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Article

Enhanced MTO performance over acid treated hierarchical SAPO-34

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ABSTRACT

Hierarchical SAPO-34 crystals were synthesized by a facile acid etching post-treatment. Butterfly-shaped porous patterns on four side faces and hierarchical pores composed of micropores, mesopores and macropores were formed after a nitric acid or oxalic acid treatment. The catalytic performance of the hierarchical SAPO-34 for the methanol to olefins (MTO) process showed that the synergistic effect of the hierarchical pores and acid sites resulted in a longer catalyst lifetime (from 210 to 390 min for the acid treated SAPO-34) and higher selectivity to light olefins of 92%–94%. The ethylene selectivity can be adjusted between 37.4% and 51.5% by the pore size. No hierarchical SAPO-34 was obtained after a treatment with butanedioic acid, and with this sample, fast deactivation was detected after 100 min.

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1. Introduction

Ethylene and propylene, traditionally produced by the petroleum route, are extremely important chemical raw materials. The methanol to olefins (MTO) process is a strategic technology for olefin production from the abundant nonpetroleum sources to balance the shortage of petroleum in China. SAPO-34 is the catalyst of choice for MTO due to its high hydrothermal stability, suitable micropores and moderate acidity [1,2]. However, it suffers from the rapid coke formation due to diffusion limitation through the small windows (0.38 nm × 0.38 nm), which would drive the process cost up with frequent catalyst regeneration [3]. Constructing SAPO-34 crystal with a hierarchical structure which contains micro-, meso- and macropores

is a promising approach to improve mass transport to decrease the regeneration frequency required [4,5].

Commonly, hierarchical pore structures are achieved by either direct synthesis with multiple templates or an indirect post-treatment. Wang et al. [4] synthesized SAPO-34 nanosheets with a hierarchical structure using the quaternary ammonium-type organosilane surfactant of [3-(trimethoxysilyl)propyl]octadecyl-dimethylammonium chloride (TPOAC) as the mesopore template and diethylamine (DEA) as the micropore template. Wu et al. [6] synthesized SAPO zeolite by adding TPOAC and C₂₂₋₄₋₄Br₂ as the organosilane surfactant for the mesopores, but their methanol conversion and catalyst lifetime were even worse than those of conventional SAPO-34 in the MTO process. Li et al. [5] synthesized hierarchical

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SAPO-34/18 zeolite by a hydrothermal method, but unfortunately only a low methanol conversion below 20% was reported. Hollow SAPO-34 cubes with butterfly-shaped spots on the faces prepared from solid precursor gels containing gelatin by a vapor phase transport method has been reported [7]. Wang et al. [4,8] synthesized hierarchical SAPO-34 catalysts using TPOAC as the mesopore template by direct hydrothermal crystallization, which exhibited a remarkably prolonged catalyst lifetime (350–500 min). A HF-assisted in situ growth etching route was developed to synthesize hierarchical SAPO-34 by the hydrothermal route [9,10], its single-run lifetime for the MTO reactions was up to 600 min. However, the secondary templates or HF used in the direct synthetic system increase the synthesis cost and environmental pollution. Post-synthetic treatment, which provides an alternative approach to get a hollow-structured micro- or nanosized SAPO-34 has been reported. Qiao et al. [11] synthesized hierarchical SAPO-34 by a hydrochloric acid and tetraethylammonium hydroxide (TEAOH) treatment, respectively, but did not report MTO performance.

Butterfly-shaped porous patterns on four side faces were formed after a nitric acid or oxalic acid treatment in our work. In our previous work, we also developed a facile TEOH etching post-treatment method to get SAPO-34 with a hierarchical pore structure and single-run MTO lifetime up to 600 min [12]. However, this method was limited by the high price of TEOH and low recovery rate (25%–42%) of SAPO-34 after the alkali treatment [11]. An acid treatment for the controllable preparation of a hierarchical SAPO-34 is a potential route to optimize the diffusion efficiency, suppress coke deposition and prolong catalyst lifetime as well as improve the recovery rate of the modified zeolite in an economic way. However, there have been only limited works on the acid treatment of SAPO-34 for the MTO application reported so far.

