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METHANOL CATALYTIC CONVERSION OVER SAPO-34 WITH DIFFERENT TYPES OF TEMPLATE

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Abstract

Light olefins are basic raw materials for petrochemical industries and the demand for them is growing rapidly. In this study, conversion of methanol to light olefins in the presence of acidic SAPO-34 with different types of template as the reaction catalyst has been investigated. SAPO-34 molecular sieves were synthesized hydrothermally, using morpholine, tetraethyl ammonium hydroxide and dipropyl amine as the template from a gel with molar composition of $1Al_2O_3:1P_2O_5:0.6\ SiO_2:2$ Template: 50 H_2O. The produced samples were characterized by XRD, SEM, NH_3-TPD and TGA-DTA techniques. These results showed that template type has effect on crystal size, morphology, crystallinity and purity of samples. NH_3-TPD results showed that different templates have effect on acidity of samples. It was found that the catalyst was synthesized with morpholine, has bigger crystal size than other. The catalysts performance to produce light ole-fins from methanol was investigated in a fixed bed reactor within the temperature range of 250–450°C and under atmospheric pressure and WHSV=1 hr^{-1}. Although all the catalysts showed similar activity and product distribution, the catalyst obtained using morpholine as the template, gave the shortest lifetime

Keywords: Methanol Conversion; SAPO-34; Template; morpholine; tetraethyl ammonium hydroxide; dipropyl amine.

1. Introduction

Small pore silicoaluminophosphate molecular sieve, SAPO34 with chabazite (CHA) structure and pore diameters of approximately 0.38 nm is well known to be one of the best catalysts in the conversion of methanol to olefins (MTO). It gives a very high selectivity (>90%) to light olefins (C_2–C_4) with almost 99% conversion of methanol, which is mainly attributed to its mild acidity, shape selective and high thermal stability catalysis by small pore entrance. In addition, due to its unique cage size and shape, SAPO-34 has been found to be suitable for selective formation of linear hydrocarbons by restricting the formation and diffusion of branched hydrocarbons. However, the main problem associated with these catalysts is rapid deactivation of SAPO-34 due to coke formation during MTO reaction and this resultantly makes the lifetime of these catalysts short [1–4].

The catalytic and sorption properties of the zeolite are often influenced by their crystal size. The acidity of SAPO-34 zeolite used as a catalyst has significant effect on reaction path and product distribution in reaction. It is known that the CHA and AFI structures compete and the content of CHA increases with concentration of the template and heteroatom. The synthesis of phase-pure molecular sieves is very important and interesting for characterization and application. Many factors affect the form the SAPO-34 molecular sieve with chabazite structure (CHA) takes, including the choice of component sources and template, the relative amount of the different component, mixing, the hydrothermal condition, e.g. temperature and reaction time.

Many research works have been reported relating to the synthesis and crystallization mechanism of SAPO-34 [5–6], its catalytic properties in MTO reaction and reaction mechanisms [7-8].

The impact of the crystal size reduction on kinetics of reaction and transport via mesoporous media could bring higher efficiency in certain catalytic and separation processes. Decreasing the crystal size is probably the simplest way to overcome the mass transport limitations and ensure high surface accessibility. Further, the possibility to use well-defined fine-crystallites with narrow particle size distributions will bring new opportunities in chemical sensing.

It is well known that template plays important roles in the synthesis of molecular sieves, such as structure-directing agent (SDA), space-filling and charge-compensating roles.

Its role was challenged, however, by the preparation of one specific structure with several SDAs, and conversely, by the existence of one SDA capable of producing more than one molecular sieves. The elemental composition, local microscopic structure and morphology of one specific molecular sieve may change with the use of different templates. The Si distribution depends on the number of framework charges, which is influenced by both the number of SDA molecules embedded within the cages and the Si atoms introduced within the framework. Moreover, the elemental composition, local microscopic structure and morphology may also change with the use of different SDAs [9-10].

Many organic amines can be used as templates for the synthesis of SAPO-34, including tetraethylammonium hydroxide (TEAOH), dipropylamine, isopropylamine, piperidine, morpholine, triethylamine (TEA), and diethylamine (DEA) [11-18], *etc.*

In this work SAPO-34 synthesized with different templates and methanol to olefin reaction was studied over the synthesized SAPO-34.

