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RESEARCH ARTICLE

Meeting Specifications of SAPO-34 Molecular Sieve with Multi-templates for MTO Reaction: Kinetic and Experimental Study

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ABSTRACT

Light olefins become are important products for polymeric and petrochemical industries. Producing olefins from oil become ineffective due to highly production cost. An alternative method for producing olefins using methanol instead of oil source become an efficient process. SAPO-34 considered as a proper zeolite catalyst used in this field. For this purpose, there were many attempts to prepare it with microwave irradiation using DEA, TEA and MOR as templates. Fixed power of 800 W for 200 min was applied in crystallization step. XRD, BET, SEM, EDX, FTIR and TGA analysis were studied for preparing catalysts. XRD analysis showed that producing SAPO-34 using DEA and TEA failed and instead of it, SAPO-41 appeared. SAPO-34 was successfully prepared using MOR template. The surface area was 123.10, 226.42 and 194.63 m^2/g using SP/DEA, SP/TEA and SP/MOR, respectively. SEM-EDX analysis showed large particles of SP/DEA and SP/TEA with relatively small particles of SP/MOR. FTIR peaks of SP/MOR were identical with SAPO-34 spectra peaks. TGA analysis revealed very high stability at high temperature. MTO kinetic results showed that the reaction obeys the first-order with activation energy of 17.383 kJ/mol. MTO conversion process was performed in fixed bed reactor with different temperatures at 350, 400, 450 and 500 °C and weight hourly space velocities at 7.7, 15 and 21.1 h^{-1}. Temperature of 400 °C recorded higher olefins selectivity at about 63% of total products and 100% conversion for 400 min. It was found that increasing temperature and WHSV cause decreasing of conversion and olefins selectivity.

Keywords: Methanol-to-Olefins, Microwave heating, SAPO-34 zeolite, Selectivity, Templates

Introduction

Light olefins such as ethylene, propylene and butylene are considered as key materials for polymeric and petrochemical industries. Commercially, light olefins are produced from oil sources. Due to the depletion of the oil reserves, high production cost and growing the demand of light olefins in industries, the scientist developed an alternative and effective process.[1,2] Producing the olefins from methanol was found as an excellent method. The process is named as methanol-to-olefin (MTO). MTO reaction is performed over zeolite catalysts. Silicoaluminophosphate (SAPO-34) molecular sieve is one of an important zeolite catalyst which has Brønest acid site that substitute of Si into neutral framework of $AlPO_4$-n.[3,4] SAPO-34 with chabazite (CHA) structure contains small pore size (0.38*0.38 nm) with 8-membered rings.[5] Since it has thermal stability, mild acidity and shape selectivity, it gives a good selectivity of methanol conversion to light olefins.[6] Many organic amines have been used in preparation of SAPO-34 as structural direct agents (SDS). This is due to reduce the cost and overcome the toxicity of some amines.[7] In another side, most of studies have been done using hydrothermal process for catalyst preparations.[8,9] The longtime of crystallization (mostly above than 48 hrs) and high power

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consumption cause high price synthesis and cannot reach the commercial demand in short time when needed.[10] An alternative method for the preparation is using microwave irradiation which shortens the crystallization time in less than 4 hours, controlling the particle morphology and saving energy, is facial method when synthesizing the catalyst. Microwave synthesis has shown to select SAPO-5 (AFI structure) rather than SAPO-34 (CHA) especially at low power and short time.[11] SAPO-5 forms at early stages of reaction since it is less stable than SAPO-34, and hence, it transforms when increasing power and time to more stable structure (i.e. SAPO-34).[12] Pure SAPO-34 is difficult to obtain with microwave heating and this needs to adjust the time and power for each synthesis process which must get further studies.[13,14] Choosing template is also an important issue when preparing zeolite catalysts. Tetraethylammonium hydroxide (TEAOH), morpholine (MOR), diethylamine (DEA) and triethylamine (TEA) are most commonly templates used for preparing SAPO-34.[15] It can be used alone or mixed with each other to have an effective catalyst with less consumption of templates.[15,16] TEAOH is perfect template for generating controlling phase with high specifications SAPO-34. But, it is very expensive material which means the final product is not cost-effective. MOR has been used an alternative template due to low price as compared to TEAOH and produce pure phase SAPO-34.[17] But in general, it forms macro-sized particles, and hence, low surface area of catalyst.[1] Recently, the organic amine templates such as DEA and TEA have been used for their availability, cost-effective and producing CHA phase of SAPO-34.[17] It is reported that the form generation of impurities accompanied with SAPO-34 such as SAPO-5 and SAPO-41 are major drawback of these templates. Also, DEA template may generate large particles with very low surface area due to aggregation of crystals.[18] The crystal size control which is affected by template, plays an important role in the specification of produced catalyst. Also, the small synthetic particles reveal a crucial factor for prolonging lifetime of prepared catalyst. In addition, the distribution of silica and the Brønsted acidic sites on the surface of catalyst are greatly affected by the type of template. As result, MTO conversion, olefins selectivity and catalyst lifetime are changed according to the template used for catalyst synthesis.[19] Sun et al.[20] prepared SAPO-34 hydrothermally using MOR template and SAPO-34 with MOR as seed. The crystal size of SAPO-34 was about 200-500 nm when using treated MOR seeds. When using MOR without seeds, the size was larger with less surface area. For MTO reaction, the catalytic conversion of the two prepared catalyst was 99%. The olefin selectivity for unseeded catalyst recorded to be 82.39% with lifetime of 3.1 h. The treated sample catalyst reported longer lifetime of 4.6 hrs with total olefins selectivity of 83.66%. Liu and Kianfar[17] investigated nano-SAPO-34 synthesis with mixture of TEAOH, MOR and TEA templates hydrothermally at several crystallization temperature and times for MTO reaction. They found that low amount impurities of SAPO-5 existed in some of prepared samples. The sample synthesized at 190 oC for 24 hrs showed higher CHA phase purity and higher crystallinity. It also reported longer lifetime reaction of 300 min with higher olefins selectivity reached to about 48.71 and 32.6% for ethylene and propylene, respectively.

In this paper, a new and novel Aluminum chloride was used as alumina source for synthesis SAPO-34 zeolite catalyst. MOR, DEA and TEA were used as templates to confirm SAPO-34 specifications. The crystallization process was achieved under microwave irradiation. The crystallization time and power were adjusted together to obtain higher purity phase of SAPO-34. Methanol to olefins conversion process was performed in fixed bed reactor was investigated.

Materials and method

SAPO-34 molecular sieves were prepared using Aluminium Chloride hexahydreated (99%, Fluka), Phosphoric acid (85%, Merk), Tetraethylorthosilane (100%, Aldrich) as Al, P and Si sources. Diethylamine (99%, Merk), Triethylamine (99%, Merk) and Morpholine (99%, Aldrich) were used as templates.

