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Article

Effect of SAPO-34 molecular sieve morphology on methanol to olefins performance

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ABSTRACT

SAPO-34 molecular sieve samples with sheet-like and cubic morphology were synthesized under microwave and hydrothermal conditions, respectively. The sheet-like SAPO-34 was 130 nm thick with a Brunauer-Emmett-Teller (BET) surface area of 593 m²/g, while the cubic sample was 1.5–2.5 μm in size with a BET surface area of 708 m²/g. Both samples exhibited a similar density for strong acid sites, while the cubic SAPO-34 possessed less weak acid sites. A methanol to olefins catalytic test carried out at 450 °C and 1.0 h⁻¹ showed that the sheet-like SAPO-34 exhibited a long stability life of 380 min and gave a high ethylene selectivity of 51.77% and a high total selectivity for ethylene, propylene, and butylene of 90.20%. However, the stability life for the cubic SAPO-34 was only 212 min, and the ethylene selectivity and total selectivity for ethylene, propylene, and butylene decreased to 49.84% and 86.81%, respectively. It is thought that the longer stability life and higher olefin selectivity for sheet-like SAPO-34 occur because of the shorter diffusion path that hinders the further conversion of produced olefins and coke formation.

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1. Introduction

SAPO-34 molecular sieves exhibit excellent catalytic performance in the methanol to olefins (MTO) reaction because of their relatively small pore diameter, moderate acid strength, and highly hydrothermal stability [1–4]. Methanol conversions can reach 100% and the total selectivity for ethylene, propylene, and butylene can be over 80%. However, SAPO-34 deactivates rapidly because of coke deposition, and this results in a short lifetime. Thus it is necessary to extend the lifetime of SAPO-34 in the MTO reaction by controlling coke deposition.

Many factors influence coke formation during the MTO reaction process, such as Si/Al ratio [5], acidity [6], and crystal

morphology [7,8]. In addition, catalytic conditions may also affect coke formation by controlling the relative distribution of products [9]. Obviously, improved MTO performance on SAPO-34 could be achieved by optimizing crystal morphology and catalytic conditions. In this work, SAPO-34 crystals with different morphologies were synthesized by controlling crystallization conditions. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX), Brunauer-Emmett-Teller (BET) surface area determination, and ammonia temperature-programmed desorption (NH₃-TPD). The effects of crystal morphology and catalytic conditions on MTO performance were also investigated.

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2. Experimental

2.1. SAPO-34 preparation

Pseudoboehmite (69 wt% of Al_2O_3 , Zibo Aluminum Co., Ltd., Zibo, China) was stirred with silica sol (31 wt% of SiO_2 , Zhejiang Yuda Chemical Co., Ltd., Shangyu, China) and deionized water at room temperature. Then phosphoric acid (85 wt%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) and organic templates (tetraethyl ammonium hydroxide (TEAOH), 25 wt%, Shanghai Nuotai Chemical Co., Ltd., Shanghai, China; or triethylamine (TEA), 99 wt%, Shanghai Qiangshun Chemical Co., Ltd., Shanghai, China) were added successively to the above-mentioned solution under vigorous stirring to obtain milky uniform gels. Finally, the gels were transferred into Teflon-lined autoclaves and heated in a microwave oven (Milestone ETHOS A) or a rotating oven with predetermined heating programs under autogenous pressure. After crystallization, the autoclaves were cooled to room temperature, and the solid products were separated by centrifugation, washed thoroughly with deionized water, dried overnight at 120 °C, and calcined at 550 °C for 6 h in a furnace. The resultant SAPO-34 samples were termed S-0, S-1, and S-2 (see Table 1 for corresponding crystallization conditions).

2.2. Characterization

XRD patterns were recorded using a powder X-ray diffractometer (Bruker AXS D8 ADVANCE) operated at 40 kV and 40 mA using $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in the range of $2\theta = 5^\circ\text{--}40^\circ$. The crystal morphology of the S-0 sample was examined using a Hitachi S-4800 field emission-SEM (FE-SEM) microscope, and the crystal morphology and chemical compositions of S-1 and S-2 were examined by SEM using a Philips XL30 equipped with an EDX.

