

The Synthesis of SAPO-34 at Different Crystallization Temperature and its Catalytic Performance for Methanol to Olefins Reaction

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Abstract

In order to enhance the catalytic performance of SAPO-34 for the reaction of methanol to light olefins (MTO), three different crystallization temperatures were used to synthesize SAPO-34. The catalysts were synthesized hydrothermally with molar composition as 1 Al_2O_3 : 1 P_2O_5 : 0.4 SiO_2 : 1 TEAOH: 0.5 TGA: 0.5 MOR: 70 H_2O . The effects of the crystallization temperature on the phase purity, morphology and functional groups of SAPO-34 were characterized by XRD, SEM and FTIR techniques. The relative crystallinity was decreased by increasing crystallization temperature and some impurities appeared at high crystallization temperature. All samples showed cubic morphology with different crystal size. The catalytic performance of synthesized SAPO-34 was investigated in a fixed-bed reactor at 410°C. For the MTO reaction, all synthesized catalysts showed similar product distribution and methanol conversion, but light olefins selectivity was greatly dependent on the crystallization condition. The sample synthesized at 170°C and 24 h, possessed the highest light olefins due to highest amount of acid sites, relative crystallinity and smallest mean crystal size.

Keywords: SAPO-34, MTO Process, Crystallization Temperature

1. Introduction

Zeolites are crystalline microporous aluminosilicates with periodic arrangements of cages and channels that find extensive industrial uses as catalysts, adsorbents and ion exchangers [1]. Silicon-substituted aluminophosphate (ALPO) molecular sieves (SAPOs) are an important class of zeolites. ALPO molecular sieves have no actual catalytic capabilities due to their neutral framework. Introduction of silicon atoms into the framework of ALPOs results in negative

imbalance in the framework's charge. Neutralization of the negatively charged centers with the proton left after decomposition of organic template in the calcination process leads to appearance of acidity as well as their catalytic application [1, 2]. Among SAPOs material, SAPO-34 with chabazite structure has received considerable attention in chemical industry in recent years. It has exhibited excellent catalytic performance in methanol-to-olefin (MTO) reaction due to the contribution of small pore, medium acidity and good thermal/hydrothermal stability [3, 4, 5].

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Chabazite is a three dimensional molecular sieve with ellipsoidal cages of $6.7 \times 10 \text{ \AA}^\circ$ interconnected via 8-membered ring windows with pore openings of $3.8 \times 3.8 \text{ \AA}^\circ$ [6]. SAPO-34 is normally synthesized hydrothermally from a gel containing an alumina source, a silica source, a phosphorous source and one or a combination of organic structure directing agents [5]. The crystallization conditions are very important factors in the hydrothermal synthesis of zeolites which researchers have paid particular attention to. Valizadeh *et al.* [7] used triethylamine as template in SAPO-34 synthesis. Crystallization temperature in this case was in the range of 170 – 220 °C. Based on their results, by increasing the temperature, the crystallinity of the SAPO-34 increased, but crystal size decreased. In their study, the sample that was synthesized at low temperature had many impurities and increasing the temperature caused impurity to transform to SAPO-34. Topuz *et al.* [8] examined the synthesis of SAPO-34 from gel synthesis containing tetraethyl ammonium hydroxide (TEAOH) as template by two-stage variable temperature method, in which the crystallization process was conducted at two different temperatures. They concluded that crystallinity and average particle size decreased with decreasing the crystallization temperature. Also, it was revealed that mixing of synthesis mixture either by stirring or recirculating promoted more homogeneous synthesis conditions and resulted in a more uniform crystal morphology.

According to the literature, crystallization temperature is one of the key parameters that can improve properties of SAPO-34 and the

performance of catalysts at MTO process may be affected by these properties. On the other hand, there are not enough researches about the effect of crystallization temperature on SAPO-34 properties and its performance in MTO reaction. In this regard, in this paper we reported the effect of crystallization temperature on the physico-chemical properties of synthesized SAPO-34 from gel synthesis containing tri-templating to obtain the best temperature of synthesis to find the proper catalyst for MTO reaction.

