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Confining Pore-mouth: an Efficient Way to Increase the Selectivity to Ethylene in the MTO Reaction

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Abstract: The chemical liquid deposition modification can decorate the pore aperture size by external surface deposition, which is a very efficient way to further improve the shape-selective performance of zeolites. Here, SAPO-34 zeolite was modified with silica by chemical liquid deposition, and then was applied in MTO reaction. It was found the Brønsted acid of SiO₂-modified SAPO-34 zeolite increased, mainly due to the transformation from Al-OH to Si-OH-Al, which can promote the selectivity to light olefins in MTO reaction. After the chemical liquid deposition, the silica located on the external surface of SAPO-34 zeolite, reduces the apparent diffusion coefficient of propylene, which will restrain the formation and diffusion of propylene. So the selectivity to ethylene and the ratio of ethylene to propylene were significantly increased over the SiO₂-modified SAPO-34 in the MTO reaction. Furthermore, the increase of the reactive sites can prolong the lifetime of catalyst effectively.

Introduction

The shape selective properties of zeolite show greatest interest for catalysis, which is the greatest advantage compared with other inorganic catalysts.^[1] Adjusting the aperture is a very efficient way to alter the diffusion restriction of zeolites, then further improves their performance in catalysis and separation. The pore size of zeolites and their adsorptive properties can be tailored by changing the crystal structure and modifying the external surface.^[2] There are two ways to modify the external surface of zeolite: chemical vapor deposition (CVD)^[3] and chemical liquid deposition (CLD)^[2c]. The separation performance of siliceous CHA membranes was improved after CVD process.^[4] Li et al. found the catalyst shown high catalytic selectivity after SiO₂-CLD modification with polysiloxane.^[5] Yang et al. using CLD to modify 4A zeolite as a size selective sorbent at 0.01 nm resolution for gas separation.^[2f] Wei et al. increased the para-xylene selectivity from the usual 23-24% to 89.6% by modifying ZSM-5 based catalyst with SiO₂.^[6] The external surface modification is a very efficient way to improve the performance of zeolites, no matter as catalysts or sorbents, so this method for modifying the zeolites or other catalysts may be never outdated.

Light olefins (ethylene and propylene) are basic chemicals in the petrochemical industry. A mass of light olefins are yielded by

thermal cracking of naphtha.^[7] Due to the limited reserve of petroleum and increasing demand for light olefins, more and more attention have been focused on methanol-to-olefin (MTO) conversion processes, the reactant of which can be produced from coal, biomass and natural gas.^[7-8] SAPO-34 exhibits excellent catalytic performance in the MTO reaction, due to its 8ring pore opening, medium to strong acidity and good thermal stability.^[9] For economical value, ethylene is more valuable than propylene. The selectivity of ethylene and ratio of ethylene to propylene increase with time on stream, due to the increasing diffusion barriers introduced by coke formation, inspired by which, some strategies have been proposed to achieve higher selectivity to ethylene, such as increasing the diffusion restriction by the cation exchange,[9c,10] changing the experimental conditions (temperature, pressure or the weight hourly space velocity). To the best of our knowledge, the CLD modification has not been used in the SAPO zeolites to improve their catalytic activity.

Here, we used CLD to reduce the effective pore mouth size on the outer surface of SAPO-34 zeolites. Polydimethylsiloxane (PDMS, CH₃-(Si(CH₃)₂-O)_n-CH₃) is the SiO₂-CLD modifier, which firstly covers on the external surface of SAPO-34 by physical and chemical adsorption, then transforms to silica after calcined.^[5] The silica modified the acidity and pore mouth of SAPO-34 zeolite, which increased the selectivity to ethylene and introduced extra diffusion limitation for bulky hydrocarbons in the MTO reaction.^[11]

Results and Discussion

The powder XRD patterns show these two samples have CHA framework topology, without other phases. These diffraction peaks at 2θ = 9.5, 12.9, 16.1, 20.6, 26.2 and 30.8° are indexed to (101), (110), (021), (121), (220) and (401) planes of SAPO-34, respectively;^[12] The crystallinity of M-SAPO-34 was maintained well, indicating the integrity of the crystallinity after the CLD process.

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Figure 1. Powder XRD patterns of P-SAPO-34 and M-SAPO-34.