The textural parameters were measured by nitrogen adsorption isotherms using the Quantachrome AUTOSORB-IQ-MP system. The samples were first degassed for 6 h under vacuum at 300 °C and then tested at liquid nitrogen temperature. The micropore volume was determined using a t -plot method, and the pore size was calculated by the Horvath-Kawazoe (HK) method. The sample acidity was determined on a TP-5080 adsorption analyzer (Tianjin Xianquan Co., Ltd., China), where a 0.05 g sample was pretreated for 1 h at 400 °C in Ar (30 ml/min) to remove the adsorbed water and then contacted with NH_3 at 10 ml/min for 30 min. Thereafter, Ar flow was introduced to remove the physically adsorbed NH_3 molecules for 40 min. The desorption process was carried out at 10 °C/min to

600 °C. The amount of coke deposited on the deactivated SAPO-34 was characterized by thermogravimetry (TG) using a NETZSCH STA 449 F3 instrument.

2.3. MTO reaction

The MTO reaction over the SAPO-34 catalyst was performed in a fixed-bed reactor (550 mm $\times$ 12 mm). SAPO-34 (3.0 g) was tableted to 20–40 mesh and then charged at the center of the reactor. Methanol aqueous solution (50 wt%) was fed into the reactor under atmospheric pressure. The volume hourly space velocity (volume of methanol aqueous solution flowing through a unit volume of catalyst in a unit time) was 0.8–4.0 h^{-1} , and the reaction temperature was 400–500 °C. The gas products were analyzed using a SHIMADZU GC-2014C gas chromatograph equipped with a flame ionization detector and a HP-PLOT/Q column (30 m $\times$ 0.53 mm). The liquid products (mainly water and containing unconverted methanol when the conversion was lower than 100%) were analyzed with a thermal conductivity detector and a PORAPAK T column (3 m $\times$ 3 mm). Dimethyl ether (DME) was converted to the corresponding amount of methanol to obtain an accurate methanol conversion.

3. Results and discussion

3.1. Characterization of SAPO-34

3.1.1. XRD

The XRD patterns of the samples are given in Fig. 1. Only two weak characteristic peaks of SAPO-34 [10] at $2\theta = 9.6^\circ$ and 20.7° appear in that of the S-0 sample. However, the characteristic peaks of SAPO-34 [10] appear at $2\theta = 9.6^\circ$, 13° , 15.9° , 20.7° , 26° , and 31° for the S-1 and S-2 sample with higher intensities, and no other peaks were detected. This implies that pure SAPO-34 is obtained. Figure 1 also shows that the peak intensities of the S-2 sample are higher than the other two samples, revealing the highest relative crystallinity of the S-2 sample.

3.1.2. SEM

Figure 2 depicts the FE-SEM and SEM images of the samples. The S-0 sample (synthesized at 165 °C for 0.75 h under micro-

Table 1
Crystallization conditions for SAPO-34 samples.

Sample	Molar composition of gel	Heating method	$T/^\circ\text{C}$	t/h
S-0	$1\text{Al}_2\text{O}_3:1.1\text{P}_2\text{O}_5:0.44\text{SiO}_2:$ $1.65\text{TEAOH}:56.9\text{H}_2\text{O}$	microwave	165	0.75
S-1	$1\text{Al}_2\text{O}_3:1.1\text{P}_2\text{O}_5:0.44\text{SiO}_2:$ $1.65\text{TEAOH}:56.9\text{H}_2\text{O}$	microwave	220	2
S-2	$1\text{Al}_2\text{O}_3:1.1\text{P}_2\text{O}_5:0.44\text{SiO}_2:$ $2.25\text{TEA}:31.4\text{H}_2\text{O}$	hydrothermal	165	30

Fig. 1. XRD patterns of SAPO-34 samples.

Fig. 2. FE-SEM (S-0) and SEM (S-1 and S-2) images of SAPO-34 samples.

wave conditions) yielded spherical SAPO-34 crystals of 20 nm diameter. By prolonging the crystallization time to 2 h at the same temperature, SAPO-34 with mixed aggregates of spherical and sheet-like crystals was formed. An increase in crystallization temperature to 220 °C for 2 h under microwave conditions (S-1) yielded 1000 nm × 1000 nm × 130 nm sheet-like SAPO-34. However, the S-2 sample (synthesized under hydrothermal conditions at 165 °C for 30 h) had a larger cubic crystal structure of 1.5–2.5 μm. The SEM results show that there was a transformation process from spherical to sheet-like crystals under microwave conditions. Spherical crystals appear at low temperature and short crystallization time and transform to sheet-like crystals at higher temperature or with longer crystallization time.