2. Experimental

2-1. SAPO-34 preparation

SAPO-34 was crystallized from mixtures with a molar composition of 1.0 Al₂O₃: 1P₂O₅: 0.4 SiO₂: 0.5 MOR: 0.5 TEA: 1TEAOH: 70 H₂O. The source of Al, P and Si were Aluminum isopropoxide (AIP, Merck), phosphoric acid (85% wt H₃PO₄, Merck), Silica gel (SiO₂, Merck) respectively. Tetraethyl ammonium hydroxide (20 wt% aqueous solution of TEAOH, Merck) and morpholine (Merck), triethylamine (Merck) were used as the organic templates. The obtained gel was aged at room temperature for 8 h with agitation. After the aging period, the gel was transferred into a Teflon lined autoclave and the crystallization process was performed with in situ agitation at three temperatures (according to Table 1) for 24 h. The synthesized material was recovered by centrifugation, washed six times, and then dried at 383 k for 10 h. The final product was calcined at 823 K for 5 h.

2-2. Characterization

The X-ray diffraction (XRD) patterns of catalysts were obtained on a powder X-ray

Table 1
Crystallization Condition for SAPO-34 Samples

Catalyst	Crystallization temperature (°C)	Time (h)
S-1	170	24
S-2	190	24
S-3	210	24

Diffractometer (Bruker D8) using CuKa radiation ($\lambda = 1.54 \text{ \AA}$). For zeolite SAPO-34, the crystallinity was calculated as the ratio of the total area under the characteristic peaks of SAPO-34. The crystal size morphology was analyzed by scanning electron microscopy (SEM) using Philips XL30 microscopes, operating at 20 kV. Diffuse reflectance FTIR was conducted using a Bruker Tensor-27 spectrophotometer. The FTIR experiments of in-situ heat-treated samples were performed on pure powder of samples without KBr under flow of nitrogen. IR spectra of the samples in the region of the framework stretching vibrations (450–4000 cm^{-1}) were measured.

2-3. Catalyst performance

Fig. 1 shows experimental setup of methanol conversion to olefins under atmospheric pressure and at 410°C. The 1 g calcined SAPO-34 catalyst and 2.5 g silicon carbide (as an inert) was packed in the center of stainless steel reactor and heated by a tubular furnace. The reactor consisted of a 45 cm long and 1.51 cm outer diameter. The depth of the catalyst bed in the reactor was 5 cm. The catalysts were pretreated with 150 ml/min flow of N_2 at 550°C for 1 hour, then

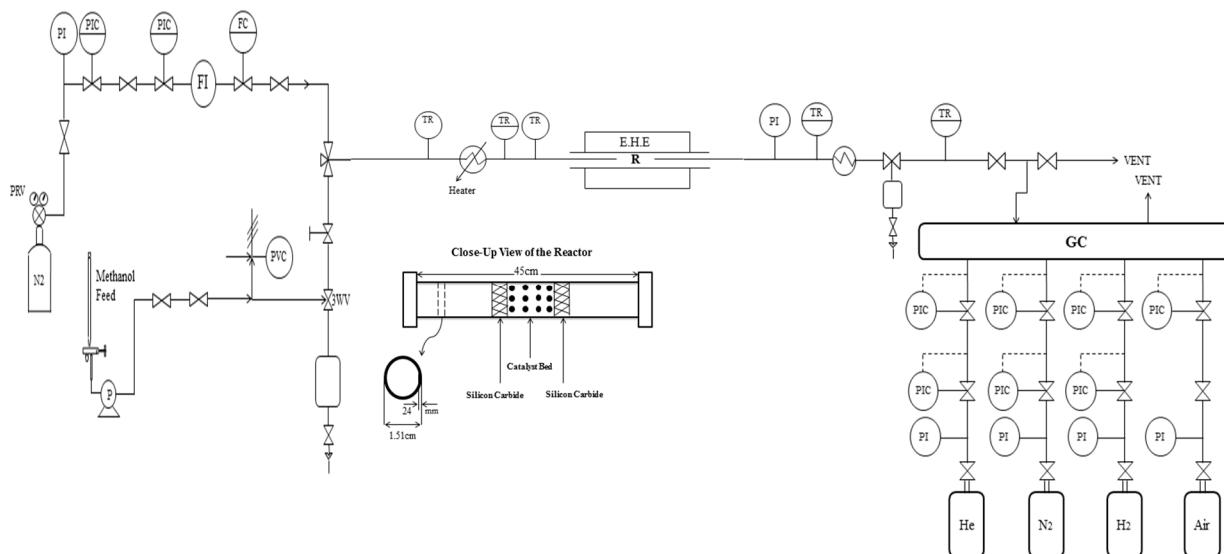
the temperature was decreased to reaction temperature (410°C). The liquid mixture of methanol in water (30 wt%) with a weight hourly space velocity (WHSV) of 6.5 h^{-1} , was fed into the reactor. The gas product was analyzed by a Hewlett-Packard 5890 flame ionization detector (FID) gas chromatograph (GC) equipped with Agilent J&W GS-alumina and plot columns. The oven was operated at 50°C, then ramped at 5°C/min up to 180°C and held for 5 min at 180°C. Finally the temperature ramped to 50°C at the same rate for the next test.

