Polyvinyl alcohol templated synthesis of hierarchical SAPO-11

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Abstract
This work reports that the polyvinyl alcohol successfully templates the intracrystal mesoporous structure of hierarchical SAPO-11 molecular sieves. The structures of prepared hierarchical SAPO-11 materials and a conventional SAPO-11 simultaneously synthesized are characterized by X-ray diffraction, \(N_2\) adsorption/desorption, scanning electron microscopy and high resolution transmission electron microscopy. The characterizations demonstrate that this synthesized hierarchical SAPO-11 possesses a mesopore structure with a much regular pore size distribution. Importantly, these mesopores are intracrystal but not intercrystal. The bifunctional isomerization catalyst with this hierarchical SAPO-11 as support shows a high selectivity in hydroisomerization reaction of hexane, evidencing that the catalytic selectivity is improved by introduction of mesopore structure into the SAPO-11 crystal. The templating mechanism of polyvinyl alcohol in formation of mesopores is well discussed at the ending. This work provides a potential template to prepare hierarchical catalyst materials.

1. Introduction
Silicoaluminophosphate molecular sieves with AEL topology (SAPO-11) [1] is a widely used porous material in the field of adsorption and separation, especially of hydrocarbon isomerization [2]. As same as the other microporous catalyst materials, its catalytic activity is heavily suppressed by reactant diffusion in micro-pores. In order to lift this limitation, numerous efforts have been made in past decades. One of the most effective accesses is to prepare SAPO-11 with intracrystal mesopores which can provide a faster mass transfer rate without losing active sites [3]. To reach this purpose, two strategies, in general, post-synthetic acid/base treatment [4, 5] and employing templating, are employed to generate mesopores. The latter can be in further divided into hard template [6] and soft template routine [7–14] according to the properties of the templating agents involved in the synthesis. Besides, some new synthetic procedures have been optimized to regulate the crystalline, as well as the acidity of the silicoaluminophosphate phosphate molecular sieves [15–17], in order to improve the performance of bifunctional catalysts based on it.

With respect to the templating synthesis of hierarchical SAPO-11, there are few publications reporting a successful synthesis with polymeric templating agent [10]. This time, we report a facial but novel preparation procedure of SAPO-11 with hierarchical architectures with hydrophilic polyvinyl alcohol (PVA) as template to direct the formation of intracrystal mesopores. The characterizations verify that the intracrystal mesoporous architecture is formed with narrow pore size distribution, turning out that PVA is an innovative and promising mesoporous directing agent.

2. Experimental
Hierarchical mesoporous SAPO-11 material was hydrothermally synthesized from tetraethoxysilane (TEOS, Energy Chemical China), aluminum iso-propoxide (AIP, 24% \(\text{Al}_2\text{O}_3\)), and phosphoric acid (85% Sinopharm Chemical Reagent), with polyvinyl alcohol (PVA, 86%–89% hydrolyzed, Alfa Aesar) as templating agent.
In a typical synthesis procedure, 1.32 g PVA was dissolved in 58 g deionized water at 55 °C. Then, this solution was cooled down to 25 °C, and 11.03 g AIP was slowly added. After an agitation of 2 h, 6.20 g phosphoric acid was added drop by drop and the mixture was stirred for another 1 h. After that, 1.13 g TEOS was slowly dropped into the flask. 3.28 g 1:1 mixture of di-propylamine and di-isopropylamine (98%, Aladdin Chemical) was added into the gel at 25 °C. After another 2 h stirring, pH of this gel was tuned to 6.5 with phosphoric acid before moved into a Teflon-lined stainless steel autoclave. The crystallization was carried out for 48 hours at 170 °C. The solid was separated by centrifugation and washed with deionized water, and then dried at 110 °C for 3 h. The ultimate product was obtained after calcination at 600 °C for 2 h in muffle oven and is named as H-SAPO-11.

For a comparison, the conventional SAPO-11 was simultaneously prepared and named as C-SAPO-11. The synthesis procedure was mostly the same to H-SAPO-11, but no PVA was involved.

3. Results

The crystalline structure of the prepared samples is analyzed by x-ray Diffraction (XRD). Their specific area and porous diameter distribution are characterized by N₂ adsorption/desorption, and the morphology is analyzed by scanning electron microscopy (SEM) and high resolution transmission electron microscopy (HR-TEM).

3.1. XRD

The crystalline structure of the prepared SAPO-11 samples are evidenced by XRD (Shimadzu, XRD-6000) with CuKα radiation at a scanning speed of 4 degree ⋅ min⁻¹. The XRD patterns of both samples are displayed in figure 1. The characteristic peaks of SAPO-11 located at 2 theta = 8.12, 9.64, 13.11, 15.88, 19.96, 22.42 and 22.56° evidence the SAPO-11 crystalline phase with AEL structure [1]. The relative crystallinility (RC) of H-SAPO-11 is slightly lower than that SAPO-11, indicating a high compatibility of PVA in directing the formation of mesopores.

3.2. N₂ adsorption/desorption characterization

The specific area and porous diameter distributions are characterized with N₂ adsorption/desorption at 77 K (Micromeritics, TriStar 3000). Those adsorption/desorption isotherms and pore size distribution of H-SAPO-11 have been shown in figure 2, and the corresponding parameters in table 1.

The specific area of this H-SAPO-11 is as high as 308.1 m² ⋅ g⁻¹, and the mesoporous surface area is 39.1 m² · g⁻¹. Strikingly, the isotherm of H-SAPO-11 reveals a classical hysteresis loop which significantly differs from C-SAPO-11 isotherm owing to packing geometry. The pore size of H-SAPO-11 shows a very narrow distribution, and the most probable pore diameter is derived to be 3.61 nm. This regular pore distribution combining with HR-TEM images can confidently confirm the presence of intracrystal mesopores.