2. Experimental

2.1. Synthesize procedure

SAPO-34 was synthesized by a hydrothermal method from a gel with molar composition of $1Al_2O_3{:}1P_2O_5{:}0.6SiO_2{:}2$ Template:50 H_2O [19]. Aluminum isopropoxide (98 wt%, Merck), ortho phosphoric acid (85 wt. % aqueous solution, Merck), and fumed silica (SiO_2, 98 wt%, Merck) were used as Al, P and Si precursors. Tetraethyl ammonium hydroxide (TEAOH, 40 wt. % in water, Merck), morpholine and dipropyleamine were used as a structure-directing agent (SDA). The first step was hydrolysis of isopropoxide. Specified amount of aluminum isopropoxide [98% $Al(O\text{-}i\text{-}C_3H_7)_3$] was mixed with distilled water. The mixture was heated to 80°C to accelerate the hydrolysis. The hydrolysis was completed in two hours with vigorous stirring, resulting in a homogeneous white gel. Isopropyl alcohol, the product of the hydrolysis, was left in the gel without further treatment. The second step was to mix phosphoric acid [85% H_3PO_4] with the white gel. Phosphoric acid was added drop wise to aluminum gel within 5 minutes with stirring. The resulting white homogenous gel was part (A) of the final mixture. The second step was to prepare part (B) of the final mixture. Morpholine [99% C_4H_9O] was mixed with specified amount of fumed silica [95% SiO_2]. The mixture was stirred until a homogenous solution was formed. Part B was then added to part A with stirring. The final mixture was further stirred for two hours, resulting in a semi-transparent homogenous white gel. The final gel mixture having the pH =7-9 depending on template source, was transferred into a high-pressure stainless steel autoclave. The autoclave was sealed and maintained at 200°C for 48 hours without stirring. The pressure inside the autoclave was equal to the autogeneous pressure of water at 200°C. The autoclave was slowly cooled down after 48 hours. As-synthesized SAPO-34 was recovered from the autoclave; washed three times with 200ml distilled water at room temperature frequently until pH approached to 7; dried at 120°C for 24 hours and calcined at 550°C for 10 hours to remove organic template molecules from zeotype framework. The product was then transformed into protonated form by ion exchange process with 2-molar ammonium chloride solution at 80°C. The synthesized catalyst dried at 120°C for 24 hours and calcined at 550°C for 10 hours.

2.2. Characterization of the product (SAPO-34)

The SAPO-34 prepared was characterized for their crystallinity, morphology, crystal size and acidity. The samples purity and crystallinity were analyzed by X-ray diffraction (XRD) for phase identification using a Philips PW 1840 type equipped with a Cu tube working at a generator potential of 40 kV and a generator current of 30 mA with a nickle filter for phase identification.

The morphology and crystal size of the samples were examined using a Philips scanning electron microscope (SEM) model XL30.

Thermal analyses to determine the amount of template trapped insides the crystals and the rate of their removal, were carried out using a Simultaneous Thermal Analyzer Model STA 1640. The temperature of the sample was raised at a rate of 10ºCmin^{-1} from ambient to 973 K in airflow of 50 cm^{3}min^{-1}.

The acidity of the samples was measured by ammonia adsorption-desorption technique using a chemical adsorption instrument of AMERICAN micrometrics 2900.

2.3. Catalytic reaction

The conversion reaction of methanol to olefins was carried out in a fixed bed micro-reactor at atmospheric pressure and in the temperature range of 250–450 ^{0}C and WHSV=1 hr^{-1}. A known weight (1 g) of HSAPO-34 catalyst (with size of 1-2 mm) was packed in the center of stainless steel (i.d.: 1 cm, length: 30 cm) reactor and heated by an electric jacket wrapped around the reactor. Reaction temperature was controlled by a PID controller and measured by a thermocouple (PT100) housed in a thermo well located at the center of the catalyst bed. The reactor's pressure was regulated by a back pressure system. Methanol liquid Flow was controlled by a dosing pump model H94X. The analysis of the reaction products was performed using an on-line gas chromatograph (Agilent model 6890).

3. Results and conclusions

3.1. X-ray diffraction

Figure 1 shows the X-ray diffraction (XRD) patterns of the as-synthesized samples prepared with different templates. Typical powder diffraction patterns corresponding to CHA-structure of SAPO-34 was found with morpholine and TEAOH as template, where intensity and peak position of each peak match well with that of reported in the literature [20]. It reveals that SAPO-34 was successfully crystallized with different SDAs, being the crysta-llinity of the samples very similar to each other. No other phase apart from SAPO-34 was found for these samples. However, with TEAOH as template, a decrease in peak intensity and line broadening is observed as is seen in Figure1 (b).

The XRD patterns of sample with pH=9 and DPA as template had a peak at 2θ=7.6°, that corresponds to the SAPO-5 with AFI structure, which consists of cylindrical channels formed by 12-membered rings with a diameter of 0.74. Major product is SAPO-5 with presence of minor one, i.e. SAPO-34. Although the DPA is a good template agent for the synthesis of SAPO-34, SAPO-5 instead of SAPO-34 is obtained as a major crystal phase due to our existing experimental conditions. The result showed that both CHA and AFI structures form with the DPA as template [21-22].

3.2. Scanning electron microscopy

The SEM photographs of SAPO-34 with different templates are presented in Figure 2. The cubic-like rhombohedra morphology could be clearly observed, which is quite similar to natural chabazite. The crystal size is in the range of 3–7 μm.

