Melting-assisted solvent-free synthesis of hierarchical SAPO-34 with enhanced methanol to olefins (MTO) performance†

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SAPO-34 zeolite with a butterfly patterned hierarchical pore system and high relative crystallinity was synthesized by a melting-assisted solvent-free route. Oxalic acid in the solid state was used as the etching agent through a facile thermal treatment of the parent SAPO-34. The resultant zeolite exhibited complete methanol conversion, high C2−C4+ selectivity (>91%) and a long lifetime in the MTO process.

Light olefins, especially ethylene and propylene, are key raw materials in the petrochemical industry, and their demand has increased significantly around the world in recent years. The silicoaluminophosphate SAPO-34 is currently the most effective MTO (methanol to olefins) catalyst because of its unique pore structure, moderate strength of acid sites, high hydrothermal stability and extraordinary activity.1−3 However, the micropores always suffer from limited diffusion and this results in fast coke deposition and short catalytic lifetime.4−6 To overcome this problem, hierarchical SAPO-34 comprising mesopores (2−50 nm) and/or macropores (>50 nm) besides the original micropores has attracted growing interest.7,8 It is reported that the introduction of mesopores or macropores into SAPO-34 zeolite crystals can enhance the MTO performance remarkably.9−11 It can not only reduce the coke formation rate, but also enlarge the coke capacity, thus enhancing the resistance to deactivation. Many related synthetic strategies, including bottom-up directed construction by soft or hard templates, and top-down post-synthesis by acid/base treatments, have been developed to produce hierarchical SAPO-34. The organosilane surfactant-directed synthesis of hierarchical SAPO-34 catalysts was reported by J. Yu et al.3 Gong et al.12 synthesized SAPO-34 with a special hollowed structure using gelatin as the precursor. A one-step hydrothermal synthesis method to prepare the hierarchically macroporous SAPO-34 via in situ growth-etching with the assistance of excess hydrogen fluoride was proposed.13 Currently, many efforts have been devoted to prepare hierarchical SAPO-34 by the top-down post-synthesis route. Qiao14 prepared hierarchical hollow SAPO-34 with a large external surface area and longer MTO lifetime via alkaline or acid etching, such as with tetraethyl ammonium hydroxide (TEAOH) and HCl. Liu et al. synthesized hierarchical SAPO-34 using TEAOH, and the single run lifetime for the MTO process of the resultant zeolite was prolonged from 320 min to 640 min.15 Chen et al. etched SAPO-34 zeolite with HF−NH4F solution, and hierarchical zeolites were obtained after ultrasonic treatment.16 In summary, hierarchical SAPO-34 zeolites formed through the post-synthesis route exhibited excellent MTO performance compared with the parent ones. However, acid or base aqueous solution was required during the post-treatment process, which produced a lot of waste water during the process. Meanwhile, the use of etching solutions also leads to low yields of hierarchical SAPO-34. In 2012, Xiao et al.17 firstly reported a solvent-free route for the synthesis of zeolites, and then Jin et al.18 prepared SAPO-34 in a similar solvent-free way. The success of the solvent-free route highlights the post-treatment route, but no hierarchical zeolites have been prepared through the solvent-free route during the post-treatment process until now.

Herein, for the first time, we present a solvent-free process to synthesize SAPO-34 with butterfly patterned hierarchical pores through a melting-assisted post-synthesis route, and solid oxalic acid was used as the etching agent. The absence of water greatly reduces the environmental pollution and improves the yield of hierarchical SAPO-34. This is the first time that a green post-processing route has been developed to
tailor the pores and morphology of SAPO-34. Furthermore, the obtained zeolite with a hierarchical structure including micro-, meso- and macro-pores can enhance the mass transfer. As a result, a much longer lifetime than that of the conventional SAPO-34 catalyst in the methanol to olefins (MTO) reaction was observed and the excellent selectivity of C₂–C₄ is well preserved. This method provides a new insight into hierarchical zeolite synthesis which only involves a simple thermal treatment process without solvent, and thus has potential for the preparation of hierarchical zeolite catalysts at the industrial level.

The parent SAPO-34 was hydrothermally synthesized from the gel with a composition of 1.0Al₂O₃:0.44SiO₂:1.1P₂O₅:2.25TEA:35.0H₂O at 165 °C for 33 hours. The solid product was washed and dried, followed by calcination at 600 °C for 5 h. The resulting sample was named as SP34. A series of hierarchical zeolites were synthesized by simply mixing solid SP34 and solid oxalic acid in different ratios, then the mixtures were transferred to autoclaves and heated at 100 °C for 6 h. These obtained samples were denoted as SP34-x, where x represents the various mass ratios of oxalic acid to parent zeolite SP34.