The P-SAPO-34 crystals show cubic morphologies with the diameter of 0.5-2 μ m (Fig. 2a). From these SEM images, there is no obvious difference between samples before and after CLD process (Figure 2a and 2b). The same result can also be obtained from these TEM images (Figure 2c and 2d). No amorphous silica particle can be found from the TEM image of M-SAPO-34 (Figure 2d).



Figure 2. SEM and TEM images of P-SAPO-34 (a, c) and M-SAPO-34 (b, d).

Infrared spectroscopy (IR) is used to identify the properties of zeolite hydroxyls of P-SAPO-34 and M-SAPO-34 (Figure 3). The peak absorbing at 1640 cm⁻¹ is ascribed to the bending mode of water adsorbed in the CHA cages.^[13] The peak at about 1100 cm⁻¹ ascribed to the O-P-O antisymmetric stretching vibration, and the characteristic peaks of the SAPO-34 appeared at 630, 580, 530, 480 cm⁻¹, which belong to the vibration of D-6 rings, T-O (T = P, AI, Si) bend.^[14] The differences of the IR spectra of these two samples are mainly reflected in the intensity of the peaks, which

shows the CLD process has negligible impact on the crystallinity of SAPO-34 zeolite.



Figure 3. IR spectra of P-SAPO-34 and M-SAPO-34.

Table 1. Textual properties of P-SAPO-34 and M-SAPO-34

Sample	S _{BET} (m²/g)ª	S _{micro} (m²/g)	S _{ext} (m²/g)	V _{total} (cm ³ /g) ^b	V _{micro} (cm ³ /g) ^c			
P-SAPO-34	633.9	630.5	3.4	0.25	0.23			
M-SAPO-34	610.7	607.9	2.8	0.24	0.22			

^eBET surface area calculated from the adsorption data obtained at *P/P*₀ between 0.05 and 0.25. ^bTotal pore volume via the single point method. ^cMicropore volume obtained through t-plot method.

The N₂ adsorption-desorption isotherms of P-SAPO-34 and M-SAPO-34 are shown in Figure S1, and the corresponding textual properties are list in Table 1. It can be found that micropore specific surface area (S_{micro}) and micropore volume (V_{micro}) of M-SAPO-34 are slightly smaller than that of P-SAPO-34, due to that bits of small cracking fragments of PDMS deposited in the micropore.^[5]

 Table 2. The composition and element distribution in P-SAPO-34 and M-SAPO-34 zeolites.

Sample	Bulk ^a	Surface⁵	Rsi ^c
P-SAPO-34	Si _{0.061} Al _{0.536} P _{0.403}	Si _{0.079} Al _{0.472} P _{0.449}	1.295
M-SAPO-34	Si _{0.082} Al _{0.532} P _{0.386}	Si0.335Al0.355P0.310	4.085

^aDetermined by XRF. ^bDetermined by XPS. ^cSurface Si enrichment index defined as [Si/(Si+P+AI)] surface/[Si/(Si+P+AI)]bulk.

The ratio of Si atom in P-SAPO-34 is very low (6.1 mol %, Table 2), and the SiO₂-CLD modifier deposited on the surface of SAPO-34 by generating new Si-O-Si bonding. So there is a small quantity of SiO₂ deposited on the surface of M-SAPO-34, leading to that it is difficult to observe the silica layer by SEM and TEM. To clarify that bits of silica was deposited on the surface of M-SAPO-34, X-ray fluorescence (XRF) and X-ray photoelectron spectroscopy (XPS) measurements were carried out (Table 2). The results obtained by XRF are bulk-content based, while those by XPS are surface-content based, \leq 10 layers of atoms in depth of surface. After modified with PDMS, the Si-content of the bulk

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slightly increased, while the Si-content on the edge of crystal significantly increased, which resulted in the R_{Si} of M-SAPO-34 is 3.2 times of P-SAPO-34. SEM coupled with energy dispersive X-ray spectroscopy (EDX) was used to prove that the silica is evenly distributed over the surface of M-SAPO-34 (Figure S2).



Figure 4. (a) NH₃-TPD curves of P-SAPO-34 and M-SAPO-34; (b) Fitted FTIR spectra of CD_3CN adsorption over calcined P-SAPO-34 and M-SAPO-34.

NH₃-TPD was used to measure the acidity of P-SAPO-34 and M-SAPO-34 (Figure 4a). The acid strength and content are represented by desorption temperature and peak area, respectively. Both samples show two desorption peaks. The low-temperature peak is ascribed to the ammonia adsorbed on the weak acid sites originated from the structural defect T-OH groups (T=P, AI, Si). The high-temperature desorption peak is attributed to the ammonia adsorbed on Brønsted acid sites in the form of bridging hydroxyl groups.^[9c,15] After CLD process, the strength and content of weak acid decreased, meanwhile the strength stay the same and the content increased for the strong acid.