As shown, the crystals of samples with morpholine and TEAOH are similar to be cubic shape of typical SAPO-34 without obvious aggregations, but distinct in crystal size. In the case of SAPO-34 synthesized with morpholine, homogeneous crystals with particle size of 5-6 μm were obtained. Moreover, the crystal particles have been observed smaller when using TEAOH.

By contrast, hexagonal crystals with different size, ranging broadly from 5 to 7 μm, were formed in the case of sample synthesized with DPA which correspond with SAPO-5 morphology. This result means that the rate of crystal growth varied closely with the type of SDAs in the initial gel. Thus, the nature of template used in synthesis not only influences the products structure patterns, but also determines the morphology of final crystals due to different rate of crystal growth [23].

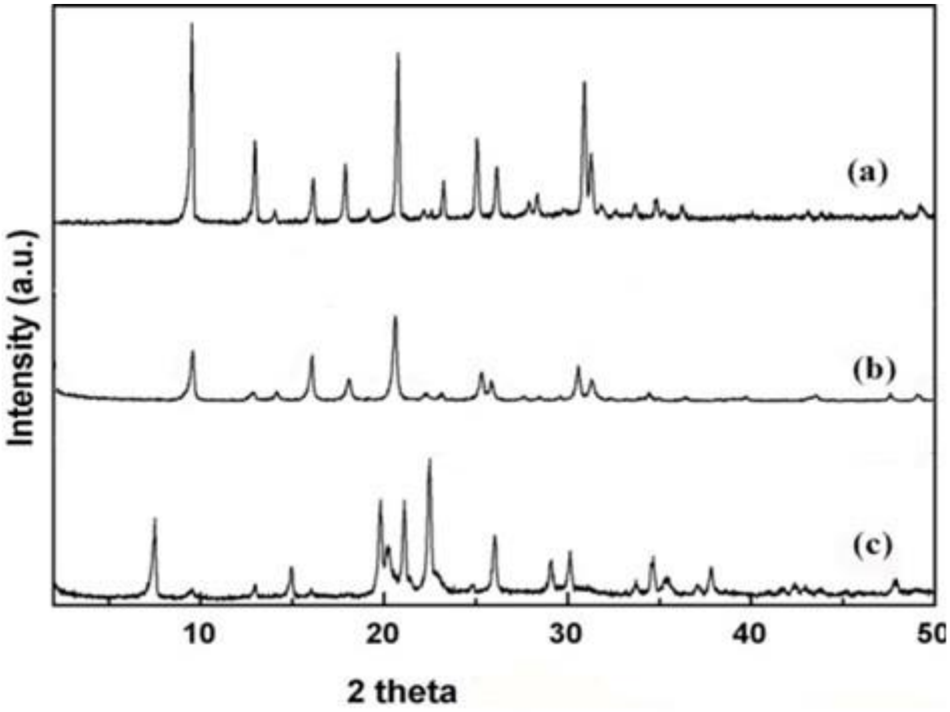

Figure 1. XRD patterns of the as-synthesized products prepared by different template (a) morpholine (b) TEAOH (c) DPA

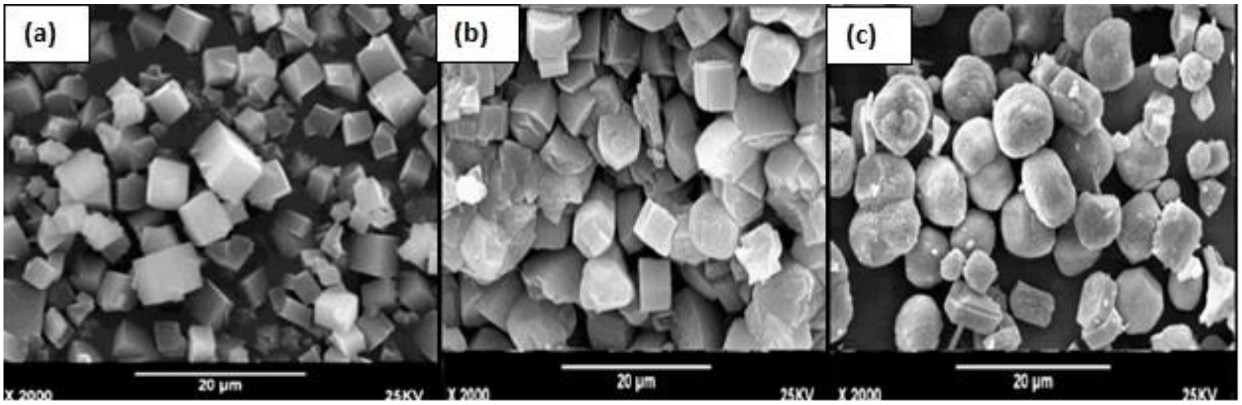

Figure 2. SEM photographs of SAPO-34 products prepared by different template (a) morpholine (b) TEAOH (c) DPA