SAPO-34 preparation

First step, aluminum chloride was dissolved in demineralized water and stirred for 1 hr at room temperature. After that, phosphoric acid was added in dropwise for 30 min and stirred virgiously. Tetraethylorthosilane the added in drops and the mixture was left in stirring for 2 hrs. Then, proper amounts of DEA, TEA or MOR templates were added separately to form SAPO-34/DEA, SAPO-34/TEA and SAPO-34/MOR gel. The reactant compositions are Al_2O_3:1P_2O_5:0.6SiO_2:4X: 60H_2O. Where X is DEA, TEA or MOR. The resultant gel was loaded in 100 ml Teflon Autoclave which sealed and placed in microwave oven. The power and time were adjusted to be 800 w and 200 min, respectively. For whole crystallization process, the reactant mixtures were kept without agitation. After crystallization, the Teflon Autoclave is cooled gradually to room temperature. The solid products were recovered by centrifugation, washed three times with distilled water, filtered and

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

SAPO-34	Template	Heating method	Power (W)	Time (min)
S-1	DEA	MW	800	200
S-2	TEA	MW	800	200
S-3	MOR	MW	800	200

dried overnight at 110 ˚C. Then it calcined in oven at 550 ˚C for 6 hrs to remove the template molecules and convert salts to oxides in the catalyst. The calcined samples were taken to analysis its characterizations. The conditions for representative cases are detailed in Table 1.

Samples characterization

The phase and crystallization of zeolite samples were identified using 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 pattern of XRD diffraction was composed by a Bruker D8 diffractmeter CuKα radiation, = 1.54060 °A in 2θ equal to 5–50. The particle morphology and size was conducted by SEM photo using instrument of Philips XL30. The particle distribution was conducted using EDX analysis. BET surface area for the catalysts were measured by N_2 isotherms analyses collected by micrometrics ASAP 2010 device. FTIR spectroscopy was performed with KBr-diluted palletized using a Bruker Tensor-27 spectroscopy. TGA–DTG data were obtained in N_2 gas using model of Shimadzu DTG-60. N_2 temperature flow and rate were set to 20 ˚C/min and 20 ml/min, respectively. The TGA–DTG tests were performed at Ondokuz Mayıs University in Turkey.

Experimental setup

The schematic of laboratory plant setup with continuous feed flow in fixed bed reactor was used in MTO study as presented in Fig. 1. The catalyst with MOR template was only performed in MTO process under atmospheric pressure. Nitrogen was used as an inert gas. 2.5 g of sample catalyst was loaded and heated to 600 ˚C for 1 hr with N_2 gas in order to remove the moisture and absorbed water. After the reactor temperature decreased to reaction temperature, the methanol/water mixture (30% w/w) was fed to the reactor. The reaction temperature of 350, 400, 450 and 500 ˚C was selected as reaction temperature. The weight hourly space velocity (WHSV) was 7.7, 15 and 21.2 hr^{-1}. The gases product were analyzed with gas chromatograph (GC BS-GC7820, BIOBASE, China) which it was equipped with Plot-U column and flame-ionization FID detector using Helium as carrier gas. Products selectivity (desired to undesired products) were expressed in weight percentage of each products among that all detected products from reaction.

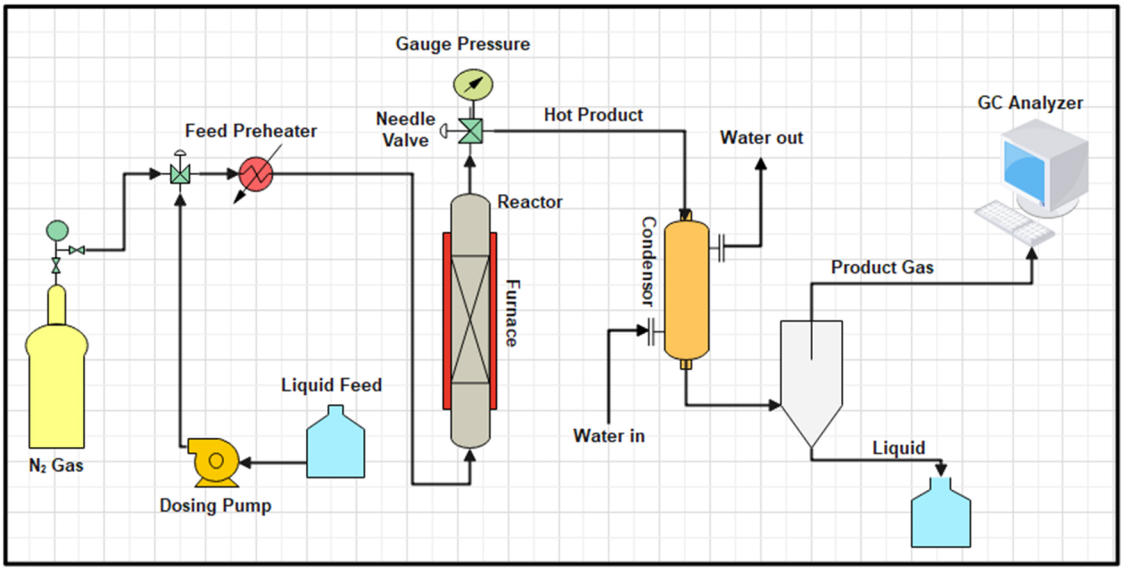


Fig. 1. Schematic diagram of MTO setup.

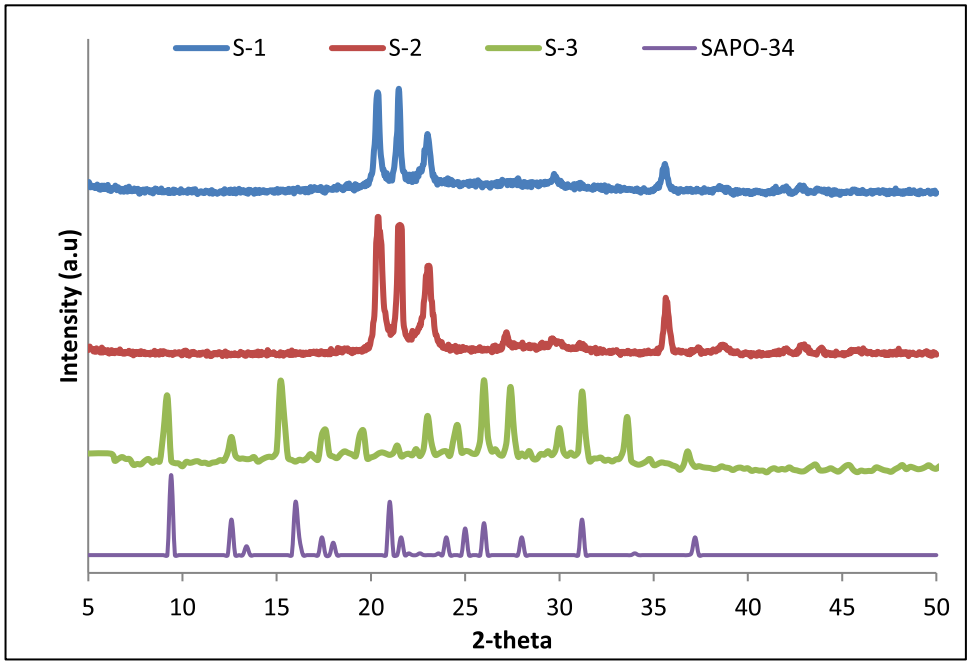


Fig. 2. XRD for S-1, S-2, S-3 and SAPO-34 standard pattern.

