MTO reaction over SAPO-34 catalysts synthesized by combination of TEAOH and morpholine templates and different silica sources

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Abstract The SAPO-34 catalyst was synthesized by the combination of TEAOH and morpholine templates, and colloidal silica and silicic acid, as the silica source under hydrothermal conditions. The effect of the template molar ratio and silica source on the physicochemical properties of each catalyst was studied by XRD, SEM, BET and TPD techniques. XRD patterns revealed the significant effect of gel composition on the crystallinity and particle size of the samples. SEM photos showed that all the catalysts have cubic morphology, but their particle size was different. According to the XRD and SEM of the catalyst prepared by silicic acid, this catalyst showed low crystallinity and large crystal size. TPD analysis indicated that the acidity reduced by increasing the morpholine content in the reaction mixture. The catalytic performance of the synthesized catalysts was tested in MTO reaction. The catalyst produced by the TEAOH/morpholine ratio of 0.5:1.5 exhibited the highest light olefins yield, as well as the longest catalyst lifetime. The maximum yield of ethylene and propylene was determined to be 94 wt%, with 100% methanol conversion.

1. Introduction

Light olefins are important intermediate products in the petrochemical industry used for the production of many useful chemicals [1]. Ethylene can be used for the preparation of polyethylene, ethylene oxide, styrene, ethylene glycol and polyvinyl chloride [2]. Propylene is the second largest petrochemical product in the world, and an important raw material for the production of many petrochemicals, such as polypropylene, propylene oxide and phenol [3,4]. According to market statistics, it is forecast that the ethylene and propylene demand for 2015 will be 160 and 110 million tons, respectively [5]. The demand for ethylene and propylene, which is predicted to grow faster than its supply, caused an increased interest in finding new processes for the production of light olefins [4]. Naphtha steam cracking is a major process for the production of light olefins [6]. The large amount of energy consumption in the steam cracking of naphtha and the carbon dioxide emissions increase the production cost of the light olefins [7]. Fluid Catalytic Cracking (FCC) is another process for the production of light olefins, but the yield of this process is low [6]. Propane dehydrogenation is the other expensive process used for the production of propylene [8]. The Methanol To Olefin (MTO) reaction is a novel process for producing light olefins. Because of the production of light olefins from natural gas or coal via methanol in the MTO process, it has been considered as an alternative process in recent years [9]. After the first report of the MTO process by Chang and Silvestri in 1977, many efforts have been directed to find the best catalyst for MTO reaction [10].

ZSM-5 is the first catalyst studied for MTO reaction. Because of the large pore openings of the MFI structure (about 5.5 Å), it was concluded that the yield of ethylene and propylene was low [11,12]. In 1982, Wilson et al. reported the synthesis of aluminophosphate (AlPO) molecular sieves for the first time [13]. The structure of this material is similar to zeolites, whereas the primary building units in these materials are formed by (Al–O–P) linkages instead of (Si–O–Al) or (Si–O–Si) in zeolite [7]. Since the framework of AlPO is neutral, they usually

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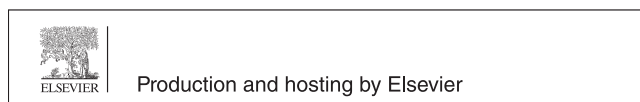
have no actual catalytic capabilities [14,15]. The introduction of silicon in the AlPO framework results in the formation of silicoaluminophosphate (SAPO) molecular sieves and leads to the production of a Bronsted acid site and, therefore, its catalytic capability [16,17]. Among SAPOs molecular sieves, SAPO-34, with a CHA structure and small pore openings (about 3.8 Å), has high ethylene and propylene yield in the MTO reaction and could be the best candidate for this process [18].

SAPO-34 is normally synthesized using a hydrothermal method from a gel that includes an alumina source, a silica source, a phosphorous source and at least one organic structure directing agent [15,19]. The structure directing agent (template) plays an important role in the synthesis of SAPO molecular sieves [20]. Many organic amines, such as tetraethylammonium hydroxide (TEAOH), triethylamine (TEA), diethylamine (DEA), dipropylamine (DPA) and morpholine, have been used in SAPO-34 synthesis [14,20–24]. Among these templates, TEAOH is the most common for the synthesis of SAPO-34. By using TEAOH as the template, a small particle size of SAPO-34 will be achieved, whereas its high price limits its application in an industrial scale [25]. The cost of morpholine is much lower than TEAOH, but its usage in the synthesis process leads to the formation of a catalyst with large particle size and poor catalytic performance in the MTO reaction [21,25]. In recent years, a combination of two templates has been used in the production of SAPO-34. The use of mixed templates was reported, firstly, by Lee et al. who prepared SAPO-34 catalysts by changing the molar ratios of two templates (TEAOH and morpholine) [26]. In that research, SAPO-34 catalysts were synthesized by pseudoboehmite and colloidal silica as the alumina and silica source, respectively. It was reported that the crystallinity and the acidity of SAPO-34 may be strongly affected depending on the different Al and Si sources used for its synthesis [27].

