

Direct K⁺ and Ag⁺ Ion-exchanged into SAPO-34 Prepared via Microwave Irradiation and Its Performance in MTO

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Abstract

Recently, light olefins became an important material for industrials, especially plastics. High olefins production cost from oil sources, made the researchers look for other methods. Methanol conversion to olefins over SAPOs was an excellent alternative. SAPO-34 molecular sieve is considered a proper catalyst used in this field. For this purpose, SAPO-34 with morpholine template was prepared under microwave irradiation. K and Ag ions were incorporated successfully by ion exchange method. The samples were analyzed by XRD, SEM, EDX, FT-IR, BET, and TGA techniques. XRD showed higher crystallinity of K-SAPO-34 and smaller crystallite size than Ag-SAPO-34. The SEM and EDX analysis indicated perfect distribution of K and Ag metal ions. Surface area reached to 287.64 and 254.59 m²/g for K-SAPO-34 and Ag-SAPO-34, respectively. TGA analysis showed high thermal stability opposite cracking at high temperature of 1100 °C. The catalyst performance on MTO was performed in trickle bed reactor at temperature of 350, 400, 450 and 500 °C at 7.7 hrs⁻¹. The conversion was 100% for the two samples. At 400 °C, olefins selectivity was 85% of K-SAPO-34. Ag-SAPO-34 showed longer lifetime of 475 min with 74% olefins selectivity. Weight hourly space velocity of 15 and 21.1 hrs⁻¹ at 450 °C for K-SAPO-34 were also investigated. As the velocity increased, the conversion and selectivity decreased. It was found that adding K and Ag by ion exchange to SAPO-34 improve surface area and enlarge the pores diffusion. This might hinder the coke deposition in pores and improve olefin selectivity.

Keywords: Ion exchange, Microwave irradiation, MTO, SAPO-34 zeolite catalyst, Selectivity.

Introduction

Light olefins like ethylene, propylene, and butylene are the key components raw material of industries. In chemical industries processes, light olefins mainly produced by fluid catalytic cracking, steam cracking, naphtha cracking and natural gas¹. The challenges forced these processes such as high price of crude oil, pollutions, high consumption of energy; create a gap between demand and supply of olefins². However; these challenges forced the researchers to search for alternative technologies for producing light olefins from non-oil sources³. Zeolite catalyst is typical type for producing oil from low-cost feedstock^{4,5}. Zeolite

can be prepared with recycled raw materials, scrap tires and papers⁶. Methanol has proved to be successful conversion to light olefins⁷. For many industrial processes, catalysts are necessary to improve products⁸. In most studies, introducing metals in the framework of catalyst give the catalyst more stability, activity and surface area⁹⁻¹¹. SAPO-34 zeolite has shown an excellent proficiency for MTO process. It has small pore diameter 0.38 nm, moderate straight acidity, high selectivity of ethylene and propylene, large surface area and high stability. Hydrothermal is the most method used to prepare

SAPO-34. Its limitations are long time of crystallization and its black box nature attracted to innovative approach of microwave heating^{12, 13}. Microwave heating showed many advantages such as fast crystallization time, small size crystals, facial homogenous morphology and eliminating heating spot. As compared to conventional hydrothermal heating, using of microwave irradiation heating shortened the time of crystallization from two or three days to several hours¹⁴. Shalmani et al.¹⁵ prepared nanosized structure of SAPO-34 catalyst with different morphologies under microwave irradiation. They studied synthesis conditions such as crystallization time, chemical composition and microwave power. They found that chemical composition was the key role of phase purity, crystal size and distribution. Also, they reported that higher microwave power yield small crystals of SAPO-34. Álvaro-Muñoz et al.¹⁴ prepared nanocrystalline SAPO-34 using microwave-assisted hydrothermal synthesis method. Significant variation in shape and size was obtained with microwave as compared to hydrothermal synthesis. The nanosized SAPO-34 synthesized in microwave irradiation exhibited a longer lifetime in MTO conversion as compared to convection oven. The results showed that olefins selectivity reached to 90% with longer lifetime of 22 hr at temperature of 673 K and weight hourly space velocity (WHSV) of 1.2 hr⁻¹. Recently, prepared nanocrystals sized of SAPO-34 using dilute zeolite solutions by microwave irradiation assisted hydrothermal method. To increase selectivity and stability of light olefins, metal ions have incorporated in the zeolite framework¹⁶. The metal ions give

SAPO-34 more activation in selective ethylene molecules and can be processed for longtime which repeals coke deposition. Xiang et al. used direct Cu⁺ ion-exchange into SAPO-34 by conventional hydrothermal method¹⁷. Their results showed that Cu-SAPO-34 display an excellent performance in the selective reduction of NO with NH₃. Merza et al. used hydrothermal method with cheap template agents. Their results showed that the crystallinity increases when adding metal ions. They reported that incorporation Ag and K ions increase ethylene selectivity to 68.56 and 80%, respectively, as compared with 56.34% of unmodified SAPO-34. They also reported that the lifetime prolongs to 10 hrs⁻¹. The surface area and weak and strong acid sited increased¹⁸. Eslami et al. synthesized nanostructured MnAPSO-34 catalyst via microwave and hydrothermal heating methods. They found that incorporating of Mn metal with hydrothermal heating enhanced olefins selectivity and lifetime. The olefins selectivity reached to 87% at 690 min. in the other hand, microwave heating produced low crystallinity of catalyst with low olefins selectivity¹⁹.