3.1.3. EDX

The $n(\text{Al}):n(\text{Si}):n(\text{P})$ for the S-1 sample obtained by EDX is 0.48:0.10:0.42, while the value for S-2 is 0.51:0.07:0.42. The P and Al contents of these two samples are almost identical while the Si content of S-1 is slightly higher than S-2.

3.1.4. Nitrogen adsorption-desorption

The nitrogen adsorption-desorption isotherms are presented in Fig. 3 with corresponding textural data listed in Table 2. Basically, both samples present the traditional type I isotherms, revealing the existence of micropores. The S-1 sample shows a hysteresis loop at high relative pressure, which may

Fig. 3. Nitrogen adsorption-desorption isotherms of SAPO-34 samples.

Table 2

Textural data of SAPO-34 samples.

Sample	BET surface area (m ² /g)	Micropore volume (cm ³ /g)	Pore size (nm)
S-1	593	0.22	0.54
S-2	708	0.26	0.54

occur because of the condensation of nitrogen molecules on the external sample surface [11].

The BET surface area of S-1 and S-2 is 593 and 708 m²/g, respectively, and the micropore volume is 0.22 and 0.26 cm³/g, respectively (Table 2). Therefore, a developed micropore system is formed in both samples. The difference in BET surface area between S-1 and S-2 may be caused by different crystallization conditions. The crystallization time for S-2 (30 h) is much longer than that for S-1 (2 h), and the relative crystallinity of S-2 is also higher than that of S-1 (shown by XRD). The micropore system in S-2 may therefore be more developed, leading to a higher BET surface area. The pore size of both samples is 0.54 nm, which is higher than the theoretical value (0.38 nm). This may occur because of connectivity between nearby channels.

3.1.5. NH₃-TPD

Figure 4 gives the NH₃-TPD profiles of the SAPO-34 samples. Both samples possess peaks at approximately 160 and 370 °C, which correspond to the weak and strong acid sites, respec-

Fig. 4. NH₃-TPD profiles of SAPO-34 samples.

tively [12,13]. The desorption peak area of the weak acid sites for S-1 is higher than that for S-2, implying that the amount of weak acid sites is higher in the former. This may be related to its higher Si content. However, the desorption peak area of the strong acid sites for both samples is almost the same, indicating the similar density for the strong acid sites in these two samples. It has been reported that the conversion of methanol to DME occurs mainly on the weak acid sites while the conversion of DME (and methanol) to light olefins occurs mainly on the strong acid sites [14,15]. The similar density for strong acid sites in these two samples reveals that acidity has little influence on the catalytic difference of the S-1 and S-2 samples.

3.2. MTO reaction over SAPO-34

3.2.1. MTO performance

Figure 5 gives the MTO performance on S-1 and S-2 under atmospheric pressure at 450 °C and 1.0 h⁻¹. The methanol conversion on S-1 is 100% for 380 min with an ethylene, propylene, and total selectivity for ethylene, propylene, and butylene of 51.77%, 36.86%, and 90.20%, respectively. In the case of S-2, the methanol conversion is 100% for 212 min with ethylene, propylene, and total selectivity for ethylene, propylene, and butylene being 49.84%, 34.22%, and 86.81%, respectively. Both the lifetime and selectivity for the light olefins on S-1 are superior to that on S-2. Taking into account their similar densi-

Fig. 5. MTO performance on SAPO-34 samples at 450 °C and 1.0 h⁻¹. (1) Methanol conversion; (2) Total selectivity for ethylene, propylene, and butylene; (3) Selectivity for ethylene; (4) Selectivity for propylene.

ty for the strong acid sites, this difference may arise from their different crystal morphologies [7]. The slice thickness of S-1 is 130 nm, so the diffusion path is short. The ethylene and propylene can diffuse out of the SAPO-34 pores easily before being converted to heavier olefins, aromatics, and coke. Thus a higher light olefin selectivity as well as a longer lifetime are achieved. For S-2, however, the crystal size is larger and the diffusion path is longer than S-1. A second reaction for the produced light olefins and severe coke formation may occur, which would lead to a lower light olefin selectivity and shorter lifetime.