The aim of this research is the preparation of the SAPO-34 catalyst at the optimal TEAOH/ morpholine molar ratio, and using a proper initial source of silica to improve the catalyst performance in MTO process. In this research, some experimental synthesis parameters, such as the source of reagents, the procedure of gel preparation, the composition of the gel, the time and temperature of the reaction and agitation during crystallization were different from similar research reported in literature.

2. Experiment

2.1. Catalyst preparation

SAPO-34 catalysts were synthesized hydrothermally from a gel composition of Al_2O_3: P_2O_5: 0.6 SiO_2: x TEAOH: y Morpholine: 60 H_2O (x:y = 1.5:0.5, 1:1, 0.5:1.5). The synthesis procedure pursued for gel preparation is described as follows. First, aluminum isopropoxide (AIP, Merck) was dissolved in a mixture of orthophosphoric acid (85 wt% H_3PO_4, Merck) and deionized water to form an aluminum sol. Thereafter, a mixture of silica source (colloidal silica (40 wt% SiO_2, Aldrich) or silicic acid (Merck)) and templates was added to the aluminum sol. In the present work, tetraethyl ammonium hydroxide (35 wt% aqueous solution of TEAOH, Aldrich) and morpholine (Merck) were used as organic templates. The obtained gel was aged at room temperature for 24 h with agitation. After the aging period, the gel was transferred into a Teflon lines autoclave and the crystallization process was performed with in situ agitation at 458 K for 48 h. The synthesized material was recovered by centrifugation, washed several times and then dried at 373 k. The final product was calcined at 873 K for 5 h. SAPO-34 was synthesized based on the hydrothermal method from a gel composition, which is presented in Table 1.

Table 1: Preparation conditions for SAPO-34 samples.

Sample	Gel composition	Silica source
S1	Al_2O_3: P_2O_5: 0.6 SiO_2: 1.5TEAOH: 0.5 morpholine:	Colloidal silica
S2	Al_2O_3: P_2O_5: 0.6 SiO_2: 1TEAOH: 1 morpholine:	Colloidal silica
S3	Al_2O_3: P_2O_5: 0.6 SiO_2: 1TEAOH: 1 morpholine:	Silicic acid
S4	Al_2O_3: P_2O_5: 0.6 SiO_2: 0.5TEAOH: 1.5 morpholine:	Colloidal silica

2.2. Catalyst characterization

The X-ray diffraction pattern was collected by a Bruker D8 diffractometer (CuKα radiation, λ = 1.54 Å) in the 2θ range of 5–40°. The relative crystallinity of SAPO-34 catalysts was calculated using sum of the intensity of the more important peaks at 2θ = 9.6, 13.0 and 20.6 on the basis of the best prepared sample as the Ref. [28]. The morphology and particle size of the catalysts was studied by a SEM photo using a Philips XL30 instrument. The BET surface area of the catalysts was measured by analyses of nitrogen isotherms collected by micromeritics ASAP 2010 apparatuses. The FTIR spectra were collected on KBr-diluted palletized catalysts using a Bruker Tensor-27 spectrophotometer. The acidity of the catalysts was determined by a NH_3–TPD technique, using a Pulsechemisorb 2705 apparatus. For TPD analysis, about 0.2 g of the catalyst was loaded into the cell of the equipment. Before ammonia adsorption, the temperature of the catalyst bed was increased to 773 K, at which the catalyst was evacuated for 2 h. Adsorption of ammonia was then carried out at 373 K passed through the catalyst bed for 1 h. After purging with helium for 90 min, the analysis was carried out at a heating rate of 12 K/min from 373 to 873 K.