3.3. Thermogravimetric-difference thermal analysis

Figure 3 shows TGA/DTA curves for all the synthesized samples. TGA/DTA results for samples with morpholine and TEAOH showed similar weight loss pattern in the temperature ranges of 25–100°C, 100–450°C and 450–800°C. The first weight loss, accompanied with endothermic peak appearing in DTA curve, is attributable to the physically adsorbed water associated with SAPO samples. The second weight loss in TGA curve centered at around 410–460°C, accompanied with strong exothermic DTA peak, is attributed to the oxidative decomposition of organic templates. The third weight loss in TGA curve centered at around 550 °C, accompanied with weak broad exothermic DTA peak, may be related to the oxidation of organic templates also. The third weight loss increased with morpholine as template in the sample, which is related due to the loss of template trapped at ion-exchange site within CHA cage of SAPO-34. It can be seen from the curves in Figure 3 that there is no weight loss and exothermic peak associating with structural collapse until 800°C. This suggests the high thermal stability of SAPO-34 synthesized in the present work, which is as good as those prepared with other templates [24].

The sample synthesized using DPA, which showed a major phase of SAPO-5, exhibited weight losses in three stages. The first stage is assigned to the desorption of water and the second stage with endothermic peak at around 300°C to the desorption of DPA and the last at temperature ranged from 370 to 800°C is attributed to the oxidative decomposition of DPA in the sample. The TGA/DTA study indicated that complete decomposition of template occurs at temperatures greater than 550°C hence the calcination was carried at the said temperature during the present investigation.

As mentioned in the introduction, in addition to structure- directing and space-filling roles, organic template is very important for the compensation of framework charge. Vomscheid *et al.* [25] have demonstrated that the template can determine the maximum charge and govern the distribution of silicon in the framework. Therefore, the high incorporation of silicon with DPA as a template in the present work seems to be related to its smaller molecular size. The higher template concentration accommodated in each cage can compensate more framework charge and thus lead to the higher silicon content in the framework [26].

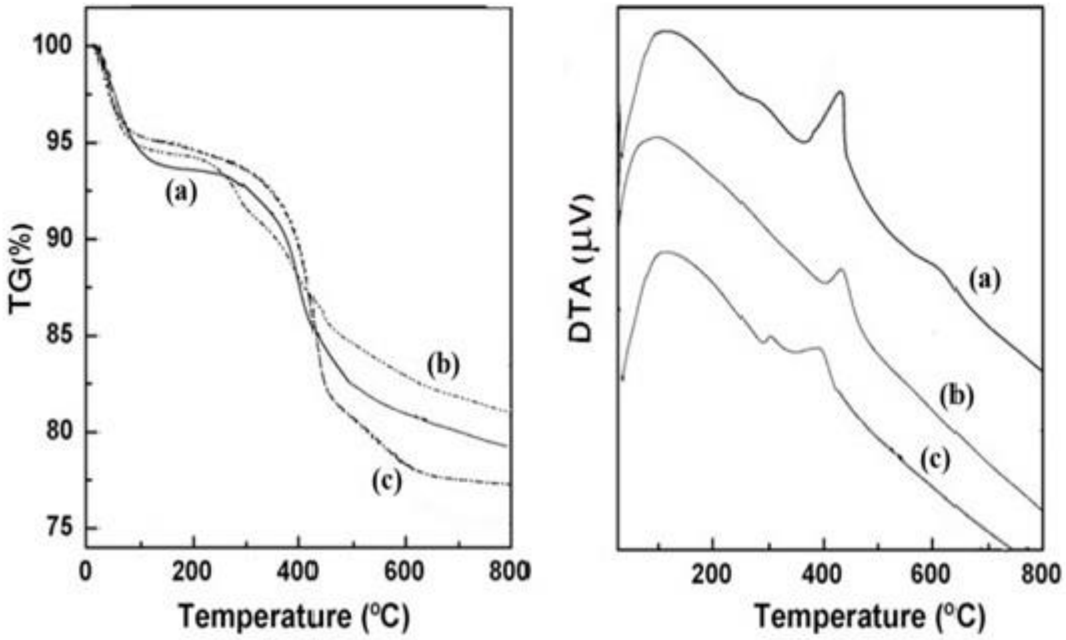

Figure 3. TG-DTA profiles of SAPO-34 with different templates (a) morpholine, (b) TEAOH and (c) DPA