In this work, we synthesized hierarchical SAPO-34 with high crystallinity by controlling the acid post-treatment conditions. The effects of the acid types (nitric acid, oxalic acid and butanedioic acid) on the hierarchical SAPO-34 structure and MTO performance were investigated. It was found that butterfly-shaped pore structures were formed after the SAPO-34 was treated by nitric acid and oxalic acid, and a significantly prolonged single-run lifetime for MTO reaction together with improved light olefin selectivity were achieved.

2. Experimental

2.1. Synthesis of parent SAPO-34

The parent SAPO-34 crystals were prepared by a hydrothermal route. The synthesis gel molar composition was $1 \text{ Al}_2\text{O}_3 : 0.44 \text{ SiO}_2 : 1.1 \text{ P}_2\text{O}_5 : 2.25 \text{ triethylamine} : 35 \text{ H}_2\text{O}$. SAPO-34 crystal seeds with a mass ratio of 1:500 to the gel were mixed in a closed autoclave. Then the mixture was heated from room temperature to 165 °C in 7 h and kept at 165 °C for 33 h before cooling. The solid product was filtered, washed and dried, and followed by calcination at 600 °C for 5 h to obtain the parent SAPO-34, which was denoted as S-0.

Hierarchical SAPO-34 was prepared by an acid etching treatment. In a typical treatment, 300 mL acid aqueous solution (0.05 mol/L) was added into a three-necked flask and heated to 90 °C. Then 15 g of parent SAPO-34 was mixed with the acid solution for 6 h under reflux. The treated SAPO-34 was subsequently separated by filtration and carefully washed with deionized water five times. The product was dried and calcined at 600 °C for 5 h before use. The samples treated by nitric acid, oxalic acid and butanedioic acid were named as S-1, S-2 and S-3, respectively.

2.2. MTO reaction

The catalytic performance of the SAPO-34 samples for the MTO reaction was tested in a tubular fixed bed stainless steel reactor with the dimension of 550 mm long and I.D. 12 mm under atmospheric pressure. 3 g catalyst (20–40 mesh) was packed into the center of reactor and a mixture of methanol and water (mass ratio of 1:1) was fed into the reactor by an HPLC pump. The feedstock was first vaporized at 150 °C before the reactor. The reaction temperature was 450 °C and the weight hourly space velocity (WHSV) of methanol was 1.0 h^{-1} . The liquid products were collected by a cooling trap. The gaseous products were analyzed by an online gas chromatograph (GC 2014C, Shimadzu) equipped with a flame ionization detector (FID) and a HP-PLLOT/Q capillary column (30 m × 0.35 mm). The liquid products were analyzed by an offline GC (GC-950, Haixin) equipped with a thermal conductivity detector (TCD) and a packed column (PORAPAK T, 3 m × 3 mm). The conversion and selectivity were calculated on a carbon balance. The selectivity for the MTO products was expressed as mass percentage of each product in all the detected products except dimethyl ether (DME), which was calculated as unreacted methanol.

2.3. Catalyst characterization

The crystal structure of SAPO-34 was measured by an X-ray diffractometer (XRD, Rigaku, ultima IV) using $\text{Cu K}\alpha$ (0.154 nm) radiation of 40 mA and 40 kV. The morphology and elemental analysis of SAPO-34 was performed by a scanning electron microscope (SEM, Zeiss SUPRA 55 SAPHIRE) equipped with an energy-dispersion X-ray spectrometer (EDS, Oxford X-max) with acceleration voltage of 2 and 20 kV, respectively. The textural properties, such as specific surface area (BET, DFT), microporous area (*t*-plot method), pore volume (BJH, DFT and HK) and pore size distribution (BJH) of the samples were derived from N_2 adsorption measurements carried out at −196 °C using an automatic physisorption analyzer (Tristar 3020, Micromeritics) after the sample was degassed at 300 °C for at least 10 h under 0.133 Pa pressure prior to each run. The macroporous size was measured by mercury intrusion porosimetry (MIP, Micromeritics Autopore V 9620). Fourier transform infrared spectroscopy (FT-IR, Thermo Scientific, Nicolet 6700) was applied to detect the functional groups of SAPO-34. The composition of samples was analyzed by X-ray fluorescence (XRF, Bruker S4PIONEER). The tablets were pre-

pared by mixing boric acid and SAPO-34 with the weight ratio of 2:1.