The morphology of SP34 before and after treatment was studied by SEM. As shown in Fig. 1a and b, the parent SP34 crystals exhibit a typical cubic shape with smooth surfaces, and the particle size is about 2 to 3 μm. After the simple melting-assisted post treatment of parent SP34 with solid oxalic acid at 100 °C for 6 h, the surface of treated SP34 became rough (Fig. 1d and e). It was interesting that the surface of the product exhibited a clear X-type pore pattern (Fig. 1d), just like a butterfly, and the surface pore size is in the range of 60–100 nm. In detail, the “butterfly” pore patterns are on the four surfaces on the sides of the cube, and the scattered pores are on the top and bottom surfaces (Fig. 1e and S1†). To show it clearly, a corresponding schematic drawing of an SP34 crystal is shown in Fig. 1f. The formation of the butterfly-patterned SP34 can be related to the experimental steps, i.e., the synthesis of the cubic parent SP34 and the subsequent etching process. It was reported that at the early stage of synthesizing cubic SP34, the crystals grew preferentially along certain directions, resulting in the formation of a particular crystal morphology composed of eight pyramidal parts and voids around the centre, and then the voids were filled up by the crystal growth, eventually forming perfect cubes (illustrated in Fig. 1c).† However, the subsequently filled parts in the SP34 cubes were less stable in energy compared with the pyramidal parts, and thus were preferentially etched to form the hierarchical structure with the so-called butterfly pattern after treatment with solid oxalic acid.

Fig. 2 shows the X-ray diffraction (XRD) patterns, N₂ adsorption–desorption isotherms, mercury intrusion porosimetry (MIP) analyses, and solid-state ²⁷Al MAS NMR spectra of SP34 and SP34-5%. The XRD patterns of both samples (Fig. 2a) show peaks at 2θ = 9.6°, 16°, 20.5°, 26° and 31° belonging to the typical chabazite (CHA) framework structure of SAPO-34.† Compared with those of the parent SAPO-34, the intensities of the characteristic peaks of SP34-x samples show a slight decrease (Fig. S2†), but no impurity phase peaks are observed even with the increasing amount of solid oxalic acid, indicating that pure SAPO-34 crystals were well preserved.

Fig. 2b shows the N₂ adsorption/desorption isotherms of the prepared samples. Each sample shows a steep increase in the curves at a relative pressure of 10⁻⁶ < P/P₀ < 0.01 due to the presence of micropores. Both isotherms display the characteristics of type I isotherms, but a little uptake near the saturation pressure in the isotherms of treated SP34-x is observed (Fig. S3†), which indicates that mesopores or macropores are present in the structures of the prepared samples. The Brunauer–Emmett–Teller (BET) surface area, total pore volume and micropore volume of SP34-5% are 673 m³ g⁻¹, 0.27 cm³ g⁻¹ and 0.24 cm³ g⁻¹, respectively (Table S1†), comparable to those of the hierarchical SAPO-34 from hydrothermal synthesis. Furthermore, the macropore size distributions of both samples determined by MIP analysis are shown in Fig. 2c, where two different sizes of macropore exist in the SP34-5% sample besides the micro- and mesopores. The peaks at 300–400 nm of both the...
conventional SAPO-34 and SP34-5% samples are attributed to the void spaces between particles. Besides, there is an additional peak at 1000 nm for the SP34-5% sample due to the solid oxalic acid etching treatment, indicating that new macropores are formed. Thus, the XRD, BET and PSD analyses together with SEM observation proved that a hierarchical SAPO-34 zeolite with micro-, meso-, and macro-pores was successfully prepared through the melting-assisted solvent-free method. The solid-state MAS NMR spectra of the conventional SP34 and SP34-5% samples are shown in Fig. 2d. The \(^{27}\text{Al}\) MAS NMR signals at 38 to 43 ppm are assigned to a tetrahedrally coordinated framework of aluminium atoms. The presence of an \(^{27}\text{Al}\) signal at a \(\delta\) of \(\sim\)10 ppm for SP34-5% suggests that the tetrahedrally coordinated framework of aluminium atoms coordinates further with two water molecules, which indicates that some Al species were moved from framework to extra-framework positions.\(^{23}\) Meanwhile, the signals of the octahedrally coordinated aluminium atoms became stronger, indicating that the oxalic acid treatment induces dealumination of the silicoaluminophosphate frameworks.