3.4. Acidity of samples

The acid sites concentration and strength of the calcined samples were characterized by temperature programmed desorption of ammonia (NH_3-TPD) technique (Figure 4). Two TPD peaks for samples at 200–250 and 430–500 °C are observed in this Fig. They are in accordance with the reported literature data for the acidity of SAPO materials [27]. The desorption temperature signifies the strength of acid sites, given that the stronger acid sites requires a higher desorption temperature, and the area under the NH_3 desorption curve indicates the amount of ammonia desorbed, which is proportional to the acidity. Low temperature peak at ca. 200°C, assigned to the weak acid sites which are probably Brönsted acid sites originating from P-OH groups not fully linked to AlO_4 tetrahedra, showed no apparent difference in peak intensity with DPA amounts. This observation is also supported by XRD data in Figure 1, where it exhibited gradual decrease in XRD peak intensity for SAPO-34 with DPA as template. In this sample a very weak desorption peak in high temperature region compared to SAPO-34 samples and strong peak at low acidity region were observed, which is similar to typical ones of SAPO-5 sample reported in literature [28].

The intensity of high temperature desorption peak appearing at 430°C assigned to the strong acidic sites which are generated by the incorporation of silicon into the framework of SAPO molecular sieve. Also, this desorption peak is assigned to the bridging hydroxyl groups, i.e., -SiOHAl-, formed by replacement of phosphorous by silicon and decreased in sample with DPA as template.

According to the peaks in Figure 4, the weak and strong acidity of samples are derived. It shows similar acid properties between these samples with morpholine and TEAOH, both in acid sites concentration and strength. However, for sample with template DPA, the peaks at low shift to low temperature with a decreased area, which can be explained by the existence of large size of silicon islands in the framework.

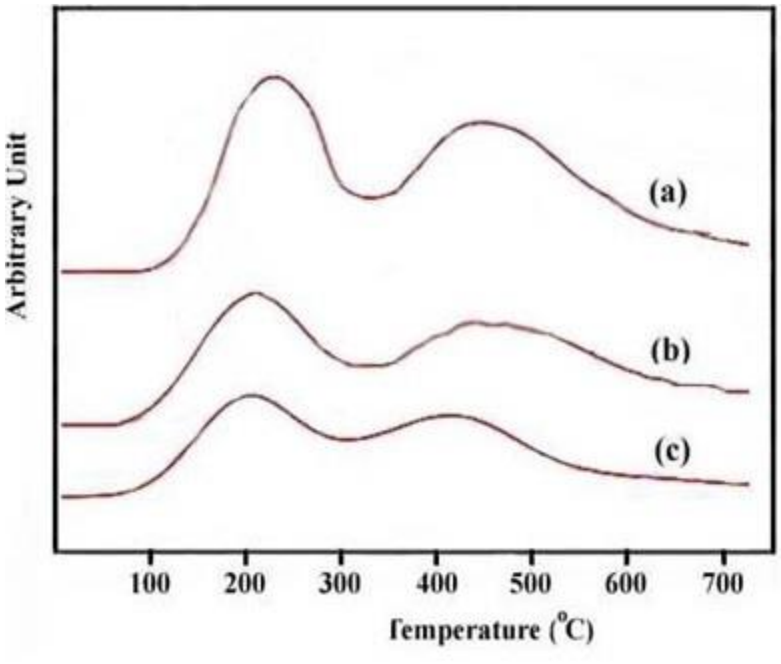

Figure 4. NH_3-TPD Profiles of SAPO-34 samples with different templates (a) morpholine (b) TEAOH and (c) DPA.

4. Activity test for MTO reaction

Figure 5 shows the product distribution for methanol conversion reaction on different catalysts at atmospheric pressure and in the temperature range of 250–450°C and WHSV=1 hr^{-1}. For every reaction, the fresh catalyst was used. At 250 °C methanol was converted mostly to dimethylether (DME) with ca. 80% yield as an intermediate product. As the temperature increased from 300 to 450°C, the MeOH conversion became complete and yield of light olefins (ethylene, propylene and butenes) was significant and became more than 80%, whereas yield of saturated hydrocarbon was maintained less than 10% in whole reaction temperature. With further increase of reaction temperature, C_4 olefins gave maximum value of about 20% at 300°C, which gradually decreased with increasing temperature. In the case of propylene, the yield increased with increasing temperature up to 400^{0}C afterward decreased at 450^{0}C, whereas yield of ethylene steadily increased in the whole reaction temperature. The reason for this phenomenon is that propylene and butenes can oligomerize to heavier oligomers, which crack to form ethylene at higher temperature. That is why yields of propylene and butenes have maximum values at low or medium temperature, while the yield of ethylene steadily increases with reaction temperature. The ethylene to propylene molar ratio increased from 0.69 at 300^{0}C to 1.31 at 450^{0}C. Yield of olefins has maximum value at 450^{0}C.