3. Results and discussion

3-1. Effect of crystallization temperature on the crystallization of SAPO-34

XRD patterns of SAPO-34 synthesized for 24 h in the 170–210°C range are shown in Fig. 2. In all samples, the characteristic peaks of SAPO-34, [8, 9, 10, 11], at $2\theta = 9.6^\circ$, 13° , 15.9° , 17.7° , 20.7° , 24.9° , 26° and 31° were identified, and some impurity peaks in sample S-3 were detected. This implies that the major phase is SAPO-34. The highest crystallinity was obtained for SAPO-34 synthesized at 170°C. This sample was also used as the reference to determine the relative crystallinity of SAPO-34 synthesized at other temperatures and results are shown in Table 2. According to Table 2, the relative crystallinity decreased with increasing the crystallization temperature from 170°C up to 210°C due to appearance of further amorphous phase, impurity and defect structure. Also, there were slight peaks at $2\theta = 7.5^\circ$, 22.5° for sample S-3 which were attributed to SAPO-5 (AFI structure).

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Notations

CV: Check Valve
E.H.E: Electrical Heating Furnace
FI: Flow Indicator
GC: Gas Chromatography

GV: Gate Valve

P: Pump
PI: Pressure Indicator
TR: Temperature Recorder
PIC: Pressure Controller

PRV: Pressure Regulator Valve

PSV: Pressure Safety Valve
R: Reactor
TR: Temperature Recorder
3WV: 3-WayValve

Figure 1. Experimental setup for activity test of SAPO-34 catalysts toward methanol to olefin.

Table 2

Properties of SAPO-34 Samples

Sample	Product Phase	Relative Crystallinity (XRD %)	Mean Crystal Size (SEM, μm)
S-1	SAPO-34	100	1.615
S-2	SAPO-34	74	1.9
S-3	SAPO-34 + SAPO-5	73	1.631