The CD₃CN-FTIR spectra (Figure 4b) shows that there is no shift in peak positions ascribed to Lewis acid and Brønsted acid sites after CLD process. From the fitting results, it can be found that there are four kinds of Brønsted acid sites: Si-OH-Al bridging hydroxyl groups (2294 cm⁻¹), Al-OH (2287 cm⁻¹), P-OH (2283 cm⁻¹) and Si-OH (2273 cm⁻¹),^[16] and the acid strength of Al-OH, P-OH and Si-OH is obviously weaker than that of Si-OH-Al bridging hydroxyl groups. According to the quantified results (Table S1), the acid strength of P-SAPO-34 is equal to M-SAPO-34, but the acid content of Brønsted acid sites in P-SAPO-34 was obviously lower than M-SAPO-34, especially for Si-OH-AI bridging hydroxyl groups. The acid content of AI-OH is decreased. The increase of the Si-OH-AI bridging hydroxyl group can be attributed to the transformation from AI-OH to Si-OH-AI with the small cracking fragments of PDMS during the CLD process. The decrease of the structural defect AI-OH groups leads to less ammonia adsorb on the weak acid sites, namely the smaller peak area of the lowtemperature peak in NH₃-TPD curve, which is corresponding to the result of NH₃-TPD.



Figure 5. In-phase (\blacksquare , \checkmark) and out-of-phase (\Box , \bigtriangledown) characteristic function curves of ethane in P-SAPO-34 and M-SAPO-34 by the single diffusion process with surface resistance model.

To investigate the influence of CLD on the pore size of micropores of M-SAPO-34, frequency-response (FR) technique was employed. The pore size of eight-membered ring in SAPO-34 zeolite is about 0.38 nm, which is comparative with the kinetic diameter of the ethane molecule (0.44 nm).^[17] Therefore, the mass transfer of ethane molecular through micropores of SAPO-34 zeolite is restricted by the pore mouth. The FR spectra of ethane in P-SAPO-34 and M-SAPO-34 zeolite at 273 K, 133 Pa was shown in Figure 5. The out-of-phase characteristic function of ethane in P-SAPO-34 gives a single peak response located at 2Hz, which can be ascribed to a pure single diffusion process of ethane molecular through the pore mouth of SAPO-34 zeolite. Comparatively, the out-of-phase characteristic function of M-SAPO-34 moved to the lower frequency zone, with the value lower than 0.2 Hz. The fitted diffusion data (Table 3, calculated by the equation in supporting information) indicated that the diffusion rate was declined obviously which can be ascribed to the pore mouth contract by the deposition of silica. Moreover, the intersection of the in-phase with the out-of-phase functions can be found in the FR spectra of both SAPO-34 zeolite samples, which indicates the transport resistance for the "skin" effect in the system.[18]



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Table 3. The diffusion properties of P-SAPO-34 and M-SAPO-34.								
Sample	ξ(a.u.)	ka	D (m ² /s)					
P-SAPO-34	0.8	0.14	4.37 X 10 ⁻¹⁶					
M-SAPO-34	15	0.19	3.17 X 10 ⁻¹⁷					



Figure 6. The selectivity to light olefins, ethylene and propylene of methanol conversion over P-SAPO-34 and M-SAPO-34. Experimental conditions: WHSV = 2.4 h^{-1} , T = 733 K, catalyst weight = 2 g.

The MTO reaction was conducted in a fixed bed reactor over P-SAPO-34 and M-SAPO-34 at 733K with WHSV of 2.4 h⁻¹. In the whole catalytic process, the conversion of methanol is higher than 99.9% over these two catalysts. The selectivity to light olefins. ethylene and propylene versus time-on-stream (TOS) are shown in Figure 6, and the detailed MTO results are summarized in Table S2. The selectivity of ethylene over M-SAPO-34 catalyst is obviously higher than that over P-SAPO-34 after methanol reaction for 30 min. The highest selectivity of ethylene attained over M-SAPO-34 is 55.5%, which is 3.4% higher than that over P-SAPO-34. Likewise, higher ratio of ethylene to propylene is obtained over the M-SAPO-34 catalysts (Table S2). With the predominant generation of ethylene, the selectivity to light olefins increase, but the selectivity to $C_3^=$, C_4 , and C_{5+} decreases. Not only the selectivity to light olefins, but also the catalyst lifetime is obviously increased over SiO₂-modified SAPO-34 catalyst.