The composition of the samples before and after the treatment was determined by X-ray fluorescence (XRF) analysis; the ratio of Si:Al:P for SP-34 is 6.7:50.2:43.1, while the ratio of Si:Al:P for SP34-5% is 6.6:49.6:43.8, confirming that some of the Al atoms were removed again. Fig. S4b† shows the \(^{29}\text{Si}\) MAS NMR spectra of SP34 and SP34-x samples, and the signals at 90 ppm are assigned to the coordination state of Si(0Si4Al). In the \(^{31}\text{P}\) MAS NMR spectra (Fig. S4c†), the dominating signals at \(\sim\)30 to \(\sim\)26 ppm can be assigned to tetrahedrally coordinated phosphorus atoms bound to four aluminium atoms,\(^{24}\) and the signals at 2 ppm can be assigned to the six-coordinated phosphorus. The weaker shoulder signals at \(\sim\)15 ppm for the hierarchical SP34-x samples are attributed to phosphorus atoms coordinated to a number of water molecules. Fig. S5† shows the NH\(_3\)-TPD curves of SP34 before and after the melting-assisted treatment. All samples show two peaks around 190 and 410 °C, ascribed to NH\(_3\) desorption from the weak and strong acid sites, respectively.\(^{25}\) Compared with the curve of SP34, similar peak areas of strong acid sites were observed after the treatment, indicating that the density of strong acid sites is unchanged. However, the peak area for the weak acid sites for SP34-5% increases slightly after the treatment, which might improve the catalytic performance for the MTO reaction.\(^{26,27}\)

The crystallization process of SP34-5% was further investigated, and the corresponding \textit{in situ} XRD patterns as well as the \textit{in situ} FT-IR analysis are shown in Fig. 3. Fig. 3A displays the change of morphology of SP34 after being treated with 5% solid oxalic acid for different treatment times at 100 °C. Compared with the parent crystals, some macropores began to appear on the surface of the SP34 crystals after being treated for 60 min. With prolonging of the treatment time to 120 min, the pore pattern kept the butterfly-shape well and there was no obvious change in the strength or position of the diffraction peaks from the \textit{in situ} XRD results (Fig. 3B). After SP34 was treated for 180 min at 100 °C, the SEM image shows that hierarchical pores appeared much more obviously in all the crystals, and higher treatment temperature promoted the formation of hierarchical pores. \textit{In situ} XRD proved that the crystal structure of SP34 was preserved during the thermal treatment process from 5 min to 180 min. Various temperature effects were also investigated by \textit{in situ} XRD analysis as shown in Fig. S6.\(^{†}\) This shows that all the samples maintained the characteristic peaks of SP34, and thus this melting-assisted method didn’t destroy the crystal structure of the parent zeolite. Furthermore, \textit{in situ} FT-IR spectra were measured to track the change of the bonds, as shown in Fig. 3C. There are some changes in the wavenumber range of 2000–4000 cm\(^{-1}\). Four vibrations appeared at 3740, 3675, 3622 and 3591 cm\(^{-1}\); the former two peaks can be attributed to terminal Si–OH and P–OH from the surface defects, respectively.\(^{28}\) The other two peaks at 3622 and 3591 cm\(^{-1}\) are from the absorbance of the bridged hydroxyl of Si(OH)Al. These two kinds of bridged hydroxyl group are considered to be the active sites of the SAPO-34 catalyst.\(^{29}\) After the treatment, all the peaks remained but the vibrations at 3675, 3622 and 3591 cm\(^{-1}\) were strengthened, indicating that the treated samples were more hydrophilic, which may be related to their hierarchical pores. Based on the above analysis, the growth mechanism of hierarchical SP34-5% can be described by a schematic illustration as shown in Fig. 3D.

Fig. 3 (A) SEM images of the samples treated after (a) 0 min, (b) 60 min, (c) 120 min, and (d) 180 min, (B) \textit{in situ} XRD patterns, (C) \textit{in situ} FT-IR spectra, and (D) schematic illustration of the growth mechanism of SP34-5%.