The acidity of the samples was determined using temperature programmed desorption of ammonia (NH_3 -TPD, Tianjin Xianquan TP-5080) automated with a TCD analysis unit under nitrogen flow. Thermal degradation measurements were performed from room temperature to 1000 °C with a heating rate of 10 °C/min in air using a thermogravimetric analyzer (TGA, NETZSCH, STA 449F3). Solid state MAS NMR experiments were performed at 5 kHz on a Bruker AVANCE 400 spectrometer operating at frequencies of 79.5, 104.22 and 161.9 MHz for ^{29}Si , ^{27}Al and ^{31}P , respectively. Chemical shifts were referenced to tetramethylsilane (TMS) for ^{29}Si , 1 mol/L of $\text{Al}(\text{NO}_3)_3$ for ^{27}Al and 85% H_3PO_4 for ^{31}P . The coke composition was analyzed by an Agilent 7890 gas chromatograph coupled to an Agilent 5975C mass spectrometer (GC-MS). Before GC-MS measurement, 0.3 g deactivated SAPO-34 zeolite was treated with 2 mL of HF (40%) followed by extraction with 4 mL methylene chloride to get the organic composition and remove HF.

3. Results and discussion

3.1. Hierarchical SAPO-34 prepared by acid post-treatment

The XRD patterns of SAPO-34 before and after acid etching are shown in Fig. 1. All the samples showed the typical diffraction peaks of the CHA structure at 9.6°, 20.7°, 26° and 31°. No impurity crystal or amorphous phase was found, which indicated that the pure SAPO-34 crystals were well preserved after the acid etching. After the acid treatment, the intensity of the diffraction peaks was reduced, suggesting poorer relative crystallinity. Compared with S-0 (taken as 100%), the relative crystallinity of the three samples after acid etching was 25%, 27% and 22% for S-1, S-2 and S-3, respectively. This was reasonable since the acid treatment dissolved part of the crystal and generated defects in the zeolite framework. The recovery rate after each etching was 70%, 72% and 66% after nitric acid, oxalic acid and butanedioic acid etching, respectively, which was about 30% higher compared with those from the alkali treatment [12].

Fig. 1. XRD patterns for SAPO-34 before and after acid treatment.

Fig. 2. SEM images of SAPO-34 crystals before and after acid etching.

Fig. 2 presents the SEM images of SAPO-34 before or after the acid treatment. Typical cubic crystals with particle sizes from 1 to 2 μm can be observed. In contrast to the parent SAPO-34 crystals with smooth faces, the faces of nitric acid and oxalic acid treated SAPO-34 presented butterfly-shaped porous patterns on the four side faces. However, no pore pattern was observed on the butanedioic acid etched sample. Moreover, the etching of nitric acid led to more obvious pores than that by oxalic acid, indicating that the generation of the pore structure was related to the kind of acid used. Although the exact formation mechanism of SAPO-34 is not known, a reasonable conjecture is that the crystal skeleton is first formed by eight pyramidal sub-crystals followed by the subsequent growth to a cubic crystal through the filling of the voids around the center of the crystal. Therefore, the subsequently formed parts of SAPO-34 were preferentially etched to give the hierarchical structure which was probably due to their poorer stability (Fig. 2, S-1, S-2) [6,12]. The composition of the SAPO-34 obtained was determined by XRF and shown in Table 1. After the acid treatment, no obvious change in the composition was found, which is a little different from the report that selective dealumination from the framework occurred [11].