The difference in catalytic activity between these two samples is mainly due to the increasing of the apparent diffusion coefficient by CLD modification. The results of FR technique indicate the silica located on the external surface of M-SAPO-34 reduces the

apparent diffusion coefficient for ethane, the kinetic diameter of which is obvious smaller than propylene, then the diffusion limitation for propylene is more remarkable. So the selectivity of propylene attained over M-SAPO-34 obviously decreases. For further revealing the effect of the diffusion restriction caused by modified silicon, the coke amount over P-SAPO-34 and M-SAPO-34 catalysts after methanol reaction for 30 min (P-SAPO-34-30min and M-SAPO-34-30min) were analyzed by TGA. The weight loss below 225 °C corresponds to the volatilization of adsorbed water, while the weight loss between 225 and 1000 °C corresponds to trapped organic species (Figure S3). The coke amount of M-SAPO-34-30min (2.6%) is obviously less than that of P-SAPO-34-30min (3.4%). Liu et al found that increasing the coke amount and introducing extra diffusion hindrance for the generated products resulted in the enhanced selectivity to ethylene in the MTO reaction.[9c,19] M-SAPO-34-30min with less coke amount shows higher selectivity of ethylene and higher ratio of ethylene to propylene compared with P-SAPO-34-30min, which is attributed to the restricted pore mouth of micropore of M-SAPO-34 by the deposition of silica.

Another reason is the changes of the acidity of M-SAPO-34. According to the hydrocarbon pool mechanism,^[20,11c] ethylene is predominantly formed via the polymethylbenzene cycle, whereas propylene is mainly produced via the alkene cycles.[11d,21] The weaker acid sites are favorable for enhancing the contribution of the alkene cycle to form more propylene.^[11d] The strength and content of weak acid of P-SAPO-34 is higher than that of M-SAPO-34, so the selectivity to propylene of P-SAPO-34 is higher than that of M-SAPO-34.[22] The increase of the acid content of strong Brønsted acid of SAPO-34 is mainly due to the increase of Si-OH-AI. The FT-IR spectra of pivalonitrile adsorption on zeolite was used to detect the acid sites on the external surface of P-SAPO-34 and M-SAPO-34 (Figure S4). The kinetic diameter of pivalonitrile is about 0.6 nm, which is much larger than the poremouth of SAPO-34 (0.38 nm). The pivalonitrile molecule could only adsorb on the surface of SAPO-34. No band of Brønsted acid can be found in the FT-IR spectras of pivalonitrile adsorption on P-SAPO-34 and M-SAPO-34 zeolite, which means no Brønsted acid on the external surface of M-SAPO-34. Bits of small cracking fragments of PDMS deposited in the micropore as mention above, so the transformation from AI-OH to Si-OH-AI might mainly take place in the cage of SAPO-34. The number of reactive sites increases, which promotes the selectivity to light olefins in MTO. The ratio of Brønsted to Lewis acid sites is increased after CLD process (Table S1), which is also beneficial to improve the selectivity of ethylene.^[22,24] Combined the increase of the diffusion hindrance of propylene and the changes of the acidity of SAPO-34 after CLD process, the selectivity to ethylene and ratio of ethylene to propylene are enhanced over M-SAPO-34 in the MTO reaction.

For SAPO-34, the typical density of acid sites is correspond to one site per cavity.^[11c] The number of isolated reactive sites increases and the strength of the Brønsted acid keeps unchanged, so the hydrogen transfer pathway, leading to alkanes, aromatics and coke in MTO,^[11c,25] is deferred over M-SAPO-34, namely enhancing the catalyst lifetime of M-SAPO-34.