3.3. SEM and HR-TEM

The SEM (JEOL, JSM-7500F) is employed to observe the morphology of prepared SAPO-11 materials, the images can be found in figure 3. Significant differences can be found between C-SAPO-11 and H-SAPO-11. From those images, the spherical aggregates of C-SAPO-11 are stacked up with numerous regular crystal bricks, and their diameters are observed to be around 10–30 μm. Those packing geometry strengthens the
aforementioned hypothesis that the mesopores in C-SAPO-11 are of intercrystal but not of intracrystal. In contrast, the microspheres of H-SAPO-11 sample show coarse surfaces, and their diameters are less than 50 μm. Remarkably, those crystal microspheres appear stuffed but not accumulated with micro-bricks. This also hints that the hysteresis loop in C-SAPO-11 isotherm is attributed to those mesopores between accumulated micro-bricks. The white domains in e and f indicate those intracrystal mesopores.

Figure 2. N₂ adsorption/desorption isotherms of SAPO-11 samples and the pore size distribution (insertion) of H-SAPO-11.

Figure 3. SEM images of C-SAPO-11 (a), (b) and of H-SAPO-11(c), (d), and HR-TEM images of H-SAPO-11 (e) and (f). It can be clearly found that the microspheres of H-SAPO-11 are stuffed and have a coarse surface but those of C-SAPO-11 are accumulated with micro-bricks. This also hints that the hysteresis loop in C-SAPO-11 isotherm is attributed to those mesopores between accumulated micro-bricks. The white domains in e and f indicate those intracrystal mesopores.

Table 1. Surface and pore structure of C-SAPO-11 and H-SAPO-11 determined from N₂ adsorption/desorption isotherms.

| Samples   | S_BET m² · g⁻¹ | S_Micro m² · g⁻¹ | S_Meso m² · g⁻¹ | V_Micro cm³ · g⁻¹ | V_Meso cm³ · c | RC   |
|-----------|----------------|------------------|-----------------|------------------|---------------|------|
| C-SAPO-11 | 162.8          | 116.9            | 54.8            | 0.052            | 0.19          | 1    |
| H-SAPO-11 | 308.1          | 269.0            | 39.1            | 0.075            | 0.129         | 95.1%|

For a better understanding to the porous structure of the crystal spheres of H-SAPO-11, HR-TEM (FEI, Tecnai-G20) is employed and the images have been showed in figure 3. Those ordered white domains with higher contrast to their vicinities can be clearly observed. This phenomenon can be attributed to the formation of intracrystal mesopores continuously or partially exposed to the observed microspheres. Those HR-TEM images joint with N₂ adsorption/desorption isotherm gives strong evidences that intracrystal mesopores have been successfully introduced into the as-prepared hierarchical SAPO-11 material.
3.4. Catalytic performance

Based on these two SAPO-11 sieves, bi-functional hydroisomerization catalysts Pt/H-SAPO-11 and Pt/C-SAPO-11 were prepared by incipient impregnation with \( \text{H}_2\text{PtCl}_6 \) solution (0.5 wt\%) for 12 h. The materials were first dried at 110 °C for 2 h and calcinated at 480 °C for another 4 h, then 1.1 g of catalyst was loaded in fixed-bed reactor to isomerize \( \text{n}-\text{hexane} \) at 2 MPa pressure. Before the hydroisomerization reaction started, the catalyst was reduced in hydrogen atmosphere at 400 °C for 4 h to obtain metal Pt. During the isomerization, the mole ratio of \( \text{H}_2/\text{C}_6 \) in the feed was 6:1, weight hourly space velocity 1.5 h\(^{-1}\), the temperature 340 °C, the reaction time was 4 h. All the species involved in the reaction were analyzed by a gas chromatograph (Agilent 7820) online.

The conversion of hexane was defined as the percentage of converted \( \text{n}-\text{hexane} \), whereas the selectivity was defined as the percentage of the branched alkanes in the converted \( \text{n}-\text{hexane} \). With the catalysis of Pt/C-SAPO-11, 52.8% \( \text{n}-\text{hexane} \) was converted and the selectivity is 93.2%. In contrast, in the reaction catalyzed by Pt/H-SAPO-11, the conversion was enhanced to 66.4% and the selectivity was raised to 96.5%. With respect to both conversion and selectivity, the isomerization catalyst based on prepared H-SAPO-11 gave a significant improvement, due to the presence of intracrystal mesopores which is favor to the diffusion but suppresses the cracking reaction of the reactant.

4. Discussion

Compared to conventional SAPO-11 molecular sieves, the prepared H-SAPO-11 exhibits a larger particle size and a highly regular intracrystal mesopore structure. Those extraordinary characteristics can only be attributed to the effects of polyvinyl alcohol. Therefore, the synthetic mechanism of H-SAPO-11 should be well discussed here. In crystallization procedure, PVA acts as mesoporous templating agent. Besides many unhydrolyzed acetic ester branches, each PVA chain has numerous hydroxyl groups that can react with phosphoric acid molecules to form phosphate ether bonds by which polymer chains are cross-linked. One phosphoric acid molecule can possibly react with one, two or three hydroxyls of PVA. In the former two cases, a phosphoric acid molecule still has two or one hydroxyl group to react further with aluminum ions released from isopropyl aluminum. As a result