The pore structure of the SAPO-34 samples was determined by N_2 adsorption (Fig. 3). All samples showed Type I isotherms, which was due to the filling of micropores [13]. Interestingly, S-2, especially S-1 exhibited a slight increase in the region $0.99 < p/p_0 < 1.0$ with an obvious hysteresis loop, indicating the formation of mesopores and macropores after the etching by nitric acid or oxalic acid, which is consistent with the SEM results [14,15]. Both the Horvath-Kawazoe (HK) distributions of

Table 1
Molar composition of bulk SAPO-34 samples.

Sample	Molar composition			Yield (%)
	Al_2O_3	P_2O_5	SiO_2	
S-0	0.46	0.42	0.12	100
S-1	0.46	0.41	0.13	70
S-2	0.46	0.41	0.13	72
S-3	0.46	0.42	0.12	66

Fig. 3. N₂ adsorption isotherms (a) and BJH pore size distributions (b) of S-0, S-1, S-2 and S-3.

S-1 and S-2 showed one sharp peak near 0.5 nm similar to that of S-0 (not shown here), confirming that no obvious change of micropores occurred after the treatment. Meanwhile, the BJH results further revealed that mesopores with the average pore size of 12.5 and 46 nm were formed in S-1 and S-2, respectively. S-1 showed a slight higher micropore surface area and micropore volume (671 m²/g and 0.26 cm³/g) than S-0 (665 m²/g and 0.27 cm³/g) due to the increase of mesopore or macropore surface area and pore volume after the treatment with nitric acid. However, the BET specific surface area and microporous volume of the oxalic acid treated SAPO-34 increased sharply to 876 m²/g and 0.32 cm³/g. In contrast, no obvious mesopores and macropores were formed in the butanedioic acid treated sample, and only a Type I isotherm was observed. Meanwhile, the lower adsorption amount of S-3 also indicated a lower surface area and pore volume, as shown in Table 2. The mercury intrusion porosimetry (MIP) curves in Fig. 4 showed one wide peak at 400 nm, which was attributed to the void spaces between the cubic particles [12]. Compared with the parent

Table 2

Textural data of SAPO-34 before and after acid etching.

Sample	S_{BET} (m ² /g)	S_{micro} (m ² /g)	V_{total} (cm ³ /g)	V_{micro} (cm ³ /g)
S-0	665	637	0.27	0.26
S-1	671	638	0.26	0.25
S-2	876	868	0.36	0.32
S-3	518	509	0.21	0.20

Fig. 4. Pore size distribution from mercury intrusion porosimetry measurements.

SAPO-34, additional peaks at 62 and 434 nm appeared on S-1 and S-2, showing that macropores were formed in the acid treated SAPO-34, which was further confirmed from its shift to higher values when the etching time was prolonged (not shown here). Therefore, in combination with the SEM results, the pore size distribution analysis proved clearly that a hierarchical pore structure consisting of micro-, meso- and macropores were successfully formed by the nitric acid and oxalic acid etching of parent SAPO-34.

Fig. 5 gives the NH₃-TPD curves of SAPO-34 before and after the acid treatment. All samples showed two peaks at 190 and 395 °C, ascribed to NH₃ desorption from weak and strong acid sites, respectively [16,17]. Compared with S-0, the acid treated SAPO-34 exhibited peaks at almost the same positions for both the weak and strong acid sites, suggesting that the acid strength was kept almost unchanged after the acid treatment. The peak area for the weak acid sites increased slightly after the acid etching, which may improve the catalytic performance of SAPO-34 for the MTO reactions [18,19]. The peak area of the strong acid sites for S-1 and S-2 was somewhat decreased, but S-3 exhibited a little larger amount of strong acid sites. The former may increase while the later may shorten the single-run MTO lifetime [18]. The FT-IR spectra in Fig. 6 indicated similar chemical groups for all samples. In detail, the bands at 1082

Fig. 5. NH₃-TPD profiles of S-0, S-1, S-2 and S-3.

Fig. 6. FT-IR profiles of S-0, S-1, S-2 and S-3.

and 724 cm^{-1} belong to the SAPO framework stretching vibration. The peaks at 640 and 490 cm^{-1} can be assigned to the vibration of double 6 rings and the bending of T-O. The band at 1220 cm^{-1} stems from the asymmetric stretch of T-O tetrahedral groups [7]. The FT-IR results allowed us to infer that the acid treatment has no obvious effect on the chemical bonds of the crystals.