Figure 5 also shows that the total selectivity for the light olefins increases with time on stream. The ethylene selectivity also increases, but the propylene selectivity increases for a short time and then decreases. This may be ascribed to the changes in pore size caused by coke deposition [5]. The coke deposition reduced the SAPO-34 pore size, and the selectivity decreased for butylene with larger molecule size. The propylene molecules are smaller than those of butylene, thus the selectivity increases at the beginning and decreases with further reduction in pore size. The selectivity for the smallest ethylene molecules increases continuously, and the extent of increase is higher than the reduced extent of propylene and butylene. This results in an increasing total selectivity for the light olefins over a certain period of time.

3.2.2. Effect of space velocity on MTO performance

The methanol conversion on SAPO-34 sample S-1 at different space velocities and at 450 °C is shown in Fig. 6. When the space velocity increases from 0.8 to 4.0 h⁻¹, the lifetime decreases from 526 to 112 min. The increasing space velocity leads to more molecules reacted per unit time, thus the coke formation rate increases, which decreases the lifetime of the SAPO-34.

3.2.3. Effect of reaction temperature on MTO performance

The methanol conversion on SAPO-34 sample S-1 at different reaction temperatures and at 1.0 h⁻¹ is shown in Fig. 7. When the reaction temperature is maintained at 400 °C, the methanol conversion is 100% for 644 min. Then the conversion decreases slowly and is maintained at 93.26% to 791 min. At

Fig. 6. Methanol conversion on SAPO-34 sample S-1 at different space velocities and at 450 °C.

Fig. 7. Methanol conversion on SAPO-34 sample S-1 at different reaction temperatures and at 1.0 h⁻¹.

450 °C, however, the methanol conversion is 100% for 380 min and then decreases rapidly. At 500 °C, the methanol conversion is 100% for only 255 min. These results indicate that the lifetime decreases with increasing reaction temperature, which may also result from the higher coke formation rate.

The selectivity for products on SAPO-34 sample S-1 at different reaction temperatures and at 1.0 h⁻¹ is shown in Fig. 8. When the reaction temperature is 500 °C, an ethylene selectivity of 56.96% can be achieved, which is far higher than the propylene selectivity. The butylene selectivity decreases from 7.81%, and the total selectivity for ethylene, propylene, and butylene is 87.24%. At 450 °C, however, the highest ethylene selectivity is 51.77%, which is still higher than the propylene selectivity but with a smaller difference compared with that at 500 °C. The butylene selectivity decreases from 9.63%, and the total selectivity of 90.20% can be achieved. The highest ethylene selectivity at 400 °C is only 41.62%, which is lower than the propylene selectivity. The butylene selectivity decreases from 14.04%, but the total selectivity can be as high as 91.16%. Figure 8 also shows that the selectivity for methane increases greatly at high temperature and can be higher than the butylene selectivity. That is, the selectivity for ethylene and methane increases, but the selectivity for propylene and butylene decreases with increasing reaction temperature; this leads to an increasing relative content of ethylene among the obtained light olefins. This phenomenon may be caused by the cracking of propylene and butylene into methane and ethylene at high temperature [16]. The above results also indicate that it is possible to control the relative olefin content by adjusting the MTO reaction temperature on the S-1 sample.

3.2.4. Coke analysis of deactivated SAPO-34

The amount of coke on the deactivated SAPO-34 in Section 3.2.1 was analyzed by TG, and the coke formation rate was calculated based on these results as well as on the other characterization results (Table 3). The coke formation rate for S-1 is 0.043 mg/(m²·h), which is half that for S-2 (0.084 mg/(m²·h)). The sheet-like crystals of S-1 can decrease the coke formation rate, thereby improving the MTO performance and prolonging the SAPO-34 lifetime.

Fig. 8. Selectivity for products on SAPO-34 sample S-1 at different reaction temperatures and at 1.0 h⁻¹. Selectivity for: (1) Ethylene, propylene, and butylene; (2) Ethylene; (3) Propylene; (4) Butylene; (5) Methane.

Table 3

Coke amount and coke formation rate of SAPO-34 samples.

Sample	Lifetime (min)	Coke amount per surface area (mg/m ²)	Coke formation rate ^a (mg/(m ² ·h))
S-1	380	0.274	0.043
S-2	212	0.296	0.084

^a Defined as the coke amount per surface area per lifetime.