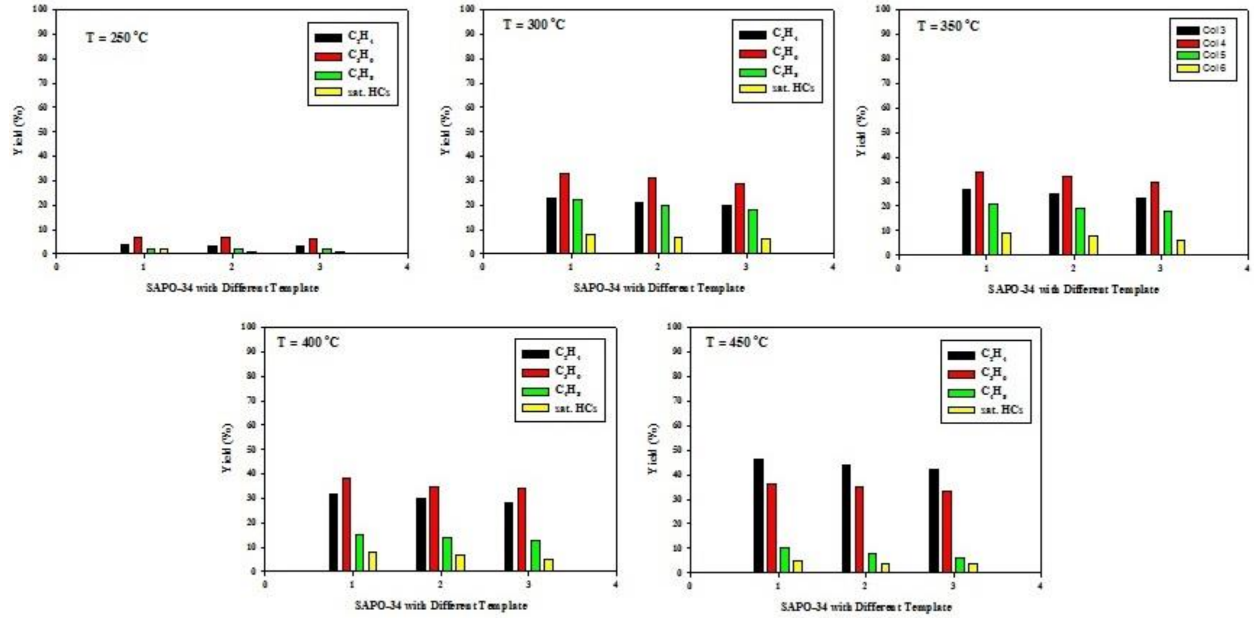

Figure 5. Product distribution yield for methanol conversion reaction on different catalysts at atmospheric pressure and in the temperature range of 250–450^{0}C and WHSV=1 hr^{-1} with TOS 1 hr (1) morpholine (2) TEAOH (3) DPA

The yield of products was studied with TOS at 450°C. The yield of light olefins was maintained over 90% until catalytic activity abruptly decreased by deactivation of catalyst. Before catalyst deactivation the yield of ethylene increased with TOS and accompanied the concomitant decrease of propylene. The DME yield in the product steeply increased with start of catalyst deactivation. DME as a reaction intermediate can easily be converted to olefins in acidic sites until the cages are occupied by coke. Once the cages are occupied by coke, yield of olefins is abruptly decreased. However, even after deactivation of the catalyst in reaction of methanol to olefins, conversion reaction of methanol to DME can take place on the weak acidic sites of external surface of SAPO-34.

All these catalysts had complete conversion of methanol and mostly conversion to light olefins in 1 h of TOS at 450^{0}C. The catalyst synthesized with morpholine only, shows shortest catalyst lifetime. These results may be explained by crystal size. Big crystal can bring diffusion limitation for reactants and products especially in small pore molecular sieve, which may result in coke formation. This supports that catalyst lifetime strongly depends on crystal size of SAPO-34. The strong acidity of this catalyst associated with big crystal size promoted hydrogen transfer reaction of olefins to saturated hydrocarbons and aromatics, which are precursors of coke formation. The catalyst with DPA as template consists of the mixture of SAPO-5 and SAPO-34. The SAPO-5 is large pore molecular sieve with AFI. Product molecules in SAPO-5 can be easily escaped in the pore without further reaction. Fig. 6 shows yield of light olefins on TOS. All the catalysts except for catalyst with DPA as template, exhibited more than 90% yield in the olefins with abrupt decrease on TOS by catalyst deactivation. Compared with other catalysts, this sample showed a slightly lower yield in olefins and a little slow decay in catalyst diminishment which is due to larger pore and lower acidity.