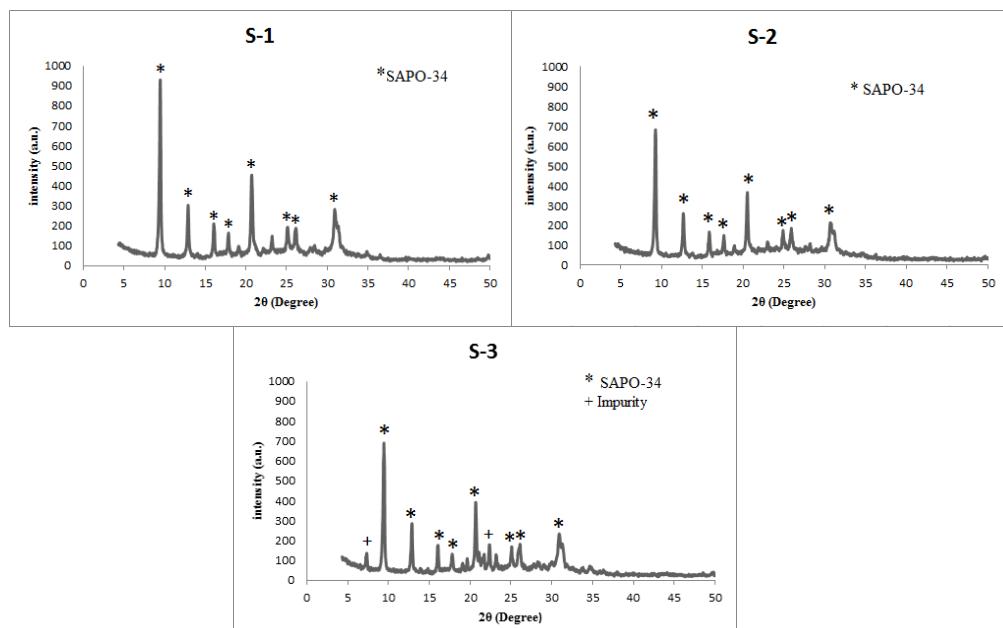


Figure 2. XRD patterns of SAPO-34 samples.

3-2. SEM characterization

The SEM micrographs (Fig. 3) showed the cubic SAPO-34 crystals with sizes in micrometer range. The average particle size of SAPO-34 synthesized at different temperature was determined by measuring the size of at least 70 crystals on the SEM images and results are shown in Table 2. According these results, with increasing crystallization temperature the average particle size increased from 1.615 to 1.9 μm but, by further increasing the temperature the crystal size decreased to 1.631. The size of

the crystals depends on the relative contribution of nucleation and growth processes. Particles with narrow particle size distribution could result from the rapid burst of all nuclei in the course of short induction period. The increase in the particle size with temperature can be the result of the shorter nucleation period that causes the decrease in the total number of nuclei formed [8]. The reduction of crystal size at 210°C resulted from more nucleation due to receiving high energy.

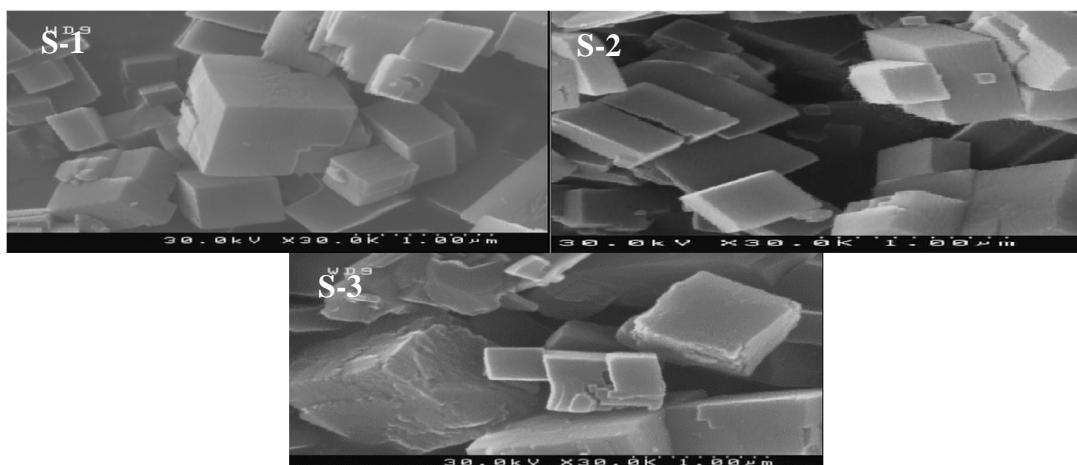


Figure 3. SEM micrographs of SAPO-34 crystals synthesized.

Table 3

Methanol conversion and products yield of synthesized catalysts

Sample	Light Olefin Selectivity (wt%)		$C_2= - C_3=$ (wt%)
	$C_2\text{H}_4$	$C_3\text{H}_6$	
S1	35	54	89
S2	40	29	69
S3	39	32	71

3-3. Infrared spectral analysis

Infrared spectra of the samples in the framework vibration frequency region are shown in Fig. 4. According to the spectra, the characteristic absorption bands of the SAPO-

34, i.e. absorption peaks at 1640 (hydroxyl groups from physically adsorbed water), 1110 (asymmetric stretch of O-P-O), 860 (protonated template), 710 (symmetric stretch of O-P-O), 640 (T-O bending in