The chemical environment in SAPO-34 before and after the acid etching was investigated by solid state ^{29}Si , ^{27}Al and ^{31}P MAS NMR (Fig. 7). In the ^{29}Si MAS NMR spectra, all the samples showed a narrow peak centered at -89 assigned to the Si(4Al) species [20,21]. The peak area of hierarchical SAPO-34 (S-2) was somewhat larger than that of the parent SAPO-34, indicating a slight increase of the amount of weak acid sites [10,11], which agreed well with the NH_3 -TPD results. Three other peaks at -82, -100 and -105 were also observed with the hierarchical SAPO-34. The signal at -82 was assigned to $\text{Si}(\text{OAl})_n(\text{OH})_{4-n}$ ($n = 1$ or 2) species from the breaking of Si-O-Al bonds [22,23]. The peaks at -100 and -105 belong to Si(3Al) and Si(2Al), respectively. The relatively higher amount of these two species suggested a somewhat increased amount of Si after the acid treatment, which agreed well with the XRF results. In the ^{27}Al MAS NMR spectra, signals at 42, 15 and -12 for all samples were detected, which were assigned to Al atoms in a tetrahedral environment [11,24], penta-coordinated Al atoms and octahedrally coordinated Al atoms formed by another two water

Fig. 8. Methanol conversion change with time on stream.

molecules, respectively [9,12,22]. However, no obvious change in the Al chemical environment was detected before and after the acid treatment. The signals between -26 to -30 in the ^{31}P MAS NMR spectra were attributed to $\text{P}(\text{OAl})_4$ species and the broad shoulder peak at -15 stemmed from P atoms coordinated with water $[\text{P}(\text{OAl})_x(\text{H}_2\text{O})_y, x + y = 4]$ [12,22,25]. The decrease of the ^{31}P MAS NMR intensity of S-2 may come from the dephosphorization effect after acid etching [26].

3.2. Catalytic performance in MTO process

The MTO performance of the SAPO-34 before and after the acid treatment was tested at 450 $^{\circ}\text{C}$ under atmospheric pressure. Methanol conversion for all samples are shown in Fig. 8. The single-run lifetime (defined as giving methanol conversion >95%) over the parent SAPO-34 was only 210 min, while it was significantly prolonged to 360 and 390 min after the nitric acid and oxalic acid etching. It was reported that the micropores of the parent SAPO-34 were easily blocked by coke species, which will obstruct the access of reagents into the catalyst [27,28]. In contrast, the abundant mesopores and macropores in hierarchical SAPO-34 (S-1 and S-2) can greatly promote the diffusion of reagents/products into and out of the crystal, which suppressed coke formation and prolong the lifetime. Moreover, the increase of weak acid sites together with the decrease of strong acid sites in hierarchical SAPO-34 probably also contributed to the longer lifetime. However, only a short lifetime of 100 min was observed on SAPO-34 after it was treated with butanedioic

Fig. 7. ^{29}Si (a), ^{27}Al (b) and ^{31}P (c) MAS NMR of S-0 and S-2.

Fig. 9. C₂=–C₄= selectivity on S-0, S-1, S-2 and S-3.

acid. The destruction of some micropores and the absence of mesopores in S-3 would be the main reason for its poor MTO performance. This was supported by the broken crystals in Fig. 2 and its decreased BET surface area. At the same time, the increased amount of strong acid sites accelerated the formation of coke species, which would contribute to rapid deactivation.

