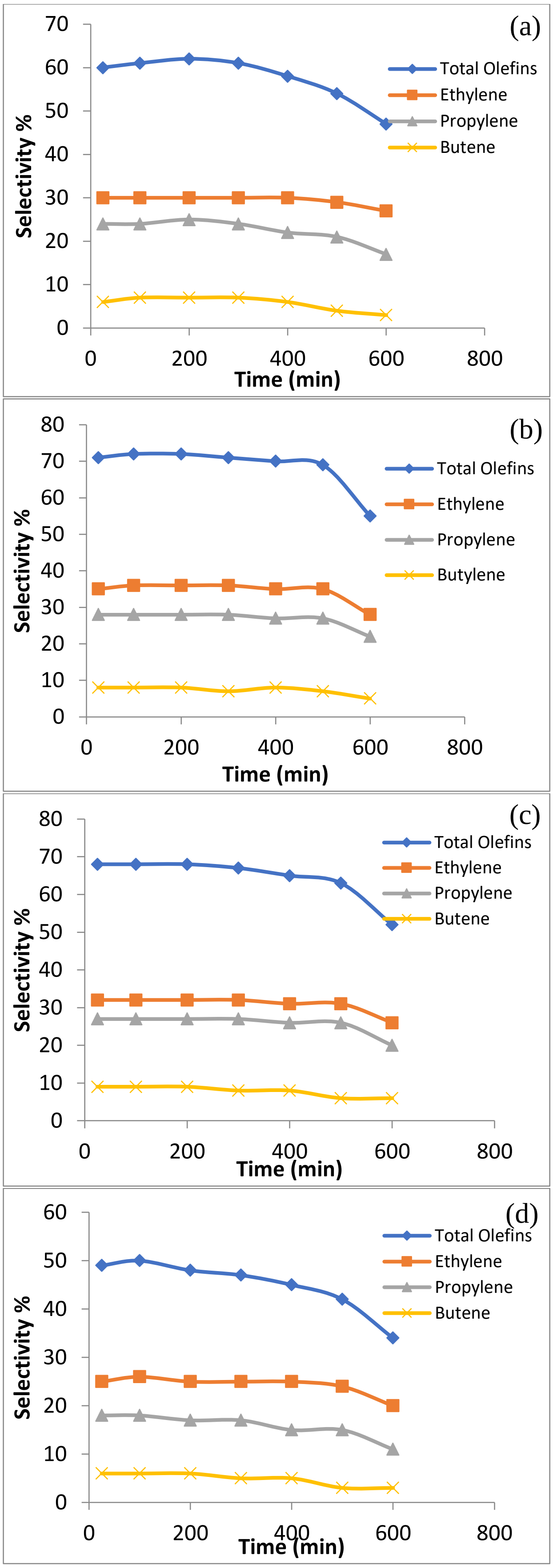

Fig. 8. Light Olefins Selectivity Over ZrAPSO-34 at Different Temperatures, (a) 350, (b) 400, (c) 450 and (d) 500 °C with 7.7 hr^{-1} under Atmospheric Pressure

3.2.3. Effect of Methanol Concentration

In order to recognize the relationship between the concentration of methanol and olefin selectivity, MTO conversion was performed over the ZrSAPO-34 catalyst. Two methanol concentrations of 30 and 70% w/w were studied at 400 °C and 7.7 h^{-1} as demonstrated in Fig. 9. It is reported that by increasing methanol concentration in the feeding stream, the lower olefins selectivity increased slightly under low water content in the raw material feed, but the selectivity decreased sharply after about 250 min of reaction. The high water content in raw material (i.e. 70% water) showed stable product selectivity with a lifetime longer than 500 min. The reporting results are approaching that reported in [24, 32, 33]. This trend of light olefins selectivity and catalyst lifetime indicates the clear effect of water content on methanol reaction over catalyst [24]. The high quantity of water prevents the coke deposition on pores and plays a role as steam around the catalyst which helps to dehydrate H_2O molecules from alcohols[33]. Also, it carries the coke formed far from the catalyst during the reaction process. The diluted feed for the MTO reaction reduces the paraffin and aromatic selectivity, hinders the coke deposition inside pores, and prolongs the catalytic lifetime [34].