Results and discussion

XRD analysis

The XRD of the prepared SAPO zeolite is shown in Fig. 2. The standard peaks of SAPO-34 at 2θ =9.5, 12.9, 16, 17.5, 20.6, 25, 26, 30.6 and 31 which are the characteristic diffraction phase according to reported patterns of SAPO-34 catalyst rhombohedra structure (JCPDS 01087-1527).[21] The XRD patterns when using DEA and TEA as templates repeals no CHA structure of SAPO-34 formation. Instead of that, SAPO-41 with AFO 10-ring channels is formed. The first peak appeared at 2θ equal to about 21°, which indicates to forming AFO structure type framework (SAPO-41).[22] That is when using microwave, large particles are formed and that inhibit the formation of chabazite structure (i.e. CHA 10-ring channels structure). In other hand, SAPO-34 zeolite catalyst with CHA 8-ring structure is formed successfully when using MOR as template. This indicates that using aluminum chloride as aluminum source with MOR template can form SAPO-34 catalyst under microwave irradiation.[1] It can be noted that synthesis of SAPO-34 with MOR template generate pure CHA phase.[23] The formation of SAPO-34 catalyst when using morpholine under microwave irradiation rather than other samples (SP/DEA and SP/TEA) can be ascribed to the complete interaction between synthetic materials which is existed in the outside of crystal framework and the precursor structure at crystallization stage.[5] Small peak deviation appears from standard peaks when use MOR as template. From XRD pattern of sample S-3, it can be noticed that little amounts of impurities exhibits in produced catalyst. That impurity is of the incomplete transforming of SAPO-5 with AFI structure framework to SAPO-34 with CHA structure. SAPO-5 is almost unstable and transforms to SAPO-34 which consider a stable phase. Despite the dominant factors influences SAPO-34 using DEA, TEA and MOR templates mentioned above, some operation variables at crystallization can alter the desired phase to another. One of most important variance, especially in microwave synthesis, is the crystallization rate. It is largely affected by the irradiation power. The high power speeds the nuclei and crystals formation. The quick generations of crystals form an amorphous as dominant in addition to another phase. Also, irradiation time is very important to obtain proper phase. With fixed time of synthesis, it can be observed that template type and synthetic method are the two basic variables for obtaining efficient, high crystallinity and pure CHA phase of SAPO-34.[5]

BET analysis

The BET surface area pores volume and pore radius of samples was measured by applying Brunauer-Emmett-Teller equation of N_2 adsorption/desorption manner as reported in Table 2. The results of surface

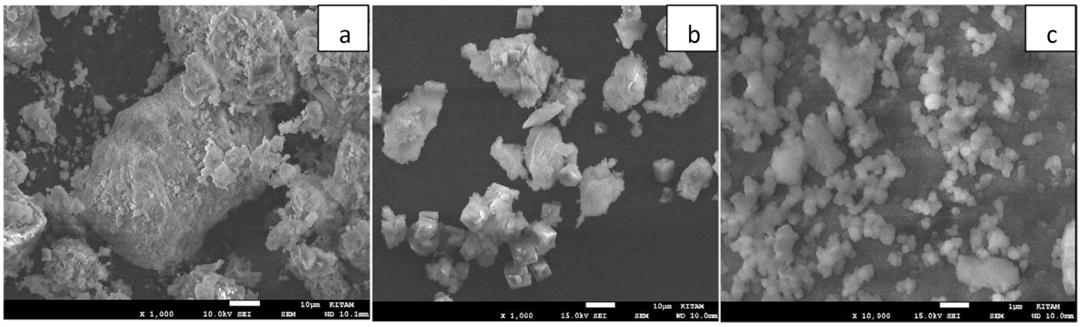


Fig. 3. SEM images of SAPO-34 samples, (a) DEA, (b) TEA and (c) MOR.

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	124.10	—	—
S-2	226.42	—	—
S-3	194.63	0.35	0.36

area indicated to a successful synthesis of SAPO-34 catalyst under microwave crystallization. It can be noticed that the surfaces area differed from one sample to another. The surface area increases from 124.10 to 226.4 m^2/g when using TEA instead of DEA. The low surface area of catalyst when using DEA is related to large ununiformed crystal particles as shown in SEM images. The increasing area is almost for the small size of particles that formed when using TEA as structure direct agent.[24] SAPO-34/MOR recorded 194.6 m^2/g surface area with high micropore volume reached to 0.35 cm^3/g. This is due to uniform spherical particle morphology and also, the growing of the crystalline surface at sufficient synthesis time with high power energy to achieve this proper type of zeolite catalyst.[25] The reduction in surface area may be ascribed to the ununiformed morphology and existence of amorphous phase.[13] Additionally, the microwave power and relatively short synthesis time affects the growing of the crystalline surface and agglomeration of crystals to each other.[5] This cause cluster, and as results, reduces the external surface area.[17]

SEM analysis

SEM images of SAPO-34 templated with DEA, TEA and MOR are depicted in Fig. 3. The S-1 sample which used DEA template yields large cubic and spherical particles because the aggregation of small particles. The aggregation is caused mainly by microwave irradiation which may explained by undistributed nuclei that formed through high power irradiation energy.[18] The SEM image for TEA template reveal a cubic-like shape and it has smaller particle cover size of 0.5–3 μm. By using TEA, a broken crystals are seen since the hierarchically zeolite structure is arranged with crisscross pore structure.[26] The aggregation is caused mainly by microwave irradiation which may explained by undistributed nuclei that formed through high power irradiation energy. By using DEA, no common cubic shape was observed, but only formed molecular sieves with flake and hexagonal columnar morphology. S-3 catalyst sample that used MOR shows spherical particles with smaller size than S-1 and S-2. The particle morphology of CHA structure of SAPO-34 is strong function of template used.[17] The silica source, i.e., TEOS has great effect in SAPO-34 morphology. The variation in particle size for the three catalyst samples can be ascribed to the double effect of silica source and template type. The interaction between Si and the SDA structure is the main factor affects the rate of crystallization and nucleation.[23] The final crystal products depend largely on crystallization rate.[13] Also, the microwave power and time influence the crystal size due to allows for aggregation of particles, which yield large particle with uninform distribution. The crystals growth and the number of created nuclei influenced by type of template, silica source and synthesis method.[12]

EDX analysis

The dot-mapping of EDX graph analysis is depicted in Fig. 4. The molar ratio of catalyst n(Al): n(Si): n(P) for the three samples are 0.88: 0.12: 0.73 for S-1 while for S-2 is 1.23: 0.178: 1.06. In other hand, the molar ratio for S-3 is 1.13: 0.15: 0.71. The Si for three samples is not identical. The perfect distribution of AL, P and Si is for sample S-3 with MOR template. This indicates to proper incorporation and distribution of silicon in the catalysts. The moderate ratio of Si in the catalyst with MOR template gives it an important structure role, acidity and catalyst performance.[15,27] The molar ratio of Al which is