D6 rings), 480 (T–O bending of silicon tetrahedrons) cm^{-1} are in good agreement with the published data and there is another peak at 3400 cm^{-1} in the three samples that is related to the structural OH, which can act as active sites for acid-catalyzing reaction, i.e. MTO process [10, 12]. This peak indicates P-OH, Si-OH, Al-OH and Si-OH-Al bonds [13]. Among these hydroxyl groups, the Si-OH-Al bound is Brønsted acidic site in which methanol and DME over this are converted to olefins. Other OH groups (P-OH, Si-OH, Al-OH) are produced in the defect structure and they are useless for the conversion of methanol to light olefins. Stronger absorbance at 3400 cm^{-1} indicates higher intensity of bridge hydroxyls. The intensity of this peak was almost equal for samples S-1 and S-3, but according to XRD analysis the crystallinity of sample S-3 was lower. It means that the high intensity of OH peak for sample S-3 in FTIR analysis is attributed to the formation of OH groups in the defect

structure. So, intensity of this peak can have an effect on catalytic performance of SAPO-34.

3-4. Catalytic performance in MTO reaction

The catalytic activity of synthesized samples in the MTO reaction was studied at 410°C with a WHSV of 6.5 h^{-1} . The product distribution for MTO reaction on different samples as a function of time on stream (TOS) is shown in Fig. 5. Table 3 gives the maximum light olefins selectivity of the SAPO-34 samples, which was measured in various TOS. All of the prepared samples have the same trend in the total light olefins selectivity, but the distribution of products and the maximum selectivity of light olefins varied. As shown in Fig. 5, at first all samples indicated low activity, thereafter, the production of ethylene and propylene rapidly increased with TOS and obtain their maximum selectivity values, then production of light olefins started to decrease.

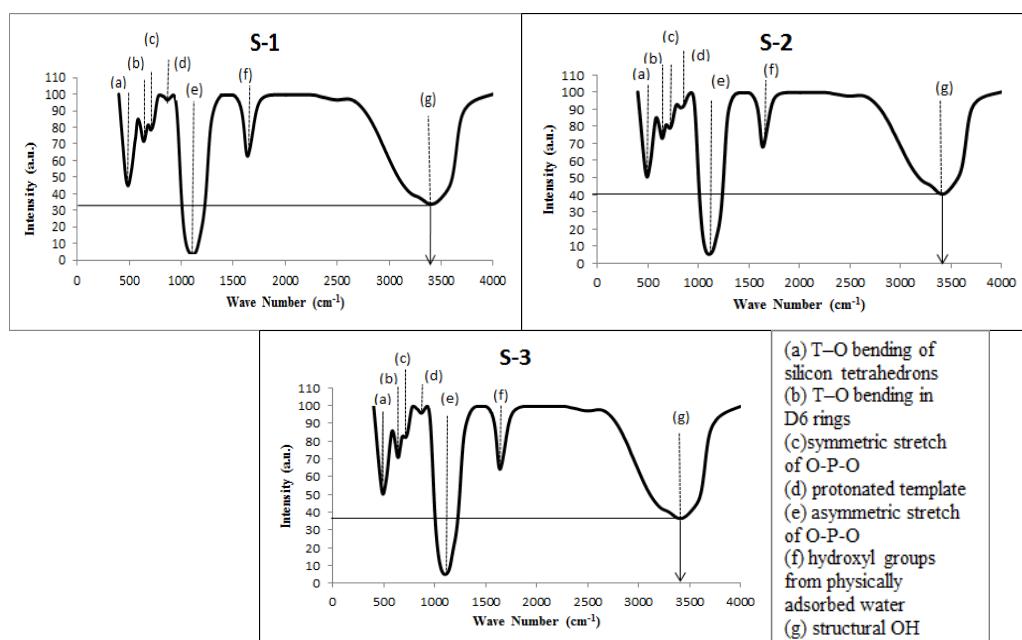


Figure 4. FTIR spectra of catalysts.