Conclusion

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In conclusion, the MTO reaction using SiO₂ modified SAPO-34 as the catalyst showed enhanced ethylene selectivity and higher ratio of ethylene to propylene than conventional SAPO-34. SiO₂-CLD modification does not destroy the framework structure of SAPO-34, which mainly occurs on the external surface of SAPO-34. The Si-OH-AI bridging hydroxyl group increased after SiO₂-CLD modification, originating from the transformation from AI-OH to Si-OH-AI. The increase of the content of Brønsted acid of M-SAPO-34 promotes the selectivity to light olefins in MTO. The decrease of weak acid of zeolite is unfavorable for the alkene cycle to forming propylene. The confined micropore introduces extra diffusion limitation for propylene. So the selectivity to propylene of M-SAPO-34 is lower than that of P-SAPO-34. Combined confining aperture and adjusted acidity, high ratio of ethylene to propylene is obtained. The increase of the reactive sites restrain the formation of alkanes, aromatics and coke, then the lifetime of catalyst enhances. Therefore, SiO₂-CLD modification of SAPO-34 is still a good strategy to alter the diffusion hindrance and product selectivity in MTO reaction, which shows high potential to modulate products for the SAPO-34 catalysts in the industrial MTO process.

Experimental Section

Materials

Orthophosphoric acid (H₃PO₄, 85 wt%), triethylamine (TEA, 99 wt%), tetraethylammonium hydroxide (TEAOH, 25 wt% in H₂O), cyclohexane (99 wt%), polydimethylsiloxane (99 wt%), colloidal silica (SiO₂, 40 wt%) and pseudoboehmite (Al₂O₃, 70 wt%) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used as received without further purification.

Synthesis of SAPO-34

A typical SAPO-34 was synthesized based on the hydrothermal method. H₃PO₄, pseudoboehmite and silica sol were added to the aqueous solution of template (TEA and TEAOH) to from the initial gel with the molar compositions of 1.0 P_2O_5 : 1.0 Al_2O_3 : 1.8TEA : 0.2TEAOH : 0.4SiO₂ : 60H₂O. Then the obtained gel was transferred into a stainless steel autoclave and heated rotationally (15 rpm/min) at 200 °C for 24h under autogenous pressure. The products were recovered by filtration, washed with deionized water and dried in air. The template was removed by calcination at 823 K for 6 h in air. The sample is referred to as P-SAPO-34.

CLD Modification of SAPO-34 Zeolite

Typically, PDMS (3 g) was dispersed in cyclohexane (65 mL). Then SAPO-34 zeolite powder (10 g) was introduced into the mixture of PDMS and cyclohexane. The CLD modification process was carried out for 4 h under stirring at ambient temperature. The mixture was dried at 373 K for 8h, then was calcined at 823 K for 6 h in air. The sample is referred to as M-SAPO-34.

Characterization

XRD patterns were obtained using Bruker D8 Advance diffractometer, with an accelerated voltage of 40 kV and detector current of 200 mA. Cu-Ka radiation (λ = 51.540589 Å) was used for a continuous scanning with the step-size of 0.02° over a 2 θ range of 5-50°. X-ray fluorescence spectroscopy was obtained on Bruker S4 Pioneer. N₂ adsorption and desorption isotherms were collected on Micromeritics TriStar3000 at 75 K.

Prior to the measurements, the sample was degassed at 350 °C until a stable vacuum of about 0.67 Pa was reached, FE-SEM (Field Emission Scanning Electron Microscopy) analysis was performed on a Hitachi S4800 electron microscope with an accelerating voltage of 2.0 kV. HRTEM was performed using JEOL JEM-2100LaB6 operating at 200 kV (Cs = 1.0 mm, point resolution of 2.3 Å). Images were recorded with a Keen View CCD camera (resolution of 1376 pixels × 1032 pixels, pixel size of 6.45 µm \times 6.45 $\mu m)$ at 50000-120000× magnification under low-dose conditions. IR were obtained on Bruker IFS88, and Samples were dried at 300 °C before testing and mixed with KBr powder and pressed to produce a transparent disk. Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed on a chemisorption analyzer (FINETEC FINSORB-3010). In situ CD₃CN and pivalonitrile spectra were recorded using a FTIR spectrometer (Bruker Vertex 70V) equipped with a stainless steel high vacuum transmission infrared cell. After dehydrated at 350-400 °C in vacuum (<2.0 \times 10⁻⁸ mbar) for 2.5 h, the samples were cooled down to room temperature, and then the background spectrum was collected. Subsequently, CD₃CN or pivalonitrile was introduced into the cell, remaining for 1 h. Finally, CD₃CN or pivalonitrile was evacuated and the corresponding spectra were collected. The frequency-response (FR) spectra, characteristic functions against frequency, were derived from the equivalent fundamental sine-wave perturbation by a Fourier transformation of the volume and pressure square-wave forms. The pressure change response to the volume perturbations was measured by a high-accuracy differential Baratron pressure transducer (MKS 698A11TRC). The experimental data was fitted by using the Yasuda sorption model or the single pure diffusion process model.