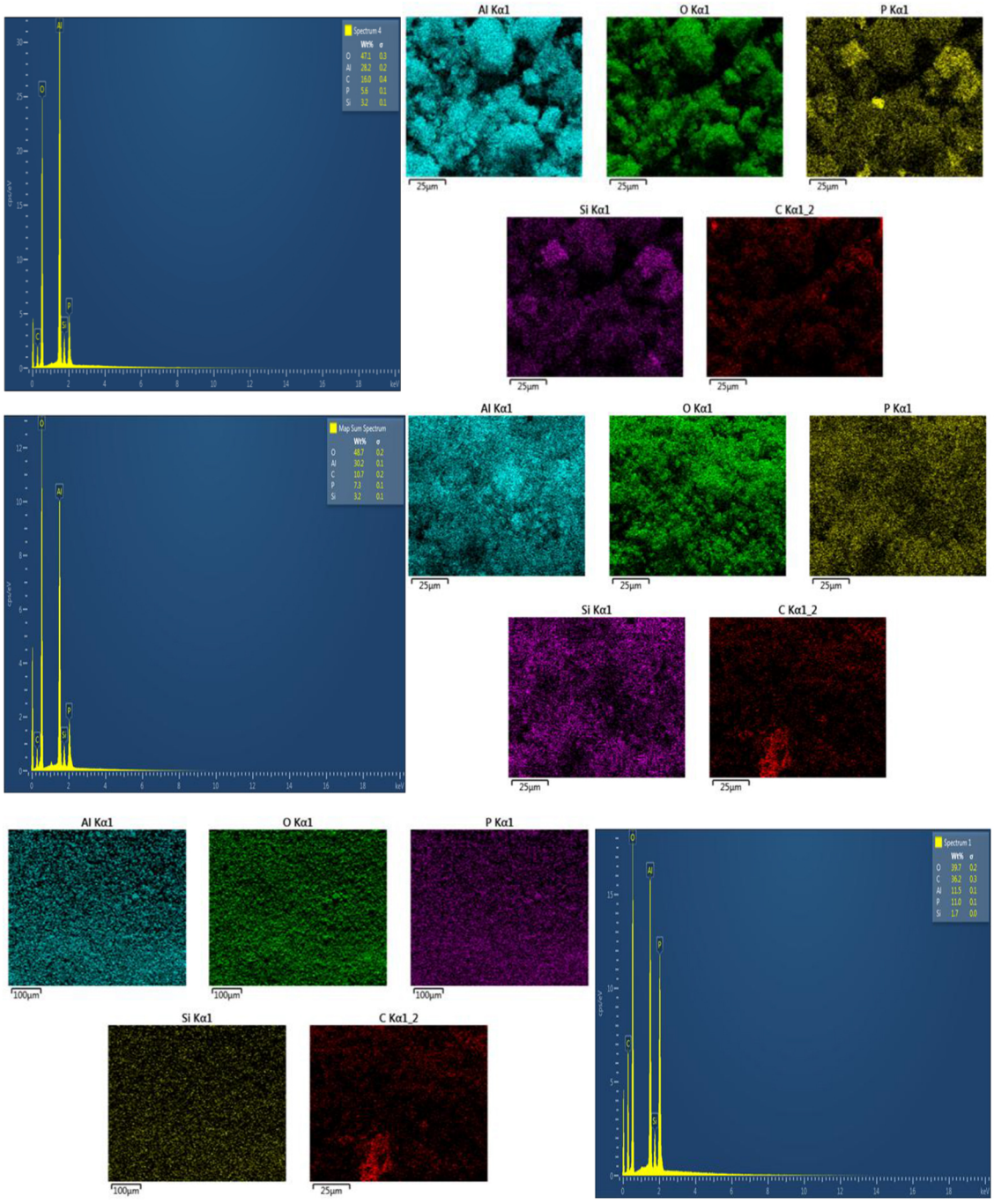


Fig. 4. EDX analysis of SAPO-34 samples S-1, S-2 and S-3, respectively.

considered as dominant and basis for other elements is in proper molar percentage. The EDX micrograph shoe better dispersion with uniform morphology of S-3 sample as compared to the others. This indicates to successful synthesis of SAPO-34 with MOR template under microwave irradiation. Si proper distribution reveals a crucial role in acidity, and hence, MTO catalytic performance. The proper distribution of elements in SAPO-34 framework creates Brønsted acidic sites inside pores. Si atoms took place inside SAPO-34 framework at crystal nucleation stage.[17] This leads to affecting the structure coordination, acid intensity for SAPO-34 and finally, the Brønsted acid sites.[13] For these reasons, it is expected a good performance of catalyst during MTO reaction with acceptable lifetime.

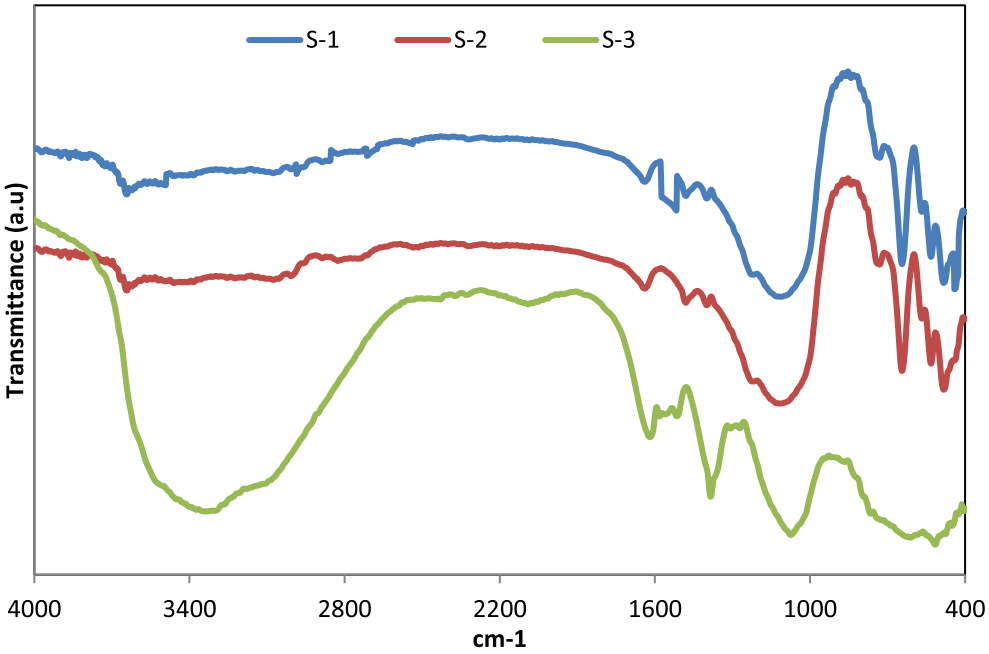


Fig. 5. FTIR spectroscopy of SAPO-34s samples.