According to these figures, propylene selectivity started to decrease much earlier than ethylene selectivity, this phenomenon is a sign of decreasing free volume in the pore structure of catalysts due to the formation of larger hydrocarbon species. This large species act as organic centers and could adsorb fewer methyl groups due to the pronounced steric hindrance imposed by pore structure of SAPO-34 catalysts and are more prone to producing ethylene instead of propylene [11]. By comparing the selectivity curves of samples, decreasing of ethylene selectivity for sample synthesized at 190°C and 24 h, (S-2) happened earlier. This result may be explained by the crystal size of catalysts. Big crystals had long intracrystalline diffusion length, enough for the reaction intermediates to react into coke

which subsequently deactivates the catalyst rapidly and decreases the light olefins selectivity. This supports the notion that catalyst lifetime strongly depends on the crystal size of SAPO-34 [14]. Hence, samples S-1 and S-3 had longer life time due to their small mean crystal size. According to Table 3, sample S-2 had lower olefins selectivity (69%) in comparison with sample S-1 (89%), due to its larger particle size and lower relative crystallinity because the presence of non-framework species decreases the number of active sites and blocks partial micropores and consequently the olefin selectivity reduced [10]. In addition, the maximum product selectivity for three samples decreased in order of S-1>S-3>S-2 which agreed with the intensity of the OH bond of these samples in FTIR analysis.

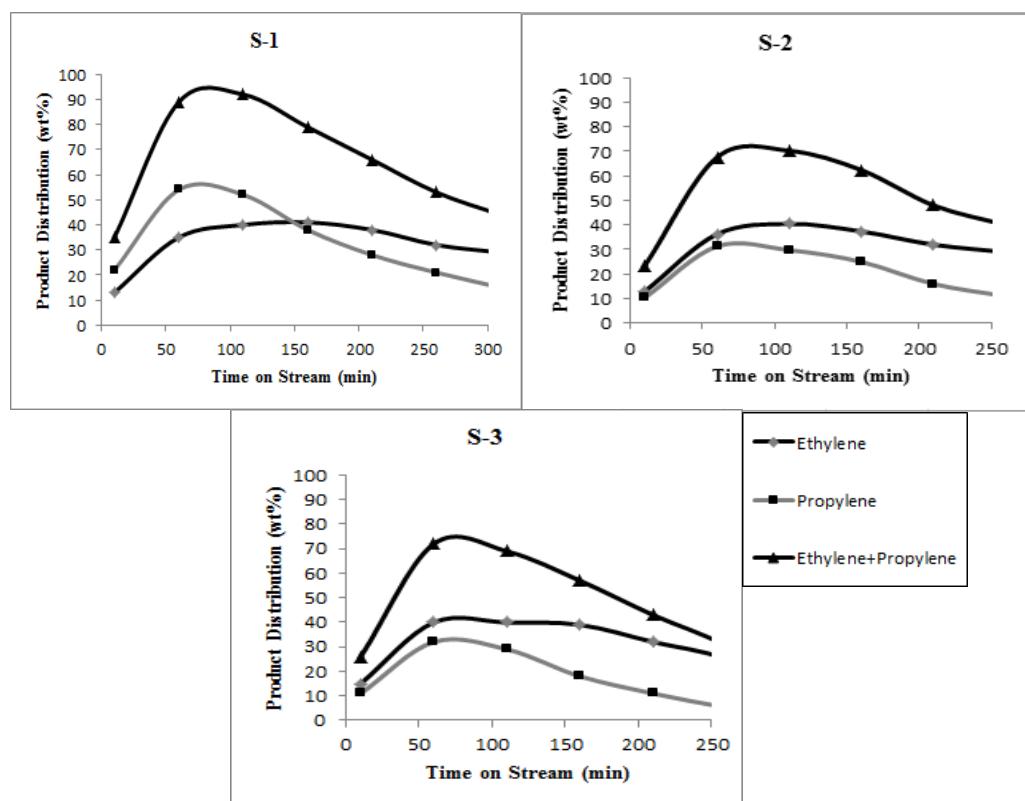


Figure 5. Product distribution with TOS over synthesized catalysts at 410°C, WHSV of 6.5 h⁻¹.

4. Conclusions

To evaluate the effect of crystallization temperature on the physico-chemical properties of SAPO-34, samples were synthesized at three different temperatures of 170, 190, 210°C and the effect of crystallization temperature on the catalytic properties such as morphology, crystallinity, crystal size, purity of catalyst and catalyst performance in MTO process were studied. According to XRD patterns, pure CHA structure was obtained in the two first synthesized temperatures and the impurity phase was observed for sample synthesized at high temperature. Also, by increasing the crystallization temperature, the relative crystallinity decreased. The results of SEM showed that the average particle size increased with increasing the crystallization temperature up to 190°C, then by further increasing the time, the crystal size decreased. Moreover, the FTIR analysis identified the desired functional groups. Based on the MTO process result, the sample synthesized at 170°C and 24 h showed the highest light olefins selectivity (89%) due to best crystallinity, small crystal size and highest acid sites concentration.