In this work, SAPO-34 zeolite molecular sieves were prepared under microwave irradiation using of Aluminium chloride with Morpholine template, cheap and available. K and Ag metal was incorporated into SAPO-34 by ion-exchanged method. The catalyst synthesis and characterization was studied. The performance of modified SAPO-34s on activity, selectivity and lifetime in MTO reaction conversion was also investigated.

Materials and Methods

In a typical microwave synthesis, aluminum chloride hexahydrated AlCl₃.6H₂O, 99%, Fluka, tetraethylorthosilicate TEOS, 100%, Aldrich, phosphoric acid H₃PO₄, 85%, Merck, potassium nitrate KNO₃, 99%, Himedia, and silver nitrate AgNO₃, 98%, Himedia, were used as Al, Si, P, K and Ag, respectively. Morpholine MOR, 99%, Aldrich, was used as structured directing agent SDS.

Synthesis of K-SAPO-34 and Ag-SAPO-34

Firstly, 9 g of AlCl₃.6H₂O was mixed 16.5 ml of demineralized water and stirred at room temperature for 30 min. 3 ml of H₃PO₄ was added in dropwise to the mixture. After that, the solution was mixed for 20 min. then, 2 ml of TEOS added to the solution. Then, 6 ml of MOR added slowly and the mixture was

stirred for 2 hrs. The gel molar ratio was Al₂O₃:P₂O₅:0.6SiO₂:4MOR:60H₂O. In next step, the mixed colloidal was transferred into 100 ml stainless steel Teflon autoclave. It then placed in microwave irradiation with 800 w for 200 min without stirring manner. In the final step, the product mixture was centrifuged in 2200 rpm for 30 min, washed three times with distilled water and filtered.

In order to prepare K-SAPO-34 and Ag-SAPO-34 catalyst, Ag and K were incorporated to SAPO-34 catalyst by direct method of ion exchange. To achieve that, Ag and K were incorporated into SAPO-34 with two times ion exchange between KNO₃ and AgNO₃ solutions in water of 0.02 M and then mixing for 1 hr. at room temperature, and then

leave the precursor overnight without stirring. Modified SAPO-34 zeolite that designed as Ag-SAPO-34 and K-SAPO-34 was centrifuged, dried at 120 °C for 24 hrs. and calcined at 560 °C for 5 hrs. in order to remove template. Finally, the as-synthesis catalysts were tableted to small particles with 2-3 mm diameter to use in methanol to olefins reaction. The methanol to olefins reaction (MTO) using the two samples of prepared zeolite catalysts was done in a laboratory trickle-bed reactor.

The experimental setup for MTO conversion test of samples consists of gas and liquid feeding section, trickle -bed reactor, furnaces and analytical section. The operation process was continuous at atmospheric pressure. Proceeding to catalytic testing, 2.5 g of crushed catalyst was overloaded inside the reactor of internal diameter = 1.2 cm, length = 48 cm. The catalyst was held on quartz balls to fix it in place. N₂ carrier flow gas at 90 ml/min opened on to the catalyst at 650 °C for 1 hr. Then it cooled to desired reaction temperature. Then, the feed solution 30 wt% methanol, 70 wt% H₂O was pumped to primary

Results and Discussion

Catalyst Characterization

The samples of zeolite were characterized by 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 (Thermogravimetric analyses) techniques. The XRD diffraction pattern was composed by a Bruker D8 diffractometer CuK α radiation, $\lambda = 1.54060 \text{ \AA}$ in 2θ range equal of 5–40. The relative crystallinity for SAPO-34 catalysts was determined by the using sum of intensities of the most important peaks of $2\theta = 9.5, 13.0$ and 20.5 . The particles morphologies and sizes were conducted by SEM photo using instrument of Philips XL30. XRD analysis is used to identify crystal phases and size. BET surface area for the catalysts were measured by N₂ isotherms analyses collected by micrometrics ASAP 2010 device. An FTIR spectrum was performed to indicate the functional groups of catalyst. It was executed in wide range wavelength vibration of 400-4000 cm⁻¹ for more accuracy. The samples were composed with KBr-diluted palletized using a Bruker Tensor-27 spectroscopy. TGA-DTG data were obtained in N₂ gas using model of Shimadzu DTG-60. The TGA temperature range test was from 20 to 1100 °C. The flow temperature and rate of N₂ gas model were set to 20 °C/min and 20 ml/min, respectively. The

heater which ascended the solution temperature to 250 °C. For each experimental test, the feedstock was changed with a fresh one to ensure that the feeding reactant concentration by bubbling the solution of methanol. The reaction temperature was 350, 400, 450 and 500 °C at 7.7 hrs⁻¹. WHSV 15 and 21.1 hr⁻¹ was studied also at 450 °C

Nitrogen gas was used carrier gas of the reactants. Gas chromatograph BS-GC7820, BIOBASE, China, equipped with Plot-U column and flame-ionization FID detector was used to analyze the product compositions. The structural properties of prepared SAPO-34 with microwave irradiation are demonstrated in Table 1.

Table 1. The structural properties of prepared SAPO-34 with microwave irradiation.

SAPO-34	Template	Ion Exchange	Microwave irradiation (W)	Time (min)
S-1	Morpholine	K	800	200
S-2	Morpholine	Ag	800	200

catalyst characterization was performed at Ondokuz Mayıs University in Turkey.