2.3. Catalyst performance

The MTO reaction was performed over SAPO-34 catalysts under atmospheric pressure in a fixed bed reactor made of stainless steel. About 2 g of powder catalyst was loaded into the reactor. The catalyst was pretreated with 100 ml/min flow of N_2 at 773 K for 3 h, and then the temperature of the reactor was reduced to the reaction temperature (673 K). Thereafter, N_2 flow was turned off, and a liquid mixture of methanol in water (30 wt%), with a weight hourly space velocity (WHSV) of 8.7 h^{-1}, was fed by a syringe pump into the reactor. The liquid and gas products were analyzed using gas chromatography. The liquid product was analyzed by an Agilent 6890 N chromatograph, and the gas product was analyzed with a CP-4900 Varian gas chromatograph equipped with a micro TCD detector. The schematic diagram of the experimental setup used for the MTO process in this study is presented in Figure 1. The conversion of methanol was determined from the outlet liquid sample as the percentage of methanol consumed in the MTO reaction. The yield of a given product was defined as the percentage of methanol consumed for its production.

3. Results and discussion

3.1. Characterization

The X-ray diffraction pattern of synthesized catalysts prepared by different gel compositions is shown in Figure 2. The
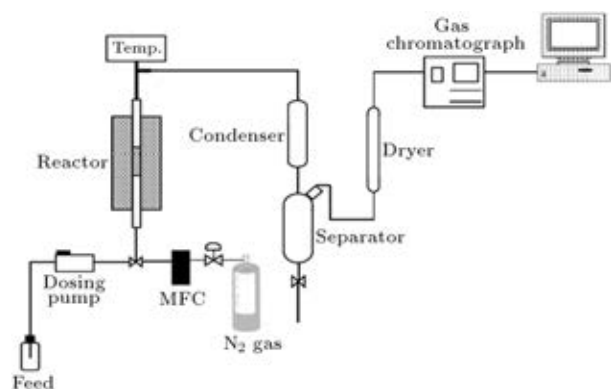
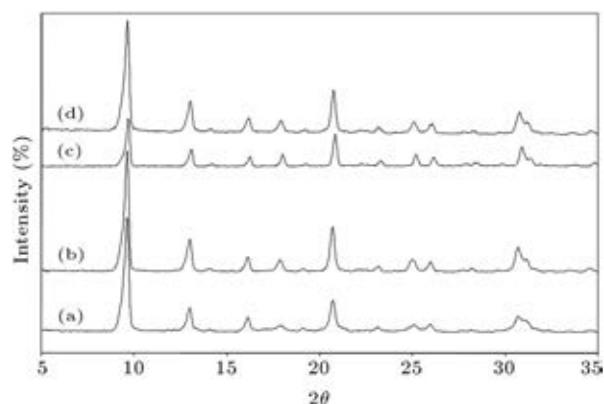Figure 1:　Experimental setup used for MTO reaction.

Table 2: Physical properties of SAPO-34 samples.

Sample	TEAOH:Mor[a]	Silica source[b]	Product phase	Relative crystallinity	Particle size distribution
S1	1.5:0.5	CS	SAPO-34	78	1.0–2.2
S2	1:1	CS	SAPO-34	90	0.9–1.2
S3	1:1	CA	SAPO-34	50	1.5–3.0
S4	0.5:1.5	CS	SAPO-34	100	0.6–1.0

[a] TEAOH:Mor means the molar ratio of TEAOH to morpholine in the synthesis gel.
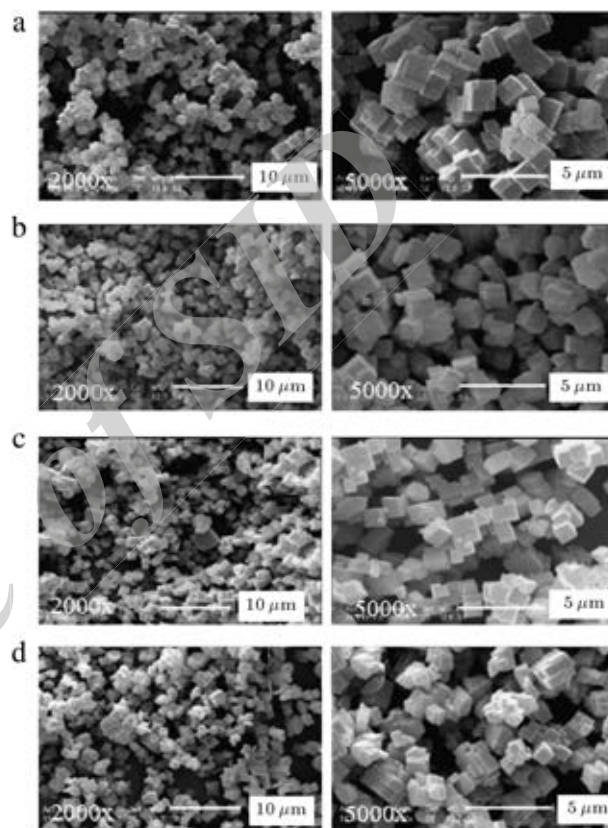[b] CS is colloidal silica and CA is silicic acid.