4. Conclusions

The sheet-like SAPO-34 synthesized at 220 °C for 2 h under microwave conditions had a thickness of 130 nm with a BET surface area of 593 m²/g, while the cubic material synthesized at 165 °C for 30 h under hydrothermal conditions was 1.5–2.5 μm in size with a BET surface area of 708 m²/g. Compared with the cubic one, the sheet-like SAPO-34 exhibited a longer lifetime of 380 min with higher ethylene selectivity of 51.77% and higher total selectivity for ethylene, propylene, and butylene of 90.20% in MTO process. The longer lifetime and higher olefin selectivity on sheet-like SAPO-34 were considered to come from the shorter diffusion path, which hindered further con-

Graphical Abstract

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Effect of SAPO-34 molecular sieve morphology on methanol to olefins performance

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Methanol to olefins performance on SAPO-34 depends on the molecular sieve morphology. The sheet-like SAPO-34 (sample S-1) exhibits a longer lifetime and higher olefin selectivity than the cubic material (sample S-2) because of the shorter diffusion path of the former.

version of produced olefins and coke formation. For the sheet-like SAPO-34 sample, a high reaction temperature and high space velocity may accelerate the coke formation rate, leading to a fast deactivation of the catalyst. At the same time, the high reaction temperature improved the ethylene selectivity and decreased the propylene and butylene selectivity. The relative content of obtained olefins could be adjusted by controlling the MTO reaction temperature.

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SAPO-34晶粒形貌对甲醇转化制低碳烯烃反应的影响

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摘要: 分别采用微波和水热法合成了具有片状及立方结构的SAPO-34分子筛。结果发现, 片状SAPO-34分子筛晶粒厚度为130 nm, 比表面积为593 m²/g; 立方结构SAPO-34分子筛粒径为1.5–2.5 μm, 比表面积为708 m²/g。二者具有数量相近的强酸中心, 后者的弱酸位数量略少。甲醇制烯烃反应结果表明, 在450 °C和1.0 h⁻¹的反应条件下, 片状SAPO-34分子筛的催化寿命可达380 min, 乙烯选择性最高为51.77%, 乙烯、丙烯及丁烯的总选择性最高为90.20%; 而立方结构SAPO-34的催化寿命仅为212 min, 乙烯选择性最高为49.84%, 乙烯、丙烯及丁烯的总选择性最高只有86.81%。这可能源于片状晶粒的扩散路径较短, 抑制了低碳烯烃的进一步转化及积碳的生成, 因此具有较高的低碳烯烃选择性及较长的寿命。

关键词: SAPO-34分子筛; 形貌; 甲醇制烯烃; 反应温度; 空速

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1. 前言

SAPO-34分子筛具有相对较小的孔道直径、适宜的酸强度以及高水热稳定性,因而在甲醇转化制低碳烯烃(MTO)反应中表现出优异的催化性能^[1-4],甲醇转化率可达100%,乙烯、丙烯和丁烯的总选择性可超过80%.但SAPO-34分子筛催化剂极易发生积碳失活,催化寿命较短,因此延长SAPO-34分子筛在MTO反应中的催化寿命具有重要意义.

积碳的生成与SAPO-34分子筛的硅铝比、酸中心的强度及数量等因素相关^[5,6],而其晶粒形貌也会影响原料及产物分子在孔道中的扩散过程,进而影响积碳的生成^[7,8];同时,MTO反应条件可通过产物的相对含量^[9]而影响积碳的生成.因此,晶粒形貌及反应条件均会影响SAPO-34分子筛上的MTO反应性能.

本文通过控制晶化条件合成了具有不同晶粒形貌的SAPO-34分子筛,采用X射线衍射(XRD)、扫描电镜(SEM)、X射线能量散射(EDX)、N₂吸附-脱附及NH₃程序升温脱附(NH₃-TPD)等手段对SAPO-34分子筛进行了表征,考察了晶粒形貌及反应条件对SAPO-34分子筛上MTO反应性能的影响.