Catalytic tests

The reaction products were analyzed using an on-line gas chromatograph (Agilent GC 7890N), equipped with a flame ionization detector (FID) and Plot-Q column (Agilent J&W GC Columns, HP-PLOT/Q 19091-Q04, 30 m × 320 μ m × 10 μ m). The conversion and selectivity were calculated on CH₂ basis and dimethyl ether (DME) was considered as reactant in the calculation.

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- [1] J. Zhou, Z. C. Liu, Y. D. Wang, D. J. Kong, Z. K. Xie, Front. Chem. Sci. Eng. 2018, 12, 103-112.
- [2] a) R. E. Morris, J. Čejka, *Nat. Chem.* 2015, 7, 381-388; b) J. Y. Li, A. Corma, J. H. Yu, *Chem. Soc. Rev.* 2015, 44, 7112-7127; c) Y. H. Yue, Y. Tang, Y. Liu, Z. Gao, *Ind. Eng. Chem. Res.* 1996, 35, 430-433; d) Y. W. Zhao, B. X. Shen, H. Sun, *Ind. Eng. Chem. Res.* 2016, 55, 6475-6480; e) D. K. J. A. Wanigarathna, B. Liu, J. J. Gao, *AlChE J.* 2018, 64, 640-648; f) Y. R. Wang, R. T. Yang, *ACS Sustainable Chem. Eng.* 2019, 7, 3301-3308.
- [3] M. Niwa, Y. Murakami, *Nippon Kagaku Kaishi* **1989**, 410-419.
- [4] E. Kim, T. Lee, H. Kim, W. J. Jung, D. Han, H. Baik, N. Choi, J. Choi, Environ. Sci. Technol. 2014, 48, 14828-14836.
- [5] Z. R. Zhu, Z. K. Xie, Q. L. Chen, D. J. Kong, W. Li, W. M. Yang, C. Li, *Microporous Mesoporous Mater.* 2007, 101, 169-175.
- [6] J. G. Zhang, W. Z. Qian, C. Y. Kong, F. Wei, ACS Catal. 2015, 5, 2982-2988.