Figure 2:　XRD pattern of catalysts: (a) S1, (b) S2, (c) S3 and (d) S4.

Figure 3:　SEM photo of catalysts: (a) S1, (b) S2, (c) S3 and (d) S4.

XRD patterns of all the catalysts were in agreement with the SAPO-34 pattern reported in the literature [28]. The relative crystallinity of each catalyst calculated from the XRD pattern, based on the S4 catalyst, is presented in Table 2. In order to investigate the effect of the silica source on the crystallinity of SAPO-34, the results of S2 and S3 samples were considered. Results showed that by changing the silica source from colloidal silica (S2 sample) to silicic acid (S3 sample), the crystallinity of SAPO-34 decreased. One of the most effective synthesis parameters on the particle size and morphology was found to be the silica source. Different silica sources have different reactivity and solubility. It was found that different surface areas of silica sources could affect the crystallization rate in the synthesis process. High surface area silica is more easily dissolved in a basic medium than a low surface area silica source [29]. The results showed that changing the TEAOH/morpholine ratio in S1, S2 and S4 samples affect the crystallinity of SAPO-34. According to XRD results, relative crystallinity increased by increasing the amount of morpholine in the preparation gel and the highest crystallinity belonged to the S4 sample prepared with the TEAOH/morpholine ratio of 0.5:1.5.

The SEM photos of synthesized samples are presented in Figure 3. As shown, all the samples had cubic like particles, but with different sizes. The S4 sample had the smallest average particle size. It indicates that the particle size has been decreased by an increase in the morpholine content from 0.5 to 1.5 in the gel mixture. In addition, the particle size of the S2 sample prepared by colloidal silica was smaller than that prepared by silicic acid as the silica source.

The BET surface area of each sample through the N_2 adsorption isotherm is listed in Table 2. The BET surface areas were about 502, 567, 500 and 677 m^2/g, for S1, S2, S3 and S4 samples, respectively. It can be observed that by increasing the morpholine content and using colloidal silica in the primary mixture, the BET surface area has been increased.

The FTIR spectra of the samples are shown in Figure 4. According to the spectra, it is obvious that there are no characteristic peaks of the amorphous phase (785, 618 and 520 cm^{-1}) in S1, S2 and S4 [15]. According to the spectra of the S3 sample, the peak in 785 cm^{-1}, means that some amorphous phase exists in this sample. Furthermore, characteristic peaks of the SAPO-34 phase, which are appeared at 480, 635, 730, 1100 and 1225 cm^{-1}, proved the synthesis of the SAPO-34 phase. The spectra of samples showed two hydroxyl stretching vibration bands at 3600 and 3625 cm^{-1}, which are assigned to Si–OH–Al groups. These hydroxyl groups are active sites in the MTO reaction. In addition, there were two other peaks at 3675 and 3743 cm^{-1}, which are related to P–OH and Si–OH weak hydroxyl groups, respectively.

The acidic properties of the samples were evaluated by NH_3-TPD and reported in Figure 5 and Table 3. The desorption
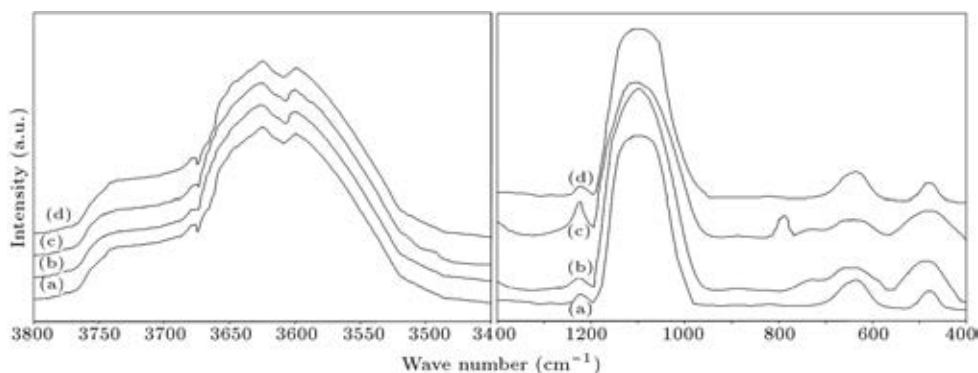
Figure 4: FTIR spectra of catalysts: (a) S1, (b) S2, (c) S3 and (d) S4.