FTIR analysis

The FT-IR spectra of S-1, S-2 and S-3 are depicted in Fig. 5. The FT-IR analysis for SAPO-34 using DEA (S-1) and TEA templates (S-2) were failed to produce desired functional groups, especially bands of about 4000 to 1650 cm^{-1}. Hence, MTO reaction over them does not included in this paper due to unidentified major peaks which greatly affects the obtained results. For SAPO-34 templated with MOR (S-3), the influence of spectra was obtained in wide rang wave number (400–4000 cm^{-1}). The major peaks were verified. The analysis shows bands of 3375, 2400, 1616, 1074, 765, 611, 516 and 450 cm^{-1}. The wave number around 3375 cm^{-1} is assigned to O-H stretching of Si(OH)Al strong band hydroxyl group.[28] The OH group gives a significant effect on Brθnsted acid sites which improves catalytic properties especially in reactions.[29] The IR spectra of 2400 cm^{-1} indicates to CO/CO_2 physically absorption and 1616 cm^{-1} indicates to physically absorption of water from atmosphere. The bands about 1074,765 and 611 cm^{-1} ascribe to O-P-O bending, promoted of MOR stretch and T-O bending in double 6-rings, respectively.[27] The bands of 516 and 450 cm^{-1} ascribe to T-O bending of silica tetrahedral that introduced in the SAPO-34 framework. The loss of intensity of SiO_2 peaks related to the fact that Si atom is strain incorporated in SAPO-34 structure when using microwave heating.[13]

TGA-DTG analysis

The TG analysis profile for the synthesized sample S-3 shows typical three regions of losing weight as illustrates in Fig. 6. The first region of weigh toss is at $T < 200$ °C which is accompanied to the endothermic heating process. It is attributed to desorption water from sample. The second region is at temperature range of 340–490 °C. The second losing weight region is that due to the combustion of the template and organic residue. There is another reason for losing weight in second region, which is further stripping of the heavy residue of organic templates molecules from channels and cages. However, the third losing weight, which is very small region, is at 900 °C, can be ascribed to the combustion of retained coke.[20] The weight loss of MOR/SAPO-34 is about 20.4% at 1100 °C which indicates to thermal stability against coke formation at high temperature. The substitution of Si in P or P-Al pair with the type of structure-direct agent enhances the catalyst stability in operation process for MTO conversion at high temperature.[18] The low amount of weight loss gives an indication of the thermal stability of the catalyst against coke deposition at high temperature in reaction process. In this case, the cocking rate is low which is agreed with longer lifetime. The substitution of Si in P or P-Al pairs with the type of structure-direct agent enhances the catalyst stability in operation process for MTO conversion at high temperature.

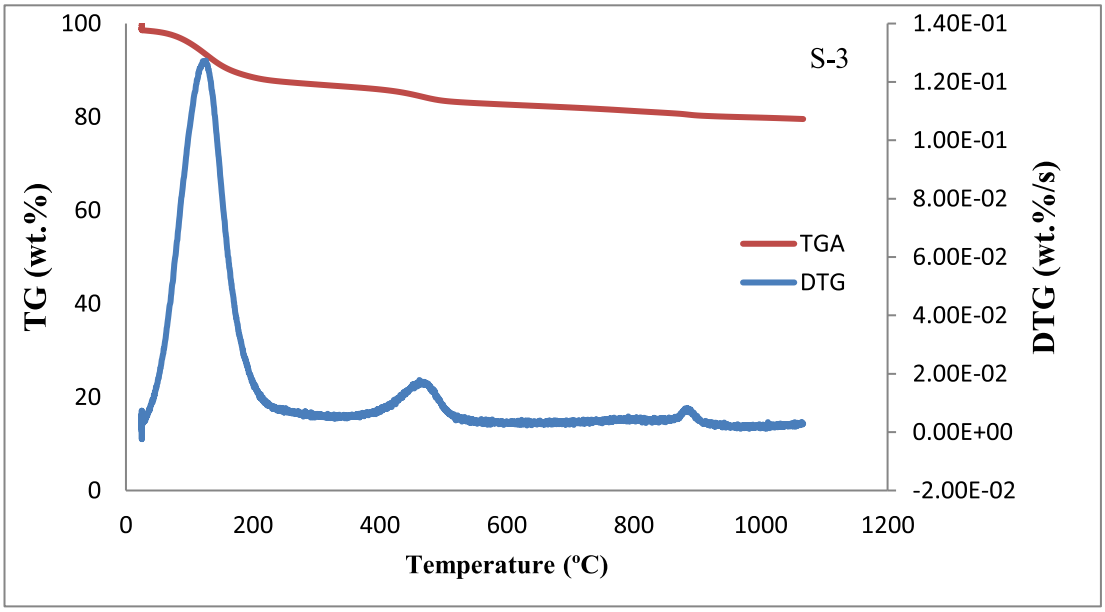


Fig. 6. TGA-DTG analysis of S-3 sample.

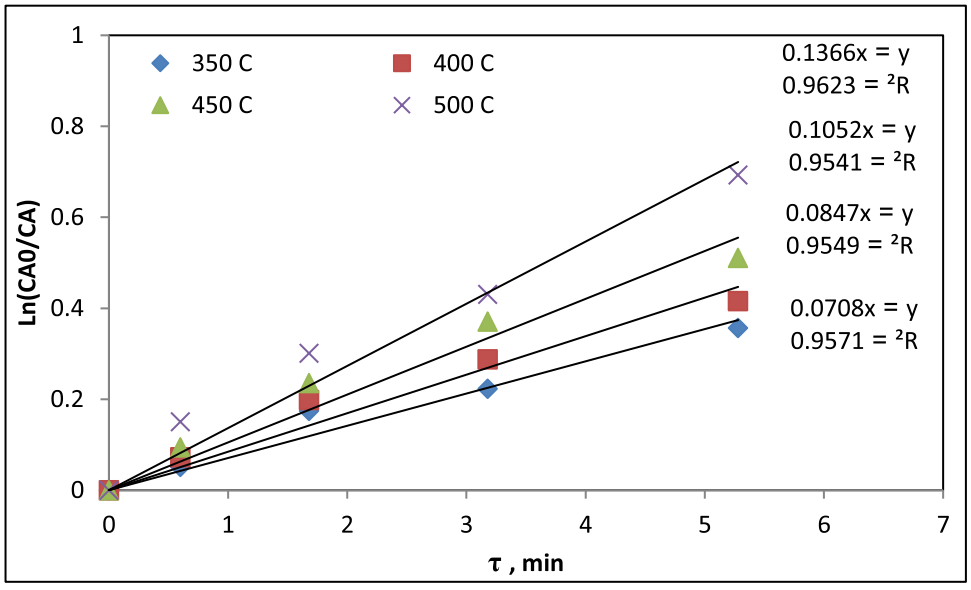


Fig. 7. First-Order kinetic fitting of MTO reaction of S-3 at 350, 400, 450 and 500 °C.

MTO kinetic study

In this section, the experimental data obtained from the kinetic study was analyzed. The kinetic experiments were carried out at four different temperatures (350, 400, 450 and 450 °C) with different space-time at atmospheric pressure. The integral method was employed for estimating the law of the reaction rate by calculating the remaining concentration and the space-time of reaction. The integral method is based on guessing a specific order of reaction, integrating the equation, and fitting the profile to a linear model. If the fit is non-linear, another rate order is guessed and tested. A first-order rate equation (n = 1) was guessed firstly. The experimental data at different temperatures have fitted in the first-order kinetic using the following Eq. (1):

$$\ln (C_{A0}/C_A) = k.\tau \quad (1)$$

Where C_{A0} and C_A represent the initial and final concentration in $g.L^{-1}$, respectively. Whereas k and τ are the reaction rate constant (min^{-1}) and space-time (min), respectively. As illustrates in Fig. 7, the data trend is well matched the first-order kinetic model for catalysts. Obviously, from 350 to 500 °C, increasing