XRD Analysis

The X-Ray diffraction of samples is shown in Fig. 1. The standard peaks of SAPO-34 with MOR template with molar ratio of 4 at $2\theta = 9.5, 12.5, 15.5, 17.7, 20.5, 26$ and 30.5 . The diffraction peaks of MOR of low molar consumption affects the presence of SiO₂ in amorphous phase at this time. The diffraction peaks of K⁺ and Ag⁺ ion exchange with morpholine template corresponds to CHA SAPO-34 phase which indicates purity phase catalyst. The peaks at $2\theta = 9.31, 12.4, 15.5, 17.7, 20.3, 25.8$ and 30.5 . The relative crystallinity that related to SAPO-34 formation of K-SAPO-34 was higher than that of Ag-SAPO-34. The average crystal size of catalyst based on Scherrer equation from the XRD instrument was found to be 23, 24.9 and 25 nm. The longtime of microwave irradiation may create an amorphous phase between crystals which decreases the crystallinity and purity of SAPO-34 zeolite templated with MOR²⁰. The incorporation of K and Ag ions improved the crystallinity and purity. It seemed that ions attributed to increase the crystal growth and crystallite surface. When heated the gel in the microwave, the reaction temperature increases rapidly and nucleation goes fast, partial of nuclei

results of amorphous phase between crystals and hence, the crystallinity becomes low²¹. The metal ions work like a seed that help of formation highly pure phase²².

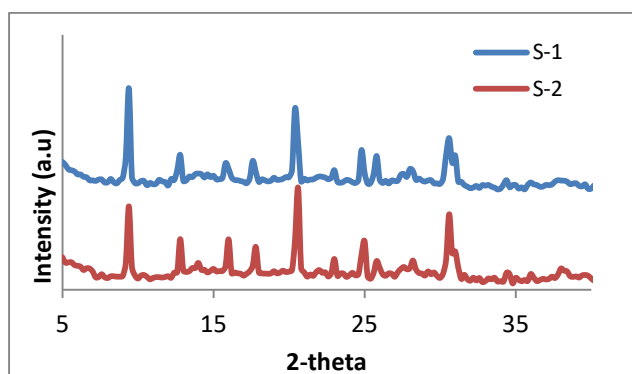


Figure 1. XRD patterns for SAPO-34 samples

BET Analysis

The BET surface area of samples was measured by applying Brunauer-Emmett-Teller equation as reported in Table 2. The results of surface area indicated to a successful synthesis of SAPO-34 catalyst under microwave crystallization. By exchanging Ag^+ , the area recorded to be $254 \text{ m}^2/\text{g}$. The surface area increased to $287 \text{ m}^2/\text{g}$ when exchanged with K^+ ions. As illustrated, K-SAPO-34 and Ag-SAPO-34 have highly pore volume about 0.32 and 0.40 ml/g, respectively. The major cause of decreasing pore volume when exchanging K^+ ions is that for the metal oxides which may narrowing or blocking some of the micropores.

Table 2. BET surface area analysis of SAPO-34 samples.

Sample	BET surface area (m^2/g)	Micropore volume (cm^3/g)	Pore radius (nm)
S-1	287.64	0.32	0.22
S-2	254.63	0.40	0.31

SEM Analysis

The scanning electron microscopy images are given in Fig. 2. As shown, the product of using Ag^+ ions of sample S-2 tended to be more aggregated compared to sample S-1. The sample that exchanged with K^+ ions revealed to be more uniform in distribution manner. The results of K-SAPO-34 and Ag-SAPO-34 were distributed and the aggregation is almost not big crystals. The changed in morphology reflected the effect of metal ions which played a crucial role in the size control and shape of SAPO-34². It is also seen

that the crystal shapes of K-SAPO-34 and Ag-SAPO-34 are almost similar to each other. This phenomenon is that the metal ions have same effect in morphology and size of crystal²³. It is also noticed that the size is smaller when using ions in microwave. This can be explained for the double effect of TEOS and metal ions. The double effect produced small particle size compared to other silica sources in absence of metal ions. In general preparation states, using MOR as template resulted in bigger crystal size¹⁵.

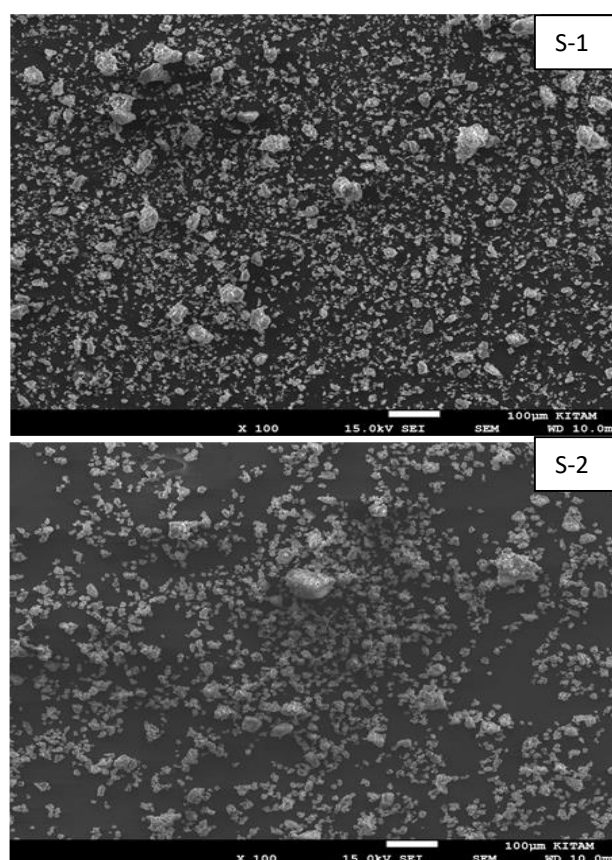


Figure 2. SEM images of S-1 and S-2 samples.