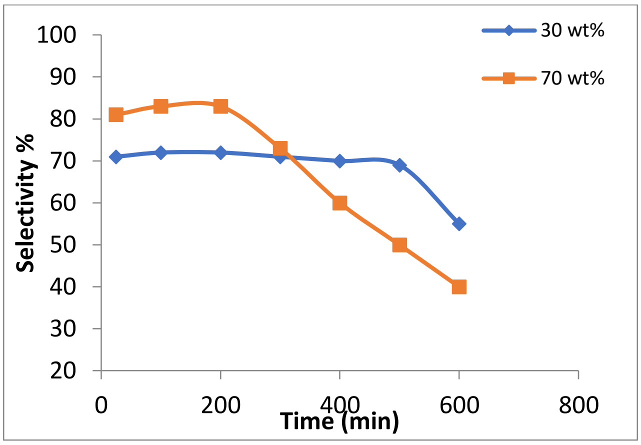

Fig. 9. Effect of Methanol Concentration on Light Olefins Selectivity at 400°C and 7.7 h^{-1} under Atmospheric Pressure

4- Conclusions

In summary, the MTO reaction is considered an alternative and effective in producing lower olefins. SAPO-34 molecular sieve catalyst improved high efficiency for this purpose. In order to enhance the catalyst activity, selectivity, and lifetime, metals were incorporated into SAPO-34 with the initial gel. For its high mechanical strength, thermal stability, and moderate acidic sites, zirconium metal was incorporated with SAPO-34. $Zr_{0.1}$APSO-34 zeolite catalyst was successfully prepared using the microwave heating method. A high irradiation power of 800 w was used for the crystallization process for 200 min. The characterization analysis of the catalyst showed high crystallinity with the typical chabazite structure of SAPO-34. The surface area of the catalyst was low for its large particles due to the effect of metal oxide which may block the pores. The catalyst showed good selectivity of light olefins in the MTO conversion process. The results showed that high reaction temperatures decrease olefin production and increase methane and alkanes. It was reported that MTO conversion was almost 100% with a long catalyst lifetime. The optimum operation temperature which yields higher conversion, selectivity, and lifetime was 400 ºC. It is also reported that increasing water content in the feeding stream plays a role in preventing the deposition of coke formed on the pores. ZrAPSO-34 showed high stability against coke formation with moderate olefin selectivity and a long lifetime in the reaction process.

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إنتزاع الماء من الكحول لتحويلها الى أوليفينات بواسطة استخدام المنخل الجزيئي ZrAPSO-34 كعامل مساعد

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الخلاصة

تعتبر الأوليفينات الخفيفة مثل الإثيلين، البروبيلين والبيوتيلين كمفتاح للصناعات البوليمرية والبتروكيميائية. إنتاج هذه الأوليفينات عن طريق إنتزاع جزيئات الماء من الكحولات بواسطة المنخل الجزيئي نوع SAPO-34 أجتذبت إهتماماً كبيراً. وجد أن إستخدام الميثانول كمادة أولية هي عملية بديلة وفعالة. من أبرز المشاكل التي تواجه SAPO-34 كعامل مساعد في هذه العميلة هو فقدان الفعالية بسرعة كبيرة. للتغلب على هذه السلبية يتم إضافة ايونات المعادن الى العامل المساعد. تم إضافة عنصر الزركونيوم الى العامل المساعد نظراً لأنه يتميز بإستقرارية عالية عند درجات الحرارة العالية كما يتميز أيضاً بخاصية الحامضية المعتدلة. تم تحضير العامل المساعد المعدل نوع زيولايتSAPO-34 بدمجه مع معدن Zr بنجاح تحت إشعاع الميكروويف و باستخدام المورفولين كقالب. طاقة التبلور المستخدمة كانت ٨٠٠ واط و بزمن ٢٠٠ دقيقة. تم تشخيص عينات العامل المساعد بواسطة تقنيات XRD, SEM ,EDX, BET, FTIR وTGA . بين تحليل XRD بنية CHA نموذجية بتبلور عالي. بينت التحاليل أن حجم الدقائق المتبلورة كبيرة مع توزيع منتظم للسيليكا في الزيولايت وبمساحة سطحية قليلة بلغت ٧٧ م^{٢}/غم. أظهرت القمم الاهتزازية للعامل المساعد المحضر توافقاً مع بنية الزيولايت SAPO-34. تم فحص أداء العامل المساعد المحضر في عملية تحويل الميثانول الى أوليفينات خفيفة في مفاعل ثلاثي طبقة الحشوة بدرجات حرارة ٣٥٠ , ٤٠٠ , ٤٥٠ و ٥٠٠ درجة مئوية عند سرعة وزنية بالساعة قدرها ٧,٧ ساعة$^{-١}$. أظهرت النتائج أن افضل إنتقائية للأوليفينات الخفيفة كانت عند ٤٠٠ درجة مئوية حيث وصلت الإنتقائية إلى ٧٠٪ مع زمن تفاعل وصل الى ٥٠٠ دقيقة. كذلك وجد أن نسبة تحول الميثانول بلغت ١٠٠٪ تقريبًا عند كل درجات حرارة التفاعل. كما تم دراسة تأثير تركيز الميثانول وأظهرت النتائج أن زيادة المحتوى المائي تلعب دورًا أساسياً في زيادة عمر العامل المساعد ومنع ترسب الفحم على المسامات.

الكلمات الدالة: عامل مساعد زيولايت SAPO-34، إضافة معدن Zr، إشعاع المايكروويف، ميثانول الى اوليفين، إنتقائية.