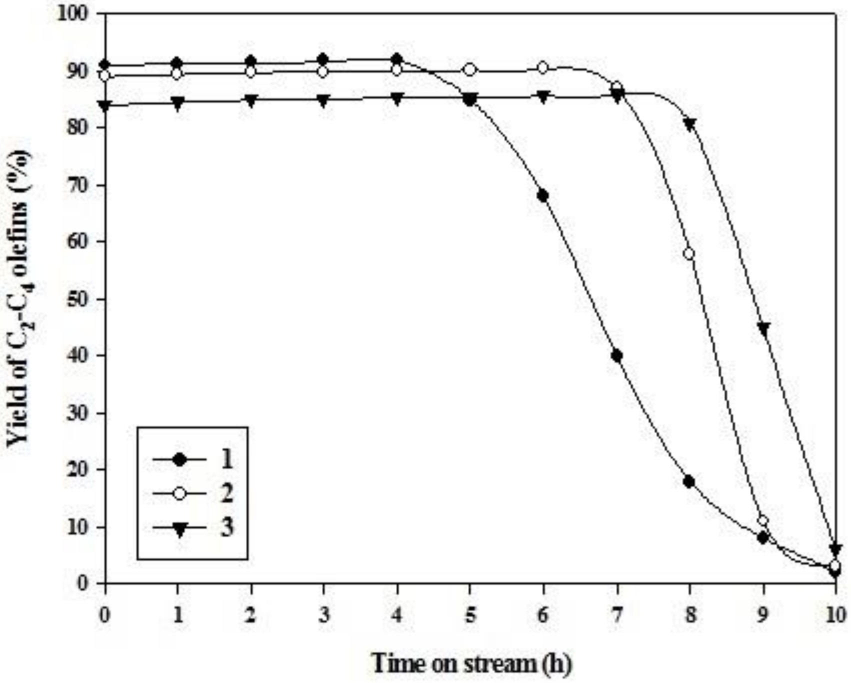

Figure 6. Yield of C_2-C_4 olefins with TOS over SAPO catalysts at 450^{0}C, atmospheric pressure and WHSV = 1 h^{-1} (1) morpholine (2) TEAOH (3) DPA

5. Conclusion

Parameters such as purity, acidity and crystal size of the SAPO-34 zeolite are highly important in their application for catalysis in industry. In this research, the crystallization of small pore molecular sieve SAPO-34 samples with different template was investigated.

The obtained results have revealed that SAPO-34 zeolitic phase has an adverse zeolitic phase of SAPO-5. This impure phase would be impoverished by the mean of template type. It is anticipated that the reduction in crystal size and unique textural and structural properties of the synthesized SAPO-34 crystals will positively impact its catalytic properties.

The crystallites of cubic shape with size in range of 3-5 µm were observed for sample with morpholine from SEM photographs. The absence of a baseline drift and high peak intensity with no line broadening indicated good crystallinity for the sample when using TEAOH as the template. SEM photographs showed that SAPO-34 crystallization by morpholine and TEAOH as a templating agent resulted in obtaining good product purity, while using DPA caused presence of impurity and oversize particles. It indicates that the nature of template used in synthesis determines the morphology of final crystals due to different rate of crystal growth. XRD analysis of the samples confirms the results obtained by SEM photographs.

From NH_3-TPD, similar acid properties were observed for SAPO-34 with morpholine and TEAOH template, but week acidity synthesized with DPA.

All the prepared SAPO-34 catalysts show similar activity and product distribution in the MTO reaction. However, the catalyst obtained using morpholine as the template, has the shortest lifetime.

References

[1] Wu X, Anthony RG. Effect of feed composition on methanol conversion to light olefins over SAPO-34. Appl. Catal. A: Gen., 218: 241- 250, 2001.
[2] Wu XC, Abraha MG, Anthony RG. Methanol conversion on SAPO-34: reaction condition for fixed-bed reactor. Appl. Catal. A General, 260: 63-69, 2004.

[3] Keil FJ. Review: "Methanol-To-Hydrocarbons: Process Technology, Microporous and mesoporous Material. 29:49-66, 1999.

[4] Chen JQ, Bozzano A, Glover B, Fuglerud T, Kvisle S. Recent advancements in ethylene and propylene production using the UOP/Hydro MTO process, Catalysis Today. 106: 103-107, 2005.

[5] Liu G, Tian P, Zhang Y, Li J, Xu L, Meng Sh, Liu Zh. Synthesis of SAPO-34 templated by diethylamine: Crystallization process and Si distribution in the crystals. Microporous and Mesoporous Materials. 114: 416-423, 2008.

[6] Liu Z, Sun C, Wang G, Wang Q, Cai G. New progress in R&D of lower olefin synthesis. Fuel Processing Technology, 62: 161-172, 2000.

[7] Wilson S, Barger P. The characteristics of SAPO-34 which influence the conversion of methanol to light olefins. Microporous and mesoporous material, 29: 117-126, 1999.

[8] Obrzut LD, Adekkanattu PM, Thundimadathil JL, Dubois DR, Guin J. Reducing methane formation in methanol to olefins reaction on metal impregnated SAPO-34 molecular sieve. React. Kinet. Catal. Lett. 80: 113-121, 2003.