EDX Analysis

The EDX micrographs for S-1 and S-2 samples templated with MOR are illustrated in Fig. 3. The metal ions of K and Ag and the elements that used to prepare SAPO-34 are all observed in EDX analysis. Elements of AL, P, Si, O and C and also K and Ag can be shown in EDX dot-mapping. The images showed highly dispersion of elements and uniform morphologies for prepared catalysts with microwave irradiation. Element O had high ratio among others because it exist in the major compounds that forming zeolite catalyst such as Al_2O_3 , P_2O_5 and SiO_2 . The EDX dot-mapping and weight content indicated the successful synthesis of SAPO-34 catalyst. Also, the

low molar percentage of K and Ag ions is as expected, and hence, the ion exchange gets in good results in SAPO-34 framework. It appears that application of high energy power reflects perfect distribution of elements in catalyst. The proper distribution of metal ions and elements in SAPO-34 framework create Brønsted acidic sites inside pores¹⁶. These new acidic sites could enhance catalyst performance with suitable silica distribution in framework. This may lead to effective conversion in MTO².

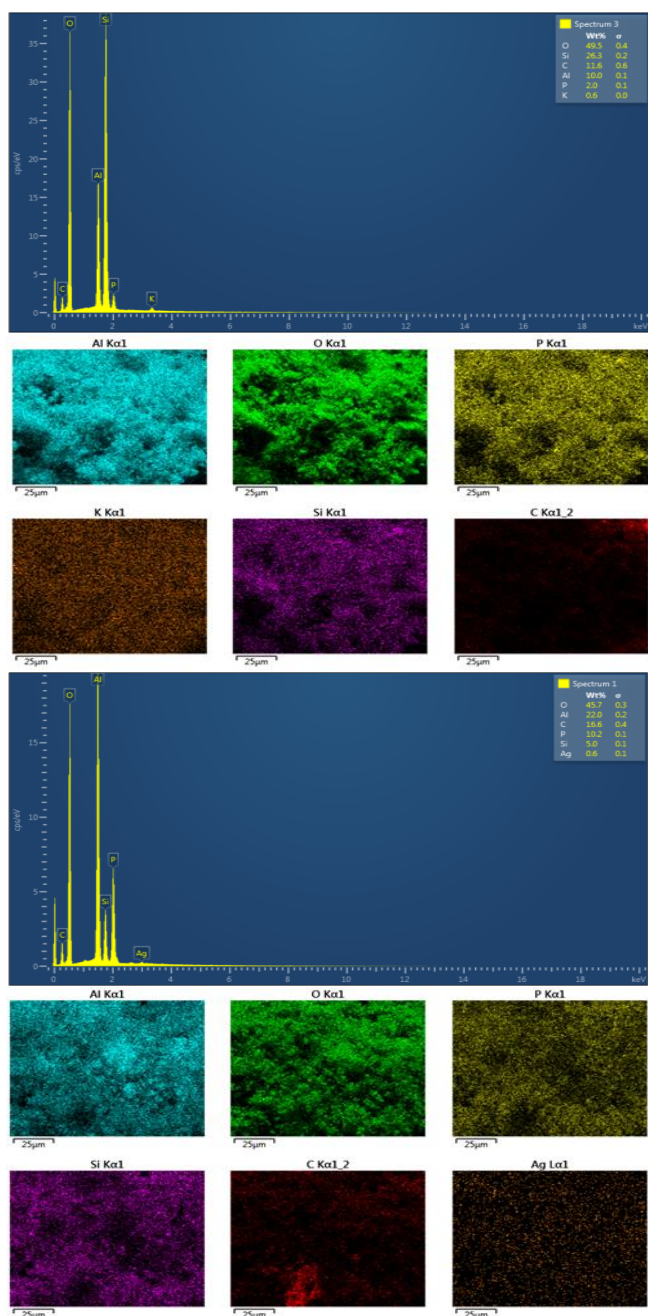


Figure 3. Energy dispersive X-ray analysis of S-1 and S-2, respectively.

FTIR Analysis

The prepared catalyst corresponding to chabazite structure which characterized by FT-IR is shown in Fig. 4. For higher accuracy, infrared spectra of 400-4000 cm^{-1} gave a wide frequency range. The vibrations that recorded are similar to CHA framework of SAPO-34. The spectra showed vibration peaks of bridge hydroxyl groups such as Si-OH and P-OH at 3400 cm^{-1} . The bands of 3150 cm^{-1} also reported of hydroxyl group. The hydroxyl groups reported played active sites roles for methanol-to-olefins conversion. The peaks of about 2440, 2190 and 2050 cm^{-1} can be assigned to CO_2 absorbed from atmosphere. The stretching vibration of 1637 cm^{-1} can be indicated as absorbed water molecules physically²⁴. The wave number peak at about 1400 cm^{-1} indicated asymmetric variation of TO_4 tetrahedral. The band of 1100 ascribed to symmetric stretching T-O-T. the wave number peaks of 730, 630, 550 and 430 cm^{-1} indicated to the protonated morpholine template, O-P-O stretching, T-O double 6-rings bend and T-O bending of tetrahedral Si, respectively^{25, 26}.