The distribution of the products is shown in Fig. 9. The C₂=–C₄= selectivity from the parent SAPO-34 was around 90% during the single-run process, and contained 37.4% of ethylene, 38.8% of propylene and 14.0% of butene. Although the distribution of C₂=–C₄= over hierarchical S-1 was similar to that of the parent SAPO-34, the total selectivity for light olefins increased to 94%. However, the distribution of the products from S-2 was quite different from those of S-0 and S-1. The selectivity to ethylene increased to 51.5% and the selectivity to propylene and butene decreased to 31.7% and 8.1%, respectively. As a result, the total C₂=–C₄= selectivity was 92%. This suggested that the distribution of C₂=–C₄= was controlled by the channel structure of the hierarchical SAPO-34. For the S-3 sample, the distribution of light olefins was not changed compared with that of S-0, but the lifetime of the catalyst was decreased dramatically. The MTO results showed that a hierarchical SAPO-34 could not only prolong the lifetime of the catalyst, but also optimize the distribution of the products, which provides the possibility to increase or decrease the ethylene ratio according to the market demand.

TGA measurements of the spent catalysts under flowing air

Fig. 10. TGA profiles of deactivated S-0 and S-2 after MTO.

Table 3

Variation of coke amount over hierarchical and conventional SAPO-34.

Sample	S-0	S-2
Coke (% g/g _{cat})	15.0	18.0
TOS (min)	210	390
R _{coke} (g/min)	0.071	0.046
P _{coke} (g/g _{MeOH})	0.059	0.038

R_{coke} = coke amount (g)/TOS (min).

P_{coke} = coke amount (g)/methanol feedstock (g).

are shown in Fig. 10. These curves exhibited two obvious weight loss steps. The weight loss before 300 °C was attributed to adsorbed water. The weight loss between 500 and 700 °C was associated with the decomposition of coke. It was found that the weight loss of water was the same for these two samples, but the amount of deposited coke was 15% and 18% for the parent and hierarchical SAPO-34, respectively, suggesting that the coke capacity of SAPO-34 was increased after the oxalic acid etching, which also contributed to its longer lifetime [29–31]. The average coke formation rate and the amount of coke deposition per methanol unit were calculated and shown in Table 3. This revealed that the coke formation rate for hierarchical SAPO-34 was much lower than that of the parent one (0.046 vs. 0.071 g/min). At the same time, the amount of coke deposition per unit of methanol decreased from 0.059 to 0.038 g/g_{MeOH}, indicating that coke formation was suppressed over hierarchical SAPO-34 due to the synergistic effect of the micro-, meso- and macroporous channels and suitable acid sites.

In order to further investigate the effect of the hierarchical pores on coke deposition, the composition of the coke in spent S-0 and S-2 was analyzed by GC-MS (Fig. 11). For the spent S-2, the coke was mainly composed of polycyclic aromatics, such as phenanthrene and pyrene, and the weight percent of these was 73%. However, the polycyclic aromatics deposited on the spent parent SAPO-34 was decreased remarkably to 49% while the lighter coke species like benzene and polymethyl benzene were increased. The higher amount of polycyclic aromatics in S-2 may come from its hierarchical structure, due to improved diffusion of the products, thus benzene or polymethyl benzene diffuse easily out of the pores while larger molecules such as polycyclic aromatics remained in the pores.

Fig. 11. GC-MS chromatograms of occluded organic species in spent hierarchical and parent SAPO-34.

4. Conclusions

Hierarchical SAPO-34 was prepared by hydrothermal synthesis followed by a nitric acid or oxalic acid post-treatment. Their catalytic performance of hierarchical SAPO-34 was investigated in MTO reaction. The SAPO-34 treated with nitric acid or oxalic acid exhibited butterfly-shaped pores on four side faces and the pores comprised micropores, mesopores (40–50 nm) and macropores (62–500 nm). The number of acid sites was also optimized after the nitric acid and oxalic acid treatment. The hierarchical SAPO-34 treated with nitric acid or oxalic acid show 100% methanol conversion and higher selectivity for light olefins (92%–94%). The synergistic effect of the hierarchical pores and acid sites helped the single-run lifetime of hierarchical SAPO-34 to increase sharply from 210 to 360 and 390 min, and ethylene selectivity changed to be between 37.4% and 51.5%. The hierarchical structure also increased the coke capacity and the ratio of smaller coke molecules, which also contributed to the longer lifetime. However, we did not get hierarchical SAPO-34 by treating SAPO-34 with butanedioic acid, and its lifetime was only 100 min. This work demonstrated a simple and efficient route to prepare hierarchical SAPO-34 with appropriate acid sites, which may be extended to make other hierarchical zeolites.