2. 实验部分

2.1. SAPO-34分子筛的合成

将一定量的拟薄水铝石(淄博铝业公司, Al₂O₃质量分数为69%)、硅溶胶(浙江宇达化工有限公司, SiO₂质量分数为31%)和去离子水混合,在室温下搅拌均匀,然后依次加入磷酸(国药集团化学试剂有限公司,质量分数为85%)和有机胺模板剂(四乙基氢氧化铵(TEAOH),上海诺泰化工有限公司,质量分数为25%;或三乙胺(TEA),上海强顺化工有限公司,质量分数为99%),搅拌均匀后制得凝胶.然后将凝胶装入带有聚四氟乙烯内衬的反应釜中,密封后将反应釜放入微波反应器(Milestone ETHOS A)或转动烘箱中,在预设加热程序和自生压力下进行晶化.晶化结束后,待反应釜冷却至室温,将晶化产物洗涤至中性,离心后将所得固体在120 °C干燥过夜,于550 °C焙烧6 h,即得SAPO-34分子筛样品,分别命名为S-0、S-1和S-2(三个样品的合成条件见表1).

2.2. SAPO-34分子筛的表征

XRD表征在Bruker公司的AXS D8 ADVANCE型X射线粉末衍射仪上进行, Cu K α 靶($\lambda = 0.154$ nm), 扫描范围 $2\theta = 5^\circ - 40^\circ$, 管电压40 kV, 管电流40 mA. 样品S-0的晶粒形貌采用Hitachi公司的S-4800型场发射电镜(FE-SEM)进行观察,而样品S-1和S-2的晶粒形貌及化学组成采用Philips公司的带有EDX的XL30型SEM进行观察和测定.样品的织构参数在Quantachrome公司的AUTOSORB-IQ-MP型物理吸附仪上测定,样品先在300 °C及真空中脱气6 h,然后在液氮温度下测定样品的N₂吸附-脱附等温曲线,分别通过 t -plot方法和HK方法算得样品的微孔体积和孔径.样品的酸性采用天津先权公司的TP-5080型吸附仪测定.测量时将0.05 g焙烧后的样品在400 °C的Ar (30 ml/min)下预处理1 h,以脱除样品上吸附的水和其它杂质;然后通入NH₃ (10 ml/min),持续30 min;再经Ar吹扫40 min,以除去样品表面物理吸附的NH₃;最后,以10 °C/min升至600 °C进行程序升温脱附.失活SAPO-34分子筛的积碳量采用NETZSCH公司的STA 449 F3型热重(TG)分析仪进行分析.

2.3. 催化剂的评价

MTO反应在固定床反应器(550 mm $\times$ 12 mm)中进行,内装3.0 g SAPO-34分子筛(20–40目).以甲醇水溶液(甲醇质量分数为50%)为原料,反应条件为400–500 °C,常压,体积空速(单位时间内流经单位体积催化剂的甲醇水溶液体积)0.8–4.0 h⁻¹.气相产物用SHIMADZU GC-2014C型气相色谱仪分析, HP-PLOT/Q毛细管柱(30 m $\times$ 0.53 mm), FID检测器;液相产物(主要为水,当转化率较低时也包含未转化的甲醇)用PORAPAK T毛细管柱(3 m $\times$ 3 mm)和TCD检测.产物中二甲醚(DME)换算成相应量的甲醇以获得真实的甲醇转化率.

3. 结果与讨论

3.1. SAPO-34分子筛的表征结果

3.1.1. XRD结果

图1为SAPO-34分子筛的XRD谱.由图可见, S-0样品在 $2\theta = 9.6^\circ$ 和 20.7° 处出现了SAPO-34的特征峰^[10],且强度较低;而S-1和S-2样品在 $2\theta = 9.6^\circ$, 13° , 15.9° , 20.7° , 26° 和 31° 处出现SAPO-34分子筛的特征峰^[10],且强度高,

没有出现其它衍射峰,表明这两个样品均为纯相的SAPO-34分子筛.还可以看出,S-2样品的衍射峰强度最高,表明其相对结晶度最高.

3.1.2. SEM结果

图2为各SAPO-34分子筛样品的FE-SEM和SEM照片.由图可见,在165 °C微波下晶化0.75 h后得到的S-0样品是球形的,其直径为20 nm左右;若将晶化时间延长到2 h,则会得到球形与片状共存的样品,说明部分球形分子筛转变为片状结构;在220 °C微波下晶化2 h后得到的样品S-1具有片状形貌,其长和宽约为1 μm ,厚度为130 nm左右;而在165 °C水热晶化30 h后得到的样品S-2是具有立方结构的SAPO-34分子筛,其粒径为1.5–2.5 μm ,明显大于S-0和S-1样品的粒径.由此可见,在微波条件下,SAPO-34分子筛的晶粒存在着由球形小颗粒向片状晶粒转化的过程:在低温短时间晶化条件下合成的是球形小颗粒;随着晶化时间的延长,晶化温度的提高,小颗粒逐渐消失,最终生成片状SAPO-34晶粒.