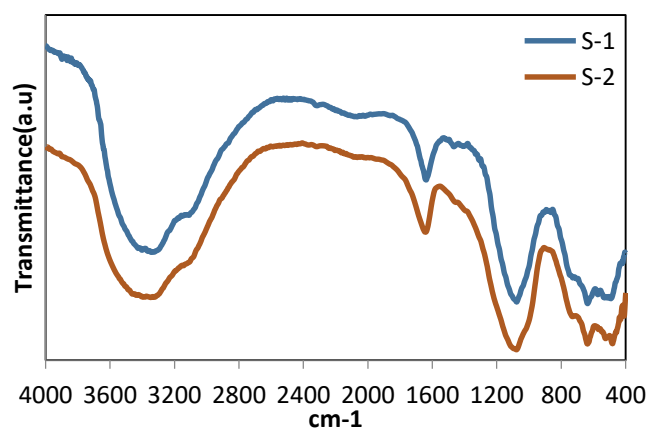


Figure 4. FTIR spectroscopy for S-1 and S-2 samples.

TGA and DTG

Thermogravimetric analyses TGA and differential temperature analyses for samples were performed in order to check the coke deposition formation on K-SAPO-34 and Ag-SAPO-34 as shown in Fig. 5. The average weight loss of all catalysts samples did not exceed 22.7% of the initial weight for high temperature reached to 1100 $^{\circ}\text{C}$. The results showed two differential regions of weight loss steps. The first occurred in temperature range of 160 to 190 $^{\circ}\text{C}$ which is attributed of endothermic of water desorption. The second region of weight loss occurred at temperature higher than 400 $^{\circ}\text{C}$, specifically in range of 420 to

490 °C. The second weight loss indicates exothermic effect which is associated to calcination of coke. The cokes species combustion temperature are in similar manner, however, the weight of coke produced in the samples are not same. The weight loss of coke calcination of K-SAPO-34 is 3.54%, while the value is 2.81% for Ag-SAPO-34. The DTG curve for all samples showed same manner of rate of decreasing weight of catalyst. It showed a high decreasing rate of region 1 and less decreasing rate of region 2. So, it is expected that SAPO-34 particles will show better performance with a longer lifetime due to higher acid site density, low mass transfer resistance and high purity.

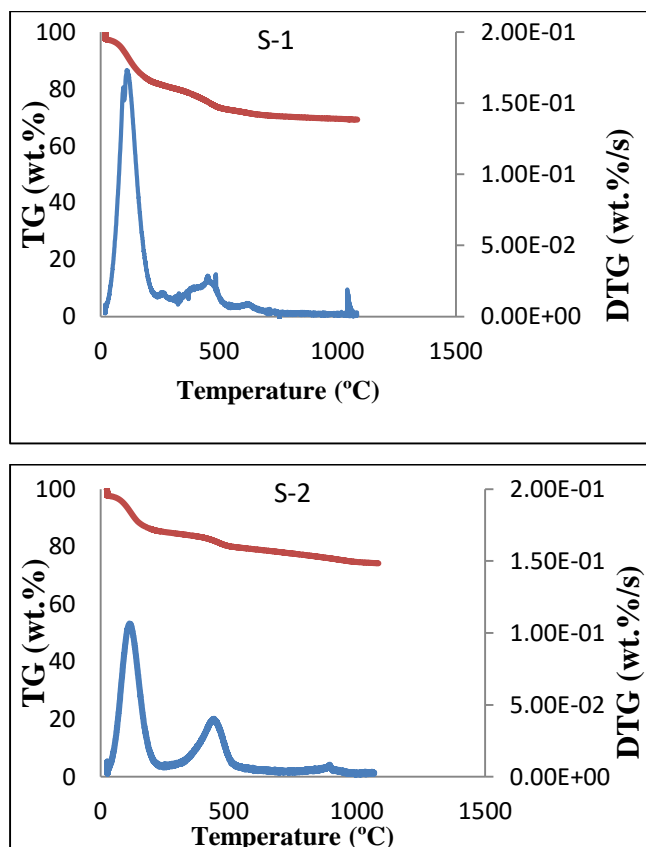


Figure 5. TGA and DTG of S-1 and S-2 samples.

Catalyst Performance

The performance of SAPO-34s synthesized with microwave irradiation for dehydration of methanol to light olefins was tested at 350, 400, 450 and 500 °C with WHSV feed of 7.7 hr⁻¹ and 30 wt% methanol. Also, the S-1 catalyst performance in space velocities of 15 and 21.1 hr⁻¹ at 450 °C was performed. The catalysts showed highly stable conversion up to 400 min. All the samples catalysts showed similar in trend into production light olefins, but on the other hand, the distribution for the

products and the lifetimes varied significantly. Reaction conversion is almost 100% in specific reaction time, then it decreases when the reaction is continue.