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- [7] J. Lefevere, S. Mullens, V. Meynen, J. Noyen, Chem. Pap. 2014, 68, 1143-1153.
- [8] a) C. D. Chang, A. J. Silvestri, *J. Catal.* **1977**, 47, 249-259; b) T. Ren, M. K. Patel, K. Blok, *Energy* **2008**, 33, 817-833.
- [9] a) P. Tian, Y. X. Wei, M. Ye, Z. M. Liu, ACS Catal. 2015, 5, 1922-1938; b)
 Q. M. Sun, Z. K. Xie, J. H. Yu, Natl. Sci. Rev. 2017, 5, 542-558; c) J. W.
 Zhong, J. F. Han, Y. X. Wei, S. T. Xu, Y. L. He, Y. J. Zheng, M. Ye, X. W.
 Guo, C. S. Song, Z. M. Liu, Chem. Commun. 2018, 54, 3146-3149.
- [10] J. W. Zhong, J. F. Han, Y. X. Wei, S. T. Xu, T. T. Sun, X. W. Guo, C. S. Song, Z. M. Liu, J. Energy Chem. 2018, 32, 174-181.
- [11] a) U. Olsbye, S. Svelle, K. P. Lillerud, Z. H. Wei, Y. Y. Chen, J. F. Li, J. G. Wang, W. B. Fan, *Chem. Soc. Rev.* 2015, 44, 7155-7176; b) S. T. Xu, Y. C. Zhi, J. F. Han, W. N. Zhang, X. Q. Wu, T. T. Sun, Y. X. Wei, Z. M. Liu, Advances in Catalysis, *Vol.* 61 (Eds.: C. Song), Academic Press, 2017, pp. 37-122; c) U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T. V. W. Janssens, F. Joensen, S. Bordiga, K. P. Lillerud, *Angew. Chem., Int. Ed.* 2012, 51, 5810-5831; d) S. Wang, Y. Y. Chen, Z. H. Wei, Z. F. Qin, H. Ma, M. Dong, J. F. Li, W. B. Fan, J. G. Wang, *J. Phys. Chem. C* 2015, 119, 28482-28498.
- [12] S. Aghamohammadi, M. Haghighi, M. Charghand, *Mater. Res. Bull.* 2014, 50, 462-475.
- [13] L. Marchese, A. Frache, E. Gianotti, G. Martra, M. Causà, S. Coluccia, *Microporous Mesoporous Mater.* **1999**, 30, 145-153.
- [14] a) S. Ashtekar, S. V. V. Chilukuri, D. K. Chakrabarty, *Chem. Inf.* **1994**, 25;
 b) J. Tan, Z. M. Liu, X. H. Bao, X. C. Liu, X. W. Han, C. Q. He, R. S. Zhai, *Microporous Mesoporous Mater.* **2002**, 53, 97-108.
- [15] M. Yang, B. Li, M. B. Gao, S. F. Lin, Y. Wang, S. T. Xu, X. B. Zhao, P. Guo, Y. X. Wei, M. Ye, P. Tian, Z. M. Liu, ACS Catal. 2020, 10, 3741-3749.
- [16] W. Daniell, N. Y. Topsøe, H. Knözinger, *Langmuir* **2001**, 17, 6233-6239.
- [17] J. R. Li, R. J. Kuppler, H. C. Zhou, Chem. Soc. Rev. 2009, 38, 1477-1504.
- [18] L. J. Song, L. V. C. Rees, *Microporous Mesoporous Mater.* 2000, 41, 193-200.
- [19] J. W. Zhong, J. F. Han, Y. X. Wei, S. T. Xu, T. T. Sun, X. W. Guo, C. S. Song, Z. M. Liu, *Chin. J. Catal.* **2018**, 39, 1821-1831.
- [20] a) I. M. Dahl, S. Kolboe, *Catal. Lett.* **1993**, 20, 329-336; b) I. M. Dahl, S. Kolboe, *J. Catal.* **1994**, 149, 458-464; c) I. M. Dahl, S. Kolboe, *J. Catal.* **1996**, 161, 304-309; d) W. G. Song, J. F. Haw, J. B. Nicholas, C. S. Heneghan, *J. Am. Chem. Soc.* **2000**, 122, 10726-10727.
- [21] a) S. Svelle, U. Olsbye, F. Joensen, M. Bjorgen, *J. Phys. Chem. C* 2007, 111, 17981-17984; b) M. Bjørgen, S. Svelle, F. Joensen, J. Nerlov, S. Kolboe, F. Bonino, L. Palumbo, S. Bordiga, U. Olsbye, *J. Catal.* 2007, 249, 195-207; c) R. M. Dessau, *J. Catal.* 1986, 99, 111-116.
- [22] I. Yarulina, K. De Wispelaere, S. Bailleul, J. Goetze, M. Radersma, E. Abou-Hamad, I. Vollmer, M. Goesten, B. Mezari, E. J. M. Hensen, J. S. Martínez-Espín, M. Morten, S. Mitchell, J. Perez-Ramirez, U. Olsbye, B. M. Weckhuysen, V. V. Speybroeck, F. Kapteijn, J. Gascon, *Nat. Chem.* **2018**, *10*, 804-812.
- [23] a) M. Cortés-Reyes, E. Finocchio, C. Herrera, M. A. Larrubia, L. J. Alemany, G. Busca, *Microporous Mesoporous Mater.* 2017, 241, 258-265; b) M. Bevilacqua, G. Busca, *Catal. Commun.* 2002, 3, 497-502.
- [24] J. Valecillos, E. Epelde, J. Albo, A. Aguayo, J. Bilbao, P. Castaño, Catal. Today 2019, 348.
- [25] a) S. Ilias, A. Bhan, J. Catal. 2012, 290, 186-192; b) S. Ilias, A. Bhan, ACS Catal. 2013, 3, 18-31; c) S. Muller, Y. Liu, F. M. Kirchberger, M. Tonigold, M. Sanchezsanchez, J. A. Lercher, J. Am. Chem. Soc. 2016, 138, 15994-16003.

FULL PAPER

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Using amphipathic molecules as co-structure-directing agent, a tri-level hierarchically porous SAPO-34 with flower-like morphology was synthesized. The co-structure-directing agent could promote the Si atoms incorporating into the AIPO₄ framework, change the morphology of particles and decrease the acidity of prepared SAPO-34 zeolite, leading to higher selectivity of C_2H_4 and C_3H_6 than conventional SAPO-34. The morphology and microstructure of samples vary with the carbon chain length of co-structure-directing agent.