Fig. 4 (a) Catalytic conversion of methanol and (b) GC-MS chromatograms of the organic species retained in spent SP34 and SP34-5% after the MTO reaction at 400 °C with a WHSV of 1 h\(^{-1}\) at atmospheric pressure.
Fig. 4a presents the catalytic performance of parent SP34 and SP34-5% catalysts in the MTO reaction as a function of time on stream (TOS) at 400 °C, with a WHSV of 1.0 h⁻¹ and at atmospheric pressure. Both catalysts exhibit complete methanol conversion (100%) up to 300 min. Notably, these two catalysts exhibit quite different catalyst lifetimes. The methanol conversion on SP34 starts to decrease at a TOS of around 315 min. However, SP34-5% exhibited a longer lifetime of 580 min, indicating that the solid acid treatment is efficient at improving the catalyst lifetime. Furthermore, the performances of the SP34-x samples treated with different amounts of oxalic acid were measured and are shown in Fig. S7.† With the help of the created hierarchical pore structures, the lifetime of the catalyst increases with the increase of solid oxalic acid up to 5%. In detail, the lifetimes of SP34-2%, SP34-3% and SP34-5% are 360, 420 and 580 min, respectively. However, the lifetime of the catalyst decreases to 540 min for SP34-10%, and is even down to 200 min for SP34-15%. These experimental results show that a suitable amount of solid oxalic acid for the thermal treatment of SP34 is 5%. In addition, the temperature effect on SP34-5% was investigated as shown in Fig. S8.† When the treatment temperature increased to 120 and 140 °C, the catalytic lifetimes of SP34-120 and SP34-140 decreased obviously to 420 and 300 min, respectively, due to excessive destruction of the zeolite framework. These results show that SP34-5% prepared by thermal treatment at 100 °C exhibits the longest catalyst lifetime. Fig. S7b and S8b† show the distribution of MTO products on SP34 treated with different amounts of oxalic acid and at different temperatures. As can be seen from Fig. S7b,† SP34 gave a selectivity to light olefins (C₂–C₄) of 90.2% with complete methanol conversion at a TOS = 120 min. Compared to the parent structure, SP34-5% exhibited a higher selectivity in 91.8%, and a slightly higher selectivity for propylene and butylene, which is in good agreement with the report that hierarchical zeolites are effective for enhancing the selectivity of propylene and butylene.30 Fig. S8b† shows that the selectivity to light olefins (C₂–C₄) of SP34-80 and SP34-100 is higher than that of the parent SP34, however, the selectivity of SP34-120 and SP34-140 is decreased to 85.3% and 87.0%, respectively, due to excessive destruction of the zeolite framework. Fig. S9† shows the TGA measurements of spent catalysts under flowing air. These curves exhibit two different weight loss steps. One can be attributed to adsorbed water and organics up to 300 °C. The other one between 300 °C and 700 °C is associated with the decomposition of the cokes. The coke formation rates on the spent catalysts were calculated based on TG analysis.31 The spent SP34-5% gave a coke formation rate of 0.28 mg h⁻¹ g⁻¹cat, which is half of that of the spent SP34 (0.49 mg h⁻¹ g⁻¹cat), as shown in Table S2.† The deposited coke species in spent catalysts were further analysed by GC-MS. Fig. 4b shows that the coke species are composed mainly of aromatic compounds which can be classified roughly by the number of benzene rings. Table S3† shows that the amounts of aromatic compounds with single and coupled rings (such as benzene and naphthalene homologues) are 17.8% and 38.1% on spent SP34 and SP34-5% respectively, and aromatic compounds with fused rings (i.e. phenanthrene, anthracene homologues, pyrene and benzantracene) occup 82.2% on spent SP34 and 62% on spent SP34-5% respectively. The reduced production of aromatic compounds with fused rings on SP34-5% is attributed to the hierarchical pores, which promote the diffusion of bigger aromatic molecules from the channels and prevent it from forming coke species with fused rings. As a result, the abundant micro-, meso- and macroporous channels in the hierarchical SP34-5% catalyst can greatly enhance the diffusion efficiency of the reagents/products into and out of the zeolite crystals, which suppresses the coke formation.

Conclusions

In summary, a simple and highly effective solvent-free process was developed for the facile synthesis of hierarchical SAPO-34 with a butterfly patterned morphology through a novel melting-assisted post-synthesis route using solid oxalic acid. The formation of crystals with such a unique morphology is through a defined etching process. After treating SP34 with solid-state oxalic acid, the obtained SP34-5% showed much better catalytic performance than the parent structure. This was due to the fact that hierarchical SP34-5% exhibited a micro-, meso-, and macroporous composite pore structure and high BET surface area. Besides, SP34-5% had more weak acid sites than SP34, which gave a methanol conversion of 100%, a C₂–C₄ selectivity of 91.8%, and an extremely long lifetime of 580 min under experimental conditions. Compared to the widely used post-treatment with solution, this route avoids the use of solvents, thus making it very convenient to scale up the production of hierarchical zeolites.

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Conflicts of interest

There are no conflicts to declare.

Notes and references