References

- [1] Askari, S. and Halladj, R., "Ultrasonic pretreatment for hydrothermal synthesis of SAPO-34 nanocrystals", *Ultrason. Sonochem.*, **19**, 554 (2012).
- [2] Salmasi, M., Fatemi, S. H. and Taheri Najafabadi, A. "Improvement of light olefins selectivity and catalyst lifetime in MTO reaction; using Ni and Mg-modified SAPO-34 synthesized by combination of two templates", *J. Indus. Eng. Chem.*, **17** 755 (2011).
- [3] Bing, L., Peng, T., Jinzhe, L., Jingrun, C., Yangyang, Y., Xiong, S., Dong, F., Yingxu, W., Yue, Q. and Zhongmin, L., "Synthesis of SAPO- 35 molecular sieve and its catalytic properties in the methanol to olefins reaction", *Chin. J. Catal.*, **34**, 798 (2013).
- [4] Dai, W., Scheibe, M., Li, L., Guan, N. and Hunger, M., "Effect of the Methanol-to-Olefin Conversion on the PFG NMR Self-Diffusivities of Ethane and Ethene in Large-Crystalline SAPO-34", *J. Phys. Chem.*, **116**, 2469 (2011).
- [5] Masoumi, S., Sedighi, M., Towfighi, J. and Mohamadalizadeh, A., "Effect of mixed templates on synthesis of SAPO-34 catalyst", The 1st nat.conf. of new technologies in chemical and chemical engineering, Tehran, Iran, 17 (2013).
- [6] Hajfarajollah, H., Askari, S. and Halladj, R. "Effects of micro and nano-sized SAPO-34 and SAPO-5 catalysts on the conversion of methanol to light olefins", *Reac. Kinet. Mech. Cat.*, **111**, 723 (2014).
- [7] Valizadeh, B., Askari, S., Halladj, R. and Haghmoradi, A., "Effect of Synthesis Conditions on Selective Formation of SAPO-5 and SAPO-34", *Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, **44**, 79 (2014).
- [8] Topuz, B., Eda, E. Oral. and Kalıpcılar, H., "Low temperature synthesis of SAPO-34 in a recirculating-flow system", *J. Porous. Mater.*, **20**, 1491 (2013).
- [9] Lei, W., Ziyu, L., Lin, X., Minghuang, Q., Xu, L., Haojia, Z. and Yuhan, S., "Effect of SAPO- 34 molecular sieve morphology on methanol to olefins performance", *Chin. J. Catal.*, **34**, 1348 (2013).
- [10] Wu, L., Liu, Z., Qiu, M., Yang, Ch., Xia, L., Liu, X. and Sun,, Y., "Morphology control of SAPO-34 by microwave synthesis and their performance in the methanol to olefins reaction", *Reac. Kinet. Mech. Cat.*, **111**, 319 (2014).
- [11] Izadbakhsh, A., Farhadi, F., Khorasheh, F., Sahebdelfar, S., Asadi, M. and Feng, Y.

- "Effect of SAPO-34's composition on its physico-chemical properties and deactivation in MTO process", *App. Catal. A: General.*, **364**, 48 (2009).
- [12] Charghand, M., Haghghi, M. and Aghamohammadi, S., "The beneficial use of ultrasound in synthesis of nanostructured Ce-doped SAPO-34 used in methanol conversion to light olefins", *Ultrason. Sonochem.*, **21**, 1827 (2014).
- [13] Wei, Y., Zhang, D., He, Y., Xu, L., Yang, Y., Su, B. and Liu, Zh., "Catalytic performance of chloromethane transformation for light olefins production over SAPO-34 with different Si content", *Catal. Lett.*, **114**, 30 (2007).
- [14] Lee, Y., Baek, S. and Jun, K., "Methanol conversion on SAPO-34 catalysts prepared by mixed template method", *App. Catal. A: General.*, **329**, 130 (2007).