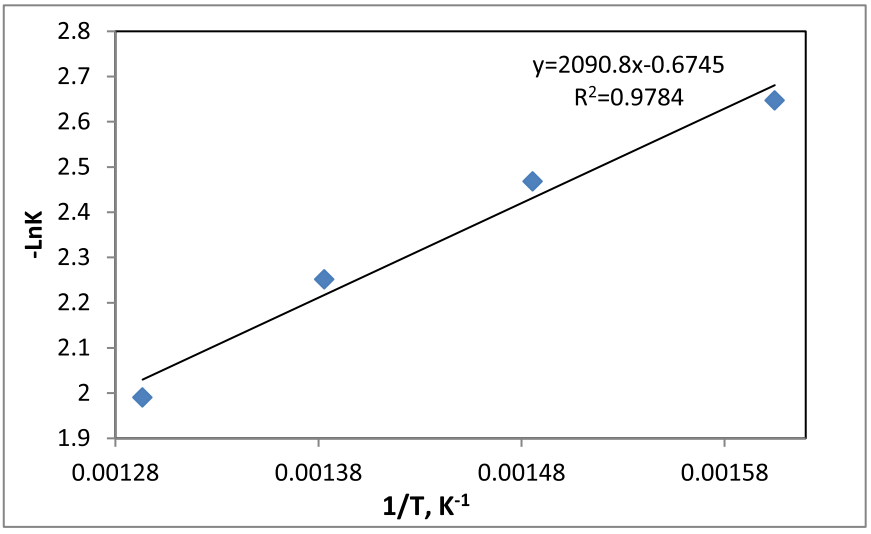


Fig. 8. Temperature dependency of methanol conversion over S-3 according to Arrhenius equation.

the temperature of a reaction generally speeds up the reaction (increases the rate) because the rate constant increases according to the Arrhenius equation. Moreover, with increasing temperature, the value of exponential part of Arrhenius equation becomes less negative, and hence, increasing the value of k. This is also conforming the characteristics of first-order kinetics.

The activation energies can be calculated from the slope of Arrhenius equation that plotted in temperatures ranges of 350–500 ˚C according to Eq. (2):

$$-\ln k = -lnk_0 + \frac{E}{RT} \quad (2)$$

Where k and k_0 are the reaction rate constant and pre-exponential factor in $g_{MeOH}\ g_{cat}^{-1}\ min^{-1}$, respectively. E is the activation energy in J/mol, R is the gas constant in J/mol and T is the reaction temperature in kelvin.

$(-\ln k)$ vs. $(1/T)$ is plotted which give straight lines as shown in Fig. 8. The values of E and K_0 are 0.08790 $g_{MeOH}\ g_{cat}^{-1}\ min^{-1}$ and 17.383 kJ/mol, respectively.

Catalyst performance

The methanol to light olefins conversion was performed with S-3 sample which used MOR template since it gave the proper SAPO-34 successfully using microwave heating method. The effect of temperature at 350, 400, 450 and 500 ˚C and the effect of WHSV with 7.7, 15 and 21.1 h^{-1} were investigated.

Effect of temperature

The conversion of methanol-to-olefins over SAPO-34 in different temperatures at 7.7 h^{-1} is depicted in Fig. 9. At 350 ˚C, the conversion is not complete and almost reached to 85% for 500 min. When the temperature increased to 400 ˚C, the best and high conversion was achieved and it maintained at 100% for 400 min, then the conversion decreased to 86% at 500 min. when the temperature raised to 450 ˚C, the conversion is 100% for 400 min and then it dropped to 81% at 500 min. At 500 ˚C, the conversion is 100% for 400 min and drops to 89% for 500 min. the high conversion in high temperature did not yield high olefins due to increase of coke formation.[30] The high conversion performance in MTO reaction can be related to proper silicon content and distribution. These results agreed with the phase environments and textural properties and specifications of S-3 sample. The moderate acidity (moderate Si content) corresponds to the effective Brønsted acid sites in the structure framework exhibited the perfect catalyst performance during MTO reaction.[29] It is also plays a crucial role in catalyst stability under high reaction temperature.[31] The incomplete conversion at relatively low and high reaction temperature can be explained by the induction period for existed mechanism during the reaction.[19] The similar conversion behavior at long reaction time and deactivation trend can be ascribed to the crystal size.[32] Larger particles cause shorter lifetime and higher deactivation must be in sight at MTO process.[33]

Product selectivity

The products selectivity on S-3 sample with different temperature at 7.7 h^{-1} is shown in Fig. 10. At 350 ˚C, the total olefin is 58% for 300 min and the ethylene selectivity is 28% of total products. The highest olefins selectivity is 63% for 300 min at 400 ˚C

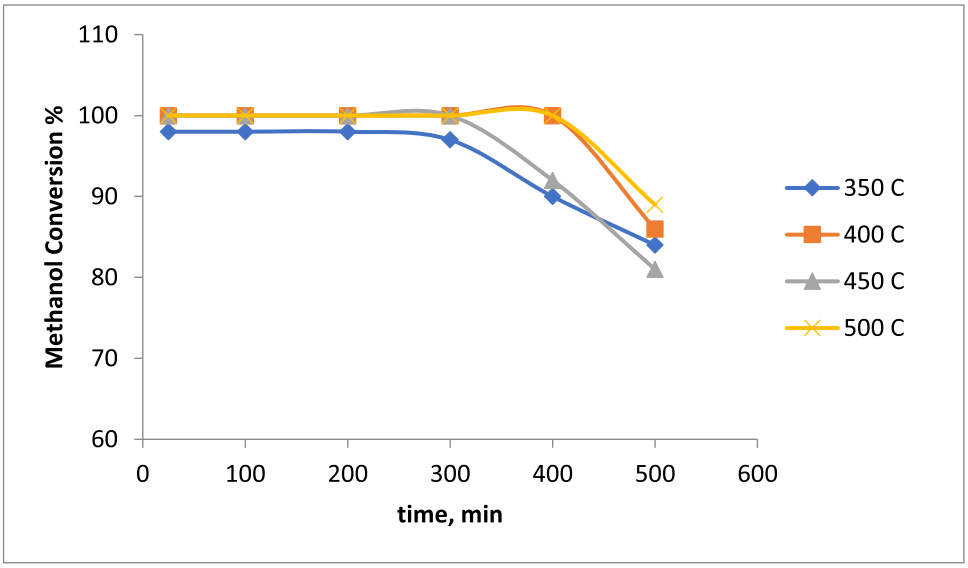
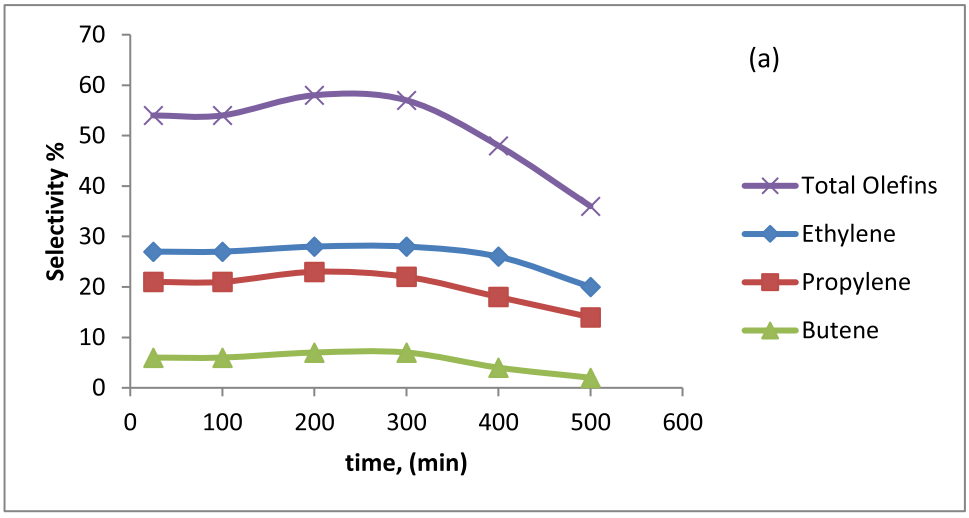


Fig. 9. Methanol conversion to light olefins over S-3 sample at different temperatures at T= 350, 400, 450 and 500 °C, WHSV= 7.7 h^{-1} and atmospheric pressure.