[9] Prakash AM, Unnikrishnan S. Synthesis of SAPO-34: high silicon incorporation in the presence of morpholine as template. J. Chem. Soc., Faraday Trans., 90: 2291-2296, 1994.

[10] Dubois DR, Obrzut DL, Liu J, Thundimadathil J, Adekkanattu PM, Guin JA, Punnoose A, Seehra MS. Conversion of methanol to olefins over cobalt-, manganese- and nickel-incorporated SAPO-34 molecular sieves. Fuel Process. Technol., 83: 203-218, 2003.

[11] Hunger M, Seiler M, Buchholz A. In situ MAS NMR spectroscopic investigation of the conversion of methanol to olefins on silicoaluminophosphates SAPO-34 and SAPO-18 under continuous flow conditions. Catalysis Letters., 74: 61-68, 2001.

[12] Lee YJ, Baek SCh, Jun KW. Methanol conversion on SAPO-34 catalysts prepared by mixed template method. Applied Catalysis A: General, 329: 130-136, 2007.

[13] Ye L, Cao F, Ying W, Fang D, Sun Q. Effect of different TEAOH/DEA combination on SAPO-34’s synthesis and catalytic performance. J Porous Mater., 18: 225-232, 2011.

[14] Salmasi M, Fatemi S, Hashemia SJ. MTO reaction over SAPO-34 catalysts synthesized by combination of TEAOH and morpholine templates and different silica sources. Scientia Iranica, 19(6): 1632–1637, 2012.

[15] Qiming S, Ning W, Guanqi G, Jihong Y. Ultrafast synthesis of nano-sized zeolite SAPO-34 with excellent MTO catalytic performance. Chem. Commun., 51: 16397-16400, 2015.

[16] Dahl IM, Kolboe S. Physicochemical characteristics of ZSM-5/SAPO-34 composite catalyst for MTO reaction. Catalysis Letters, 20(3): 329-336, 1993.

[17] Kang E, Kim T, Chae H, Kim M, Jeong K, Kim J, Kim C, Jeong S. Synthesis of mesoporous SAPO-34 zeolite from mesoporous silica materials for methanol to light olefins. J. Nanosci Nanotechnol, 13(11): 7498-503, 2013.

[18] Liping L, Xiaojing C, Junfen L, Jianguo W. Synthesis of SAPO-34/ZSM-5 Composite and Its Catalytic Performance in the Conversion of Methanol to Hydrocarbons. J. Braz. Chem. Soc., 26(2): 2015.

[19] Lok BM, Messina CA, Patton RL, Gajek RT, Cannan TR, Flanigen EM. Crystalline silicoaluminophosphates. US Patent 4440871, 1984.

[20] Liang J, Li H, Zhao S, Guo W, Wang R, Ying M. Characteristics and performance of SAPO-34 catalyst for methanol-to-olefin conversion. Applied Catalysis, 64: 31-40, 1990.

[21] Dahl IM, Mostad H, Akporiaye D, Wendelbo R. Structural and chemical influences on the MTO reaction: a comparison of chabazite and SAPO-34 as MTO catalysts. Microporous and Mesoporous Materials, 29: 185-190, 1999.

[22] Dumitriu E, Azzous A, Hulea V, Lutic D, Kessler H. Synthesis, characterization and catalytic activity of SAPO-34 obtained with piperidine as templating agent. Microporous Materials, Vol. 10, : 1-12, 1997.

[23] Parlitz B, Schreier E, Zubowa HL, Eckelt R, Lieschke E, Fricke R. Isomerization of n-Heptane over Pd-Loaded Silico-Alumino-Phosphate Molecular Sieves. J. Catal., 155: 1-11, 1995.

[24] Xiao TC, An LD, Wang HL. Dependence of the nature and catalytic performance on the synthesis factors of SAPO-5 molecular sieve. Appl. Catal. A: Gen., 130: 187-194, 1995.

[25] Vomscheid R, Briend M, Peltre MJ, Man PP and Barthomeuf D. The Role of the Template in Directing the Si Distribution in SAPO Zeolites. J. Phys. Chem., 98(38): 9614–9618, 1994.

[26] Chen D, Moljord K, Fuglerud T, Holmen A. The effect of crystal size of SAPO-34 on the selectivity and deactivation of the MTO reaction. Microporous Mesoporous Mater., 29: 191-203, 1999.

[27] Kang M. Synthesis and catalytic performance on methanol conversion of NiSAPO-34 crystals (II): catalytic performance under various reaction conditions. Journal of Molecular Catalysis A: Chemical, 150: 205-212, 1999.

[28] Liu G, Tian P, Li J, Zhang D, Zhou F, Liu Zh. Synthesis, characterization and catalytic properties of SAPO-34 synthesized using diethylamine as a template. Microporous and Mesoporous Materials, 111: 143-149, 2008.

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