Reaction Temperature of 350 °C

K-SAPO-34 and Ag-SAPO-34 performance on MTO conversion at 350 °C with 7.7 hr⁻¹ space velocity are shown in Fig. 6. The reaction conversion for two catalysts not reaches to 100%, then they drops after 300 min. The conversion on K-SAPO-34 yield maximum value of light olefins reached to 78% at 200 min, while Ag-SAPO-34 yield total light olefins of 71% for 400 min and then drop to 57% after 500 min of reaction. It indicated that Ag ions give the catalyst more stability against decompositions and coke formation but also yield less amounts of olefins than K ions that promoted zeolite catalyst at low reaction temperature, i.e. 350 °C.

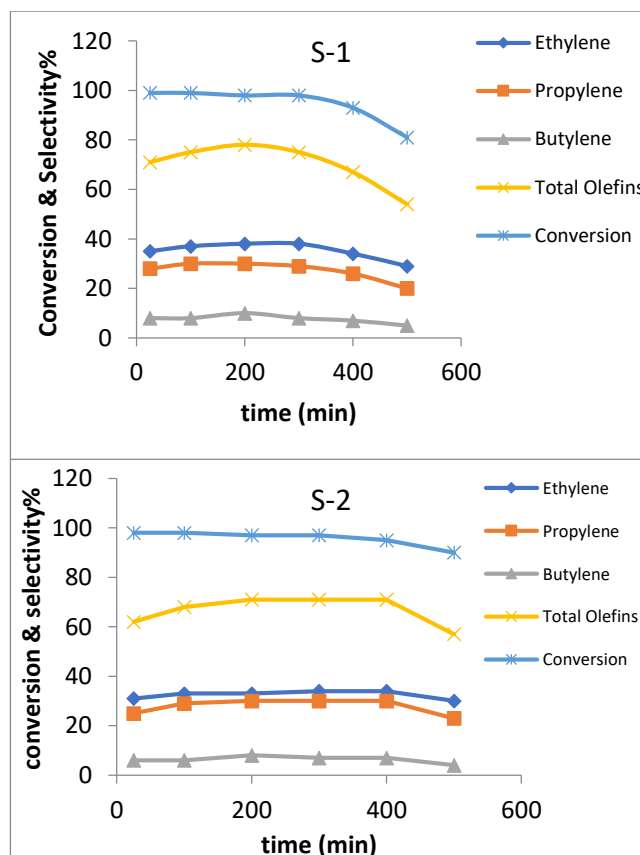


Figure 6. Methanol conversion and product selectivity over K-SAPO-34 and Ag-SAPO-34 catalysts: T=350 °C, WHSV=7.7 h⁻¹.

Reaction Temperature of 400 °C

Fig. 7 illustrates the catalysts performance on MTO at 400 °C with WHSV of 7.7 hr⁻¹ under

atmospheric pressure. The methanol conversion on S-1, S-2 is 100% for 300 min, 100% for 400 min, respectively. The total selectivity is the summation of selectivity of light olefins ethylene, propylene and butylene. The total selectivity recorded for S-1 and S-2 is 78% for 400 min and 74% for 475 min, respectively.

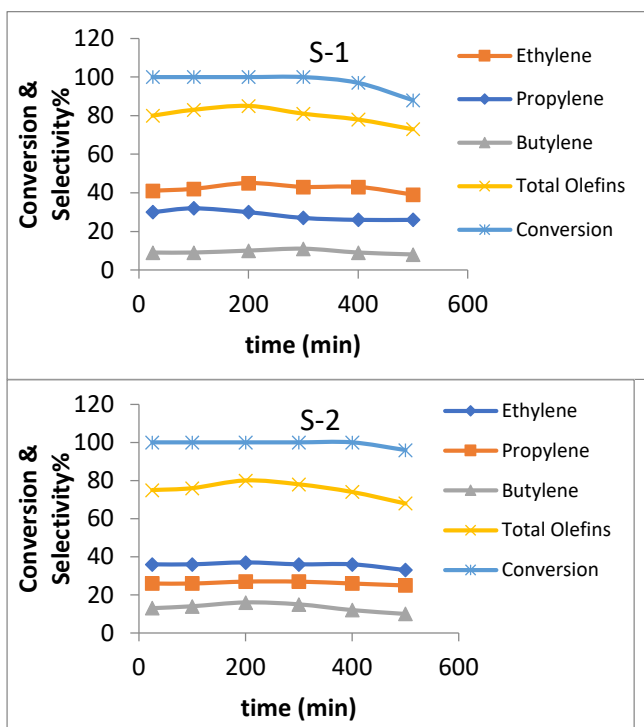


Figure 7. Methanol conversion and product selectivity over K-SAPO-34 and Ag-SAPO-34 catalysts: T=400 °C, WHSV=7.7 h⁻¹.

Reaction Temperature of 450 °C

Fig. 8 demonstrates the S-1 and S-2 catalyst samples performance on methanol conversion to light olefins at 450 °C and 7.7 hr⁻¹. The conversion of S-1 and S-2 is 100% for 400 min and 99% for 400 min. The total olefins selectivity is 85% for 300 min and 81% for 300 min for S-1 and S-2, respectively.