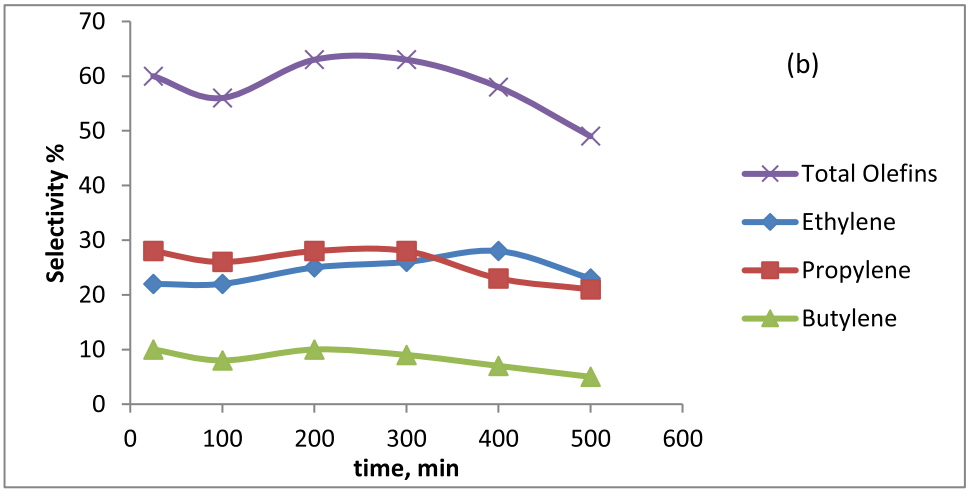


Fig. 10. Continued.

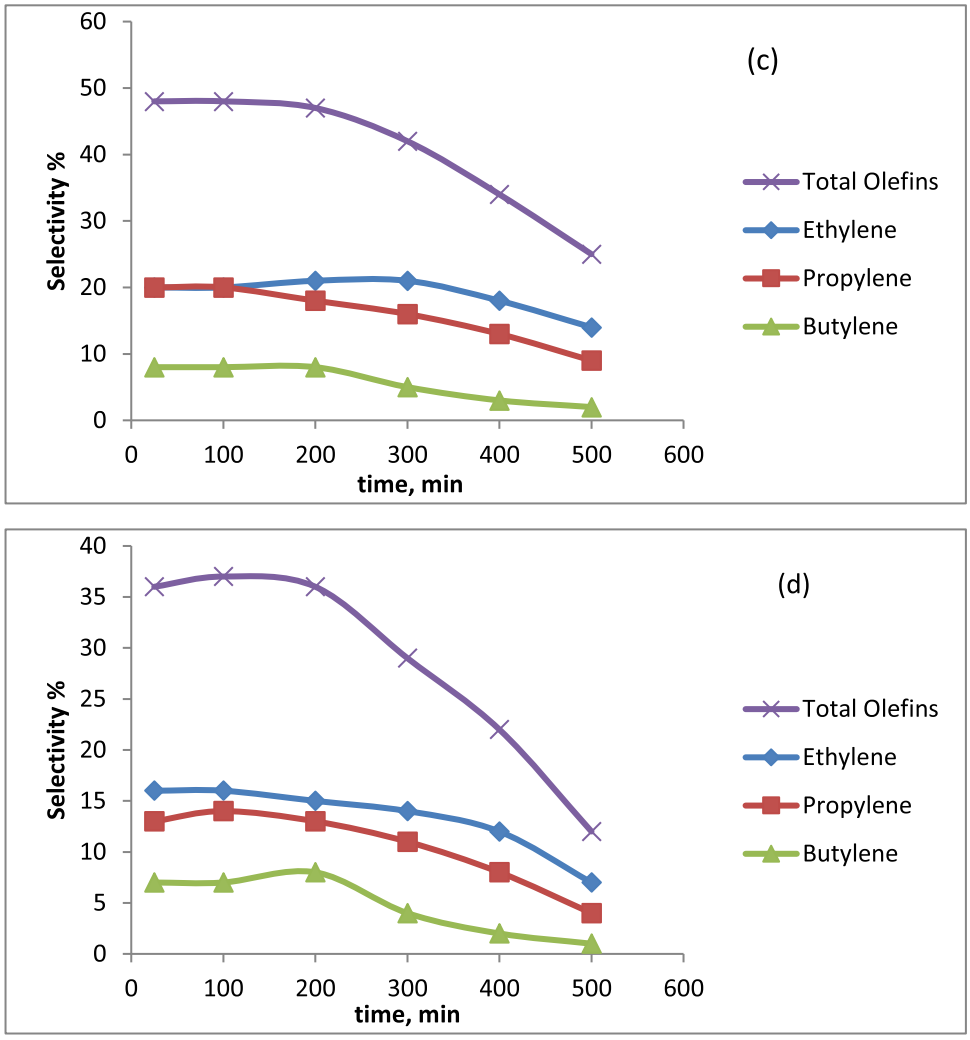


Fig. 10. Light olefins selectivity of S-3 sample at different temperatures of)a) 350, (b) 400, (c) 450 and (d) 500 °C, WHSV = 7.7 h^{-1} and atmospheric pressure.

as compared to other temperatures. When raising temperature to 450 and 500 ˚C, the products selectivity of light olefins decreased. The selectivity is 48% for 200 min at 450 ˚C. Then, it drops fast to a value of 36% for 200 min and the ethylene selectivity reduces to very low value of 16% for 200 min at temperature of 500 ˚C. This phenomenon may be explained by the cracking of some amount of olefins to other products like methane at high temperature.[12,34] These results depict that it can be control the olefins product by adjusting reaction temperature in MTO operation process.[17,21] By comparison, the selectivity of lower olefins at reaction temperature of 400 ˚C is better than others. This may be attributed to limit coke formation at this temperature. The relationship between the pore cages and the coke deposition is an important factor for increasing catalyst lifetime.[32] Despite the coke deposition, the acid strength is another crucial factor which promotes the olefin selectivity and reduces coke formation.[29] This achieves by reducing hydrogen transfer from reacted methanol to saturated aromatics and hydrocarbons, which result in increasing the olefin selectivity and reducing the coke formations. Also, the structure of SAPO-34 of cage pores which existed in eight-membered rings helps to select light olefins and restrict the carbon atoms to accumulate inside pores.[31] At reaction temperature lower and higher than 400 ˚C, the olefin selectivity decreased in same trend. This can be introduced to the diffusion limitations of the reactants and products, especially for small pores, which cause coke deposition.[32] Subsequently, catalyst deactivates fast due to occupy coke at cages. As a result, the olefin yield decreases abruptly.[35]