3.1.3. EDX结果

EDX测得S-1和S-2样品中 $n(\text{Al}):n(\text{Si}):n(\text{P})$ 分别为0.48:0.10:0.42和0.51:0.07:0.42,两者P和Al的含量基本相当,只是S-1样品的Si含量略高.

3.1.4. N_2 吸附-脱附结果

图3为SAPO-34分子筛的 N_2 吸附-脱附等温线,表2为相应的结构参数.由图可见,S-1和S-2样品的等温线均为典型的I型,表明所合成的SAPO-34分子筛为微孔结构;S-1样品在高比压区内的弱迟滞环可能来源于 N_2 在样品外表面上的凝聚^[11].S-1和S-2样品的比表面积分别达到593和708 m^2/g ,相应的微孔体积分别为0.22和0.26 cm^3/g (见表2),表明这两个SAPO-34分子筛样品均形成了发达的微孔体系;S-2的比表面积更高则可能是由其晶化条件的差别所致.S-1样品在微波条件下晶化时间较短,而S-2样品在水热条件下晶化时间较长.因此S-2样品的相对结晶度较高(见图1),其内部微孔体系可能更为发达,因而其比表面积更大.两者的孔径均为0.54 nm,比理论值(0.38 nm)偏高,这可能是分子筛孔道之间有部分连通所致.

3.1.5. NH_3 -TPD结果

图4为S-1和S-2样品的 NH_3 -TPD谱.由图可见,两样品均出现两个脱附峰,其中160 °C左右的脱附峰对应于弱酸中心,370 °C左右的则对应于强酸中心^[12,13].相比之下,S-1样品的弱酸中心脱附峰面积大于S-2样品,表明其弱酸中心数量略多,这应与S-1样品中Si含量较多相

关;而二者对应于强酸中心的脱附峰位置和峰面积差别不明显,表明其强酸中心强度和数量较接近.一般说来,弱酸中心主要使甲醇脱水生成DME,而强酸中心则主要将甲醇和DME的混合物转化为低碳烯烃^[14,15].二者强酸中心的强度和数量较为接近,表明在MTO反应中二者酸中心的影响相差较小.

3.2. SAPO-34分子筛的MTO反应结果

3.2.1. MTO反应结果

在常压、450 °C以及空速 1.0 h^{-1} 的条件下各SAPO-34样品上MTO反应结果见图5.从图中可以看出,S-1样品上甲醇转化率保持100%的时间为380 min,乙烯选择性最高为51.77%,丙烯选择性最高为36.86%,乙烯、丙烯及丁烯的总选择性最高为90.20%;而S-2样品上甲醇转化率保持100%的时间仅为212 min,乙烯选择性最高为49.84%,丙烯选择性最高为34.22%,乙烯、丙烯及丁烯的总选择性最高为86.81%.可见,S-1样品的催化性能和稳定性明显优于S-2样品.考虑到这两个样品中对DME转化为低碳烯烃起决定作用的强酸位数量较接近,因此其催化性能的差异应主要源自不同的晶粒形貌^[7].S-1样品晶粒厚度为130 nm,扩散路径较短,因此生成的乙烯、丙烯等低碳烯烃迅速扩散出孔道,有效抑制了其进一步生成高碳烯烃、芳烃以及形成积碳的反应,因此低碳烯烃的选择性较高,催化寿命较长.而S-2样品晶粒较大,扩散路径较长,不利于乙烯、丙烯等低碳烯烃从孔道中及时扩散出来,使得低碳烯烃较易进一步反应,生成积碳的速率较快,导致低碳烯烃的选择性较低,催化寿命较短.

还可以发现,在一定的反应阶段内S-1上烯烃的总选择性随着反应时间的延长而增加,同时乙烯选择性增加,而丙烯选择性则经历一段很短时间的增加后开始降低.这主要是由于积碳导致的孔道变化所致^[5].反应过程中生成的积碳使SAPO-34的孔径减小,丁烯的分子直径较大,因此其选择性逐渐下降;丙烯的分子直径居中,因此其选择性开始时逐渐增加,而随着SAPO-34孔径的进一步减小,其生成被抑制,选择性下降;乙烯的选择性则一直增加,并且其增加量大于丙烯和丁烯的减少量,使得烯烃的总选择性在一定的阶段内随着反应时间的延长而提高.