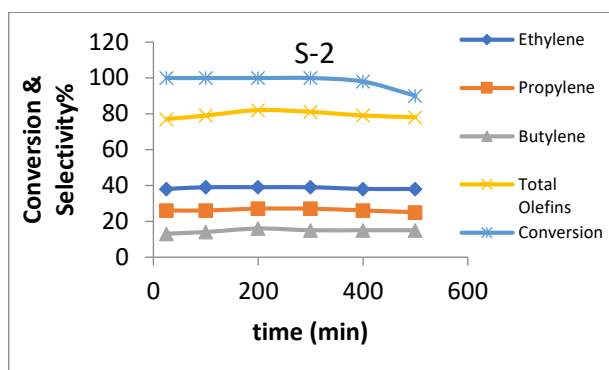
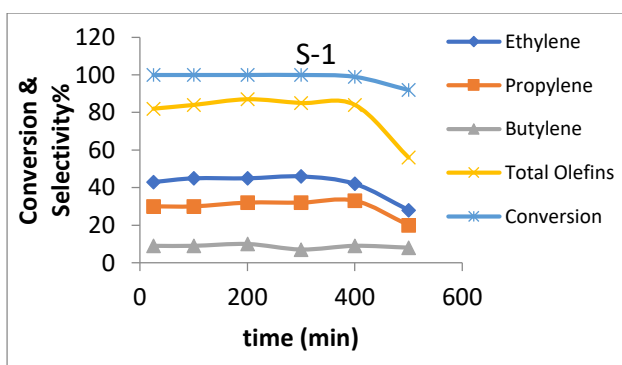


Figure 8. Methanol conversion and product selectivity over K-SAPO-34 and Ag-SAPO-34 catalysts: T=450 °C, WHSV=7.7 h⁻¹.

Reaction Temperature of 500 °C

Fig. 9 depicts the MTO conversion and light olefin selectivity on S-1 and S-2 samples at 500 °C and 7.7 hr⁻¹. It is shown that the conversion is high at long reaction time with less selectivity of total light olefin. It is noticed that selectivity is drop after 200 min of reaction which recorded about 55 to 51% for the two reactions. These results indicated that the temperature of 500 °C occurs in the range of second region of coke formation which allows the coke to deposit the pores which reflects inverse results in olefins products.

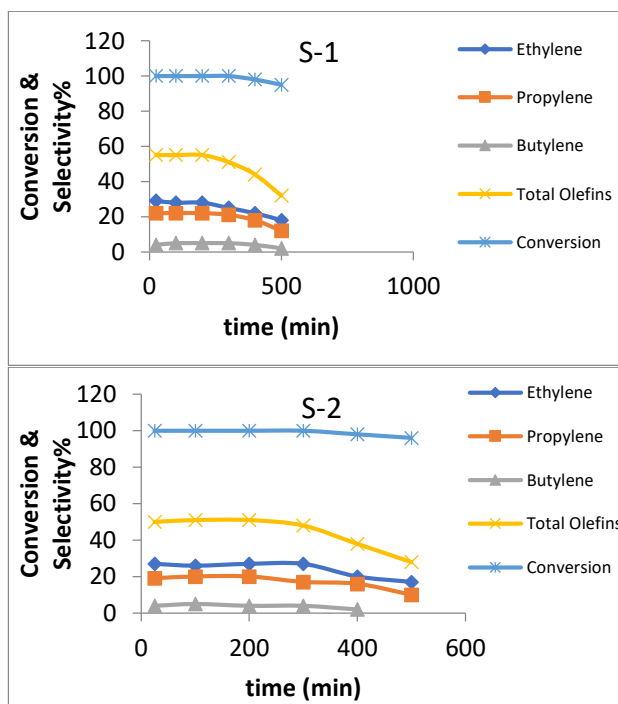


Figure 9. Methanol conversion and product selectivity over K-SAPO-34 and Ag-SAPO-34 catalysts: T=500 °C, WHSV=7.7 h⁻¹.

In general, the lifetime of catalysts of reaction temperature of 450 and 500 °C is less than 300 and 400 °C, but the total light olefins selectivity of 300, 400 and 500 °C is less than 450 °C. Incorporation of K and Ag ions in the catalysts improve the conversion of methanol and also enhance the light olefins selectivity. K ions improve the light olefins production more than Ag ions, but the last one improves the lifetime. The major expected reason for reducing lifetime when increasing temperature is that the reaction occurs in the second region of coke formation 420-490 °C^{27,28}. The cokes that deposit on the active sites reduce the diffusion of reactant to the pores of the catalysts²⁵. The reactions give high yield of light olefins in initial time but on continue reaction and increase coke formation, the quantities of olefins reduced and accompanied of that, the lifetime reduced in all types of catalysts^{25, 26}. SAPO-34 incorporated with Ag ions showed more stability than other types. This might be ascribed to its lower acid strength which leads to reduce cracking of ethylene and propylene¹⁸. Also, using microwave for preparing SAPO-34 enhanced lifetime for methanol conversion².

Conclusion

Due to the growing the demand of the light olefins in industry, an alternative method for producing light olefins using methanol as source instead of oil becomes an effective process. Dehydration of alcohols over zeolite catalyst like SAPOs was an alternative and effective method. SAPO-34 showed an excellent and effective feature for MTO conversion process. SAPO-34 was prepared via microwave heating method. The catalyst was incorporated with K and Ag metals by direct ion-exchanged method. The catalyst characterization showed higher crystallinity and uniform distribution of metal ions. The surface area was 287.64 and 245.59 m²/g for S-1 and S-2, respectively. TGA analysis showed high thermal stability against coke

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Authors' Declaration

- Conflicts of Interest: None.