Table 3: Chemical properties of SAPO-34 samples.

Catalysts	BET surface area (m^2/g)	Acidity concentration (mmol NH_3/g)	
		Weak	Strong
S1	502	0.5831	1.1288
S2	567	0.7930	1.1203
S3	500	–	–
S4	677	0.7726	1.1150

temperature indicates the acidic strength of the sites, whereas the area under the curve indicates the acidity of the samples. SAPO-34 catalyst provides two desorption peaks; the first peak at the range of 180–210 °C corresponding to weak acid sites, which is attributed to P–OH hydroxyl groups; the second peak appears at high temperatures (in the range of 370–410 °C), and it indicates the presence of strong acid sites, which would be active in the MTO reaction [28]. As shown in Figure 5, the temperature of the desorption peak related to strong acid sites, appeared at 377, 408 and 371 °C for S1, S2 and S4 samples, respectively. The areas under the high temperature desorption peak corresponding to the acidity of strong acid sites decreased in the order of S1, S2 and S4. These results show that the concentration of strong Brønsted acid sites decreased by increasing the amount of morpholine in the preparation gel.

3.2. Catalytic performance in MTO reaction

The performance of catalysts was tested at 673 K with a feed WHSV of 8.7 h^{-1}. All the catalysts had the same trend in light olefins production, but the distribution of the products and their lifetimes varied significantly. The products distribution of the S4 catalyst with reaction Time On The Stream (TOS) is shown in Figure 6. For the TOS between 10 and 90 min, all the catalysts showed activity as being too low. Thereafter, the production of ethylene increased gradually with TOS, getting its maximum value at TOS between 125 and 200 min, which decreased afterwards. The production of propylene increased by the reduction of ethylene produced. Propylene can be converted to higher olefins and aromatics afterwards. These higher products cannot diffuse from SAPO-34 pores and lead to the deactivation of the catalyst. After TOS = 150 min, the ethylene selectivity decreased, but the propylene selectivity, especially for the S4 catalyst, increased. So, the light olefins selectivity is approximately constant.

The methanol conversion, yield and selectivity of light olefins and catalytic lifetime are listed in Table 4. It was observed that the S3 catalyst, in comparison with others,
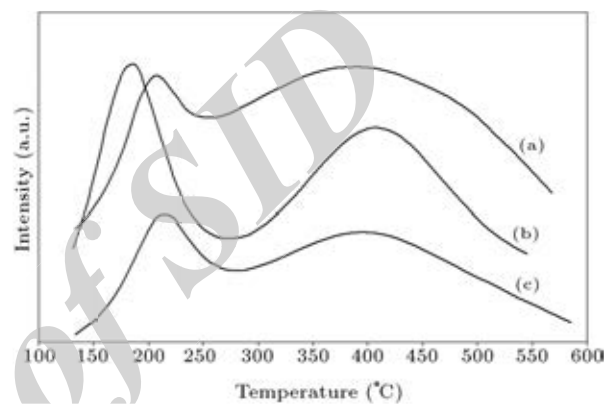
Figure 5: NH3-TPD profile of catalysts: (a) S1, (b) S2 and (c) S4.
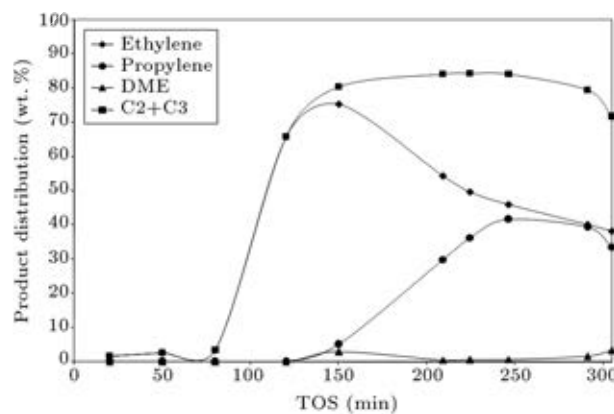
Figure 6: Products distribution with TOS over S4 catalyst at 400 °C and WHSV of 8.7 h^{-1}.