3.2.2. 空速的影响

图6为不同空速下S-1样品上甲醇转化率随反应时间的变化.由图可见,当原料的体积空速从 0.8 h^{-1} 升至 4.0 h^{-1} 时,SAPO-34分子筛的催化寿命从526 min逐渐降

至112 min. 这是因为随着空速的增加, 单位时间内发生反应的分子数量逐渐增多, 使得积碳的生成量增加, 导致SAPO-34分子筛的催化寿命逐渐降低.

3.2.3. 反应温度的影响

图7为不同反应温度下S-1样品上甲醇转化率随反应时间的变化. 由图可见, 当反应温度为400 °C时, 甲醇转化率保持100%的时间为644 min, 随后开始下降, 但降幅较小, 至791 min时, 甲醇转化率仍可达93.26%; 但当反应温度为450 °C时, 甲醇转化率保持100%的时间为380 min, 之后迅速下降; 而当反应温度为500 °C时, 甲醇转化率保持100%的时间仅为255 min. 由此可见, 随着反应温度的升高, 催化剂的寿命逐渐缩短. 这可能是由高温下积碳的生成速率加快所致.

图8为不同反应温度下S-1样品上MTO反应产物的选择性随反应时间的变化. 由图可见, 500 °C下乙烯选择性最高为56.96%, 乙烯选择性明显高于丙烯, 丁烯选择性从初始的7.81%逐渐下降, 乙烯、丙烯及丁烯的总选择性最高为87.24%; 在450 °C下, 乙烯选择性最高为51.77%, 乙烯选择性仍高于丙烯, 但两者之间的差值较500 °C时的小, 丁烯选择性从9.63%逐渐下降, 乙烯、丙烯及丁烯的总选择性最高为90.20%; 而在400 °C下, 乙烯选择性最高仅为41.62%, 始终低于丙烯, 丁烯选择性从14.04%逐渐下降, 但乙烯、丙烯及丁烯的总选择性高达91.16%. 另外, 高温下甲烷的选择性随着反应时间的延长而明显上升, 在反应后期甚至高于丁烯选择性. 可见, 随着反应温度的升高, 乙烯和甲烷的选择性逐渐上升, 而丙烯和丁烯的选择性逐渐降低, 使得乙烯在低碳烯烃中的相对含量逐渐提高. 这可能是由于在高温条件

下丙烯和丁烯会发生裂解成甲烷和乙烯所致^[16]. 上述结果表明, 可以通过控制片状结构的SAPO-34分子筛上MTO反应温度来调节产物中各烯烃的相对含量, 以获得不同的目标产物.

3.2.4. 失活SAPO-34分子筛的积碳分析

将3.2.1节中失活的SAPO-34分子筛通过TG分析其积碳量, 并结合其它表征方法计算其积碳生成速率, 结果见表3. 可以看出, S-1样品的积碳生成速率为0.043 mg/(m²·h), 远小于S-2样品的0.084 mg/(m²·h), 即S-1样品的片状晶粒能有效抑制积碳的生成, 从而提高其催化性能并延长催化剂的寿命.

4. 结论

220 °C微波条件下晶化2 h后所得的SAPO-34分子筛晶粒呈片状, 其厚度为130 nm, 比表面积为593 m²/g; 而165 °C水热条件下晶化30 h后所得的SAPO-34分子筛晶粒呈立方结构, 粒径为1.5–2.5 μm, 比表面积为708 m²/g. 片状SAPO-34分子筛的MTO催化寿命可达380 min, 乙烯选择性最高为51.77%, 乙烯、丙烯及丁烯的总选择性最高为90.20%, 均明显优于立方结构的SAPO-34分子筛. 由于片状SAPO-34分子筛具有更短的扩散路径, 能有效抑制低碳烯烃的进一步转化及积碳的生成, 因此具有较高的低碳烯烃选择性及较长的寿命. 对片状SAPO-34分子筛来说, 较高的反应空速及较高的反应温度将加快积碳的生成, 从而加速催化剂的失活. 同时, 高温条件有利于提高MTO产物中乙烯的选择性, 降低丙烯和丁烯的选择性, 因此可以通过控制反应温度来调节MTO产物中各烯烃的相对含量.