Effect of Weight Hourly Space Velocity

The effect of WHSV of 7.7, 15 and 21.1 hrs⁻¹ at 450 °C on MTO conversion are studied on K-SAPO-34 catalyst and shown in Fig. 10. As increasing in space velocity from 7.7 to 21.1 hr⁻¹, the catalyst lifetime decreasing from 400 to 100 min. When space velocity increased, the molecules that reacted per time also increased, and hence, the rate of coke formations are increased simultaneously, which then decreases the SAPO-34 catalyst lifetime².

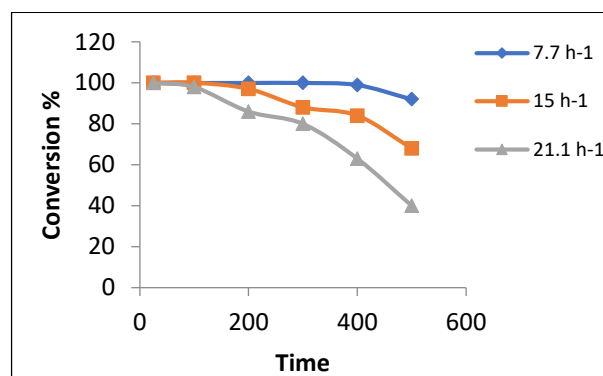


Figure 10. Methanol conversion over K-SAPO-34 with different WHSV at T=450 °C.

formation at high temperature of 1100 °C. Methanol to olefins conversion was performed in trickle bed reactor. Reaction temperatures of 350, 400, 450 and 500 °C at 7.7 hrs⁻¹ were investigated. The results showed high conversion for all samples reached to 100%. The higher light olefins selectivity was 85% at 450 °C for S-1 sample. Longer lifetime was 475 min for S-2 sample with 74% light olefin selectivity. Increasing or decreasing temperature than 450 °C reduced selectivity of light olefins. Weight hourly space velocity of 15 and 21.1 hrs⁻¹ at 450 °C were also investigated. It was found that increasing space velocity had a reverse effect on olefins selectivity. The coke deposition on catalyst increased when increasing space velocity.

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- We hereby confirm that all the Figures and Tables in the manuscript are ours. Furthermore, any

Figures and Images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.

- Ethical Clearance: The project was approved by the local ethical committee at College of Engineering, University of Baghdad.

- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- No potentially identified images or data are present in the manuscript.

Authors' Contribution Statement

This work was carried out in collaboration between all authors. M. J. M diagnosed the cases then collected the samples and did the tests and also wrote

the manuscript. N. S. M, edited the manuscript with revised the idea. N. S. M, analyzed the data. All authors read and approved the final manuscript.

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التبادل المباشر لأيونات البوتاسيوم والفضة في SAPO-34 المحضر بواسطة إشعاع المايكروويف وأدائها في تحويل الميثانول الى أوليفينات

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الخلاصة

حديثاً، أصبحت الأوليفينات مادة مهمة للصناعات، وخاصة في البلاستيك. إن التكلفة العالية لإنتاج الأوليفينات من مصادر نفطية جعلت الباحثين يفتشون عن طرق بديلة. إن تحويل الكحولات إلى أوليفينات بواسطة العامل المساعد هي طريقة ممتازة. يعتبر زيولايت SAPO-34 عوامل مساعدة مناسبة في هذا المجال. لذلك، تم تحضيرها باستخدام المورفولين كقالب بواسطة إشعاع المايكروويف. تم إدخال أيونات البوتاسيوم والفضة بنجاح عن طريق التبادل الأيوني. تم تشخيص العينات بتقنيات FT-IR, BET, EDX, SEM, XRD. أظهر تحليل XRD تبلور أعلى لـ K-SAPO-34 وحجم بلوري أصغر من Ag-SAPO-34. في حين أشارت تحاليل TGA و DTG. أظهر توزيع المثالي لأيونات المعادن K و Ag. وصلت المساحة السطحية إلى 287.64 و 254.59 م²/غم لـ K-SAPO-34 و Ag-SAPO-34 على التوالي. أظهر تحليل TGA ثباتاً حرارياً عالياً مقابل التكسير عند درجة حرارية وصلت الى 1100 مئوية. أجريت إختبارات كفاءة النماذج المحضرة من العامل المساعد في عملية تحويل الميثانول الى أوليفينات خفيفة MTO في مفاعل ثلاثي طبقة الحشوة عند درجات حرارة 350, 400, 450 و 500 مئوية بسرعة وزنية WHSV بلغت 7.7 ساعة⁻¹. بلغ التحويل للنموذجين 100% عند درجة 400 مئوية بانتقائية وصلت الى 85% لنموذج K-SAPO-34 في حين أظهر النموذج Ag-SAPO-34 عمراً أطول وصل إلى 475 دقيقة مع انتقائية إجمالية للأوليفينات بلغت 74%. تم دراسة السرعة الوزنية للميثانول الداخل للنموذج K-SAPO-34 بالساعة عند 15 و 21.1 ساعة⁻¹. وجد أنه بزيادة السرعة الوزنية، انخفض تحويل الميثانول وانتقائية الأوليفينات. أن إضافة K و Ag إلى SAPO-34 يزيد المساحة السطحية ويحسن انتشار المواد المتفاعلة داخل المسام. بهذا تحدث إعاقه للفحم المترسب في المسام و يحسن انتقائية الأوليفين.

الكلمات المفتاحية: تبادل أيوني، أشعاع المايكروويف، ميثانول الى أوليفين، عامل مساعد زيولايت نوع SAPO-34، إنتقائية.