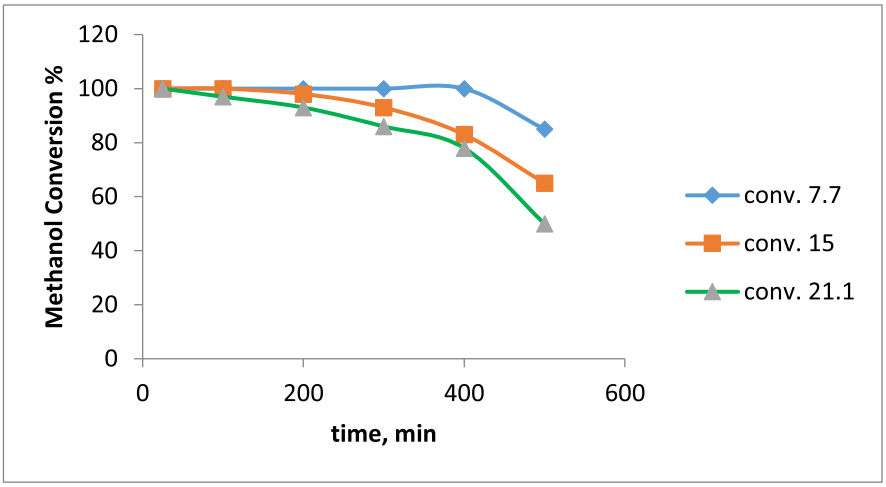


Fig. 11. MTO conversion over S-3 at T = 400 °C, WHSV = 7.7, 15 and 21.1 h^{-1} under atmospheric pressure.

Effect of space velocity

Fig. 11 illustrates the effect of different weight hourly space velocities on MTO conversion over SAPO-34 sample S-3 at 400 °C. As it is shown, the lowest space velocity of 7.7 h^{-1} leads to highest conversion, while the methanol conversion decreases when increases the space velocity to 15 h^{-1}. As increases WHSV to 21.1 h^{-1}, the conversion be the lowest and reaches at 500 min to about 40%. The decreasing of methanol conversion to low values when increasing space velocity can be explained by two reasons. The first is that at high space velocity, the methanol reaction over catalyst is uncompleted and more quantity of feed appears in products. The second is that by increasing the space velocity, more molecules are reacting per unit time, and hence, the rate of coke formation is also increase which results in decreasing the lifetime of SAPO-34 catalyst.[12,17] With long residence time of methanol reactant, the diffusion inside pores becomes better. At low space velocity, the long diffusion path fills of reactant species and hinders the formation of coke. The product be in high valuable quality and high yield. As increasing reactant flow, shorter diffusional path involves in reaction inside cages.[31] This allows the coke to form inside unused volume path, which means reducing of olefins product, coke deposition and deactivation of catalyst rapidly.[32]

Conclusion

Three samples of zeolite catalysts were prepared using DEA, TEA and MOR template with microwave irradiation in order to synthesize SAPO-34 molecular sieve. DEA and TEA failed to produce SAPO-34 while it produced SAPO-41. SAPO-34 was successfully prepared using MOR with smaller crystal size as compared with the other samples. The XRD, SEM, EDX, BET, FTIR and TGA analysis of S-3 sample showed perfect characterization of SAPO-34 zeolite catalyst. MTO kinetics was studied over SAPO-34/MOR (S-3). The results revealed of first-order kinetic reaction and the activation energy for the reaction was 17.383 kJ/mol. MTO process over SAPO-34 sample S-3 was performed in trickle bed reactor at different temperatures and space velocities. From results, it can be concluded that at 400 °C with 7.7 h^{-1} produce higher amount of light olefins, high conversion and long lifetime. The reason can be explained as that temperature of 400 °C hinders the coke formation at early time which can produce more amounts of olefins. The low space velocity helps to complete the reaction over catalyst. The high temperature and high space velocity accelerate the rate of coke formation which leads to fast deactivation of catalyst. To get higher olefins selectivity, it can be adjusting the temperature and space velocity to more specific value in MTO process.

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Authors' declaration

- Conflicts of Interest: None.
- 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.
- No animal studies are present in the manuscript.
- No human studies are present in the manuscript.
- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

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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تحقيق مواصفات المنخل الجزيئي SAPO-34 بقوالب متعددة لعملية تحويل الميثانول الى أوليفينات: دراسة حركية وتجريبية

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الخلاصة

أصبحت الأوليفينات الخفيفة من المواد المهمة التي تدخل في الصناعات البوليمرية والبتروكيميائية. نظراً لإرتفاع تكلفة إنتاج الأوليفات من المصادر النفطية فإنه تم إيجاد البديل المناسب لذلك وهو انتاجها من مصادر غير نفطية مثل كحول الميثانول. يعتبر استخدام زيولايت SAPO-34 كعامل مساعد مناسب في هذا المجال. لهذا الغرض, تمت محاولة تحضير هذا النوع بواسطة إشعاع المايكروويف بإستخدام DEA, TEA و MOR كقالب للتحضير. أجريت فحوصات XRD, BEA, SEM, EDX, FTIR و TGA غلى النماذج المحضرة. أستخدمت طاقة 800 واط للتحضير ولمدة 200 دقيقة. أظهر تحليل XRD فشل تكون SAPO-34 عند استخدام DEA و TEA و تكون SAPO-41 بدلاً عنه. بينما تم تحضير SAPO-34 بنجاح بإستخدام MOR. وجد أن المساحة السطحية (م2/غم) للنماذج S-1, S-2 و S-3 كانت 124.10, 226.42 و194.6. أظهر تحليلSEM-EDX أحجام بلورت كبيرة للنموذجين S-1 و S-3 بينما كانت صغيرة نسبياً للنموذج S-2. أظهر فحص FTIR للنموذج S-3 تطابقاً كبيراً مع القمم القياسية للعامل المساعد SAPO-34. بين فحص TGAللنموذج S-3 ثباتاً ممتازاً في درجات الحراة العالية التي تصل الى 1100 درجة مئوية وجد أن التفاعل يتبع حركية من الدرجة الأولى وبطاقة تنشيط 17.383 كيلوجول/مول. تم إجراء عملية تحول الميثانول الى اوليفينات MTO بواسطة مفاعل ذو طبقة ثابتة في درجات حرارة 350, 400, 450 و 500 مئوية وبسرع وزنية 7.7 و 15 ساعة-1. سجلت أن درجة حرارة 400 مئوية بسرعة وزنية 7.7 ساعة-1 أعلى قيمة لإنتقائية الاوليفينات حيث وصلت الى 63% من الناتج الكلي وبتحول 100% لمدة 400 دقيقة. وجد أن زيادة الحرارة وزيادة السرعة تؤثر سلباً على التحول الكلي وكذلك تقلل من إنتقائية الاوليفينات الخفيفة.

الكلمات المفتاحية: ميثانول الى اوليفينات، تسخين بالمايكروويف، زيولايت SAPO-34، إنتقائية، قوالب.