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Graphical Abstract

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Enhanced MTO performance over acid treated hierarchical SAPO-34

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Hierarchical SAPO-34 crystals with butterfly-shaped faces were synthesized by acid etching, which increased the catalyst lifetime and light olefin yield in the MTO reaction.

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酸处理可控制备多级孔 SAPO-34 及其甲醇制烯烃性能

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摘要: 甲醇制低碳烯烃(MTO)技术既可实施石油替代路线, 又能解决低碳烯烃不足的问题, 因而具有重要意义. 在 MTO 技术中, SAPO-34 分子筛因其高水热稳定性、适宜的微孔结构和酸强度而展现了优异的 MTO 性能. 但 SAPO-34 分子筛孔道较小, 易形成积碳物种而覆盖活性中心, 导致分子筛催化剂失活快, 反应流程复杂. 延长 SAPO-34 催化剂的单程寿命可减少其再生频率, 降低能耗并节约成本. 在微孔 SAPO-34 分子筛中引入介孔或大孔孔道来组成多级孔道结构, 可大大促进反应物及产物分子在孔道内的扩散, 从而降低积碳速率, 延长催化剂寿命. 目前, 文献中主要采用直接合成路线制备多级孔 SAPO-34 分子筛, 该过程所用的二级模板剂价格较贵, 且合成步骤复杂. 而采用后处理方法, 即先合成 SAPO-34 分子筛母体, 再进行酸碱后处理来制备多级孔 SAPO-34 分子筛是非常有前景的技术路线.

本文首先通过水热合成法制备了立方晶形 SAPO-34 分子筛, 再采用不同种类的酸溶液(硝酸、草酸及丁二酸)对其进行后处理, 制备了具有良好相对结晶度的多级孔 SAPO-34, 考察了酸种类对所得多级孔 SAPO-34 结构及其 MTO 性能的影响. 研究发现, 经硝酸和草酸处理后的样品在特定晶面上出现了蝴蝶状孔道, 形成了由微孔、介孔(40–50 nm)和大孔(400–500 nm)组成的多级孔分子筛; 其比表面积高达 876 m²/g, 孔容为 0.36 cm³/g, 该多级孔道大幅改善了 MTO 过程中的分子扩散性能. 酸后处理过程并没有影响分子筛的化学环境及酸中心强度, 却降低了分子筛的强酸中心数量并增加了弱酸中心数量. 在多级孔结构及酸中心的协同作用下, 其 MTO 性能得到了大幅度提升: 经硝酸和草酸处理后所得多级孔 SAPO-34, 其 MTO 寿命(400 °C, 1 atm, 甲醇空速 1 h⁻¹)分别由母体的 210 min 增至 360 和 390 min, 低碳烯烃的总选择性由母体的 90% 提高至 92%–94%, 并可根据孔道大小调整产物组成, 使乙烯选择性在 37.4%–51.5% 内调变. 对比发现, MTO 过程中多级孔 SAPO-34 上的积碳量由母体的 15% 提高到 18%, 但积碳速率却由 0.071 降至 0.046 g/min. 失活多级孔 SAPO-34 内的积碳物种主要为较大的分子, 其中茈及茈取代物的含量高达 73%, 而母体 SAPO-34 中茈及茈取代物的含量则降低至 49%. 这是因为多级孔 SAPO-34 内部更大的孔道空间可容纳更多的大分子积碳物种所致. 丁二酸处理后的样品未产生多级孔道, 却使部分微孔受损且增加了强酸中心数量, 导致其更易失活, MTO 寿命也降至 100 min. 选择合适种类的酸溶液进行后处理可控制备多级孔 SAPO-34, 可大幅改善其 MTO 性能.

关键词: 酸处理; 多级孔; SAPO-34; 甲醇制烯烃; 单程寿命

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