did not achieve a noticeable performance (short catalyst lifetime and low olefins yield). The particle size and relative crystallinity of this catalyst were larger and lower than the others, respectively. By increasing the particle size, diffusion resistance will be increased and, therefore, the reactants cannot easily reach the center of the catalyst. As a result, the available surface, methanol conversion and yield of light olefins will be decreased. On the other hand, for the large particles, successive polymerization easily occurs because of the long diffusion length, and the catalyst will deactivate rapidly [24,30]. The yield of methane, ethylene, propylene, DME and higher hydrocarbons for each catalyst is shown in Figure 7. The S2 catalyst showed lower methanol conversion and low ethylene
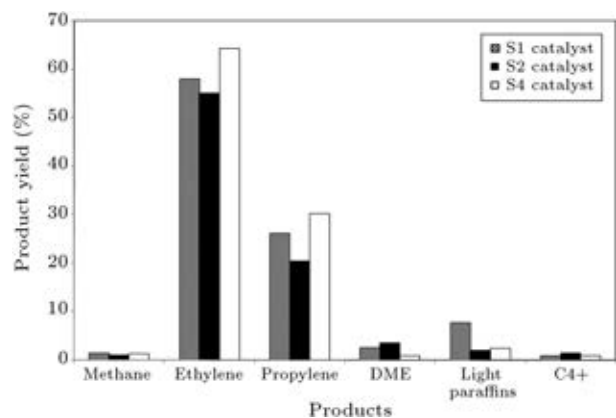
Figure 7: Yield of products over S1, S2 and S4 catalysts at 400 °C and WHSV of 8.7 h^{-1}.

Table 4: Methanol conversion and products yield of SAPO-34 catalysts.

Samples	Conversion (%)	Catalyst lifetime (min)	Light olefins yield (wt.%)		Light olefins selectivity
			C_2H_4	C_3H_6	
S1	98	240	58.10	26.25	3.1
S2	80	190	55.02	20.36	2.0
S4	100	300	64.34	30.11	3.8

and propylene yield, as well as faster declining activity. The S4 catalyst, compared to other catalysts, had the highest methanol conversion and yield of light olefins. The yield of light olefins for this catalyst (94%) was higher than that reported in similar research (88%) [26]. As shown in Table 4, the lifetimes of S1, S2 and S4 catalysts were 240, 190 and 300 min, respectively. In this work, a lifetime was defined as the time in which the yield of light olefins dropped down to 80% of its maximum. For all catalysts, deactivation is evidenced by the decline in olefin production, together with the appearance of the intermediate DME, and subsequent decrease of methanol conversion.

The selectivity of light olefins was defined as the ratio of the sum of produced ethylene and propylene to undesirable products. It is concluded that the S4 catalyst with the light olefins selectivity of 3.8 had the best performance and longer catalyst lifetime under the studied operational conditions. In addition, the S4 catalyst prepared by a combination of the TEAOH/morpholine ratio of 0.5:1.5, had smaller particle size, higher methanol conversion and higher yield of ethylene and propylene compared to other catalysts.

4. Conclusion

SAPO-34 catalysts were synthesized with three different molar ratios of TEAOH/morpholine and two different silica sources (colloidal silica and silicic acid) under hydrothermal conditions. The prepared catalysts were different in average particle size, surface area, acidity and catalytic performance. The particle size of SAPO-34 was decreased by increasing the morpholine ratio and addition of colloidal silica instead of silicic acid as the silica source. It is concluded that SAPO-34 produced by a combination of templates assisted with agitation during the crystallization could be an appropriate method for controlling particle size. The TPD analysis indicated that the concentration of strong acid sites (acidity) decreased by enhancement of the morpholine content from 0.5 to 1.5.

The catalytic performance of each catalyst was tested in the MTO process at 673 K and feed WHSV of 8.7 h^{-1}. The SAPO-34 catalysts prepared with a 0.5:1.5 molar ratio of TEAOH/morpholine exhibited the highest selectivity of light olefins and the longest catalyst lifetime. This kind of synthesized catalyst with its inexpensive template would be proposed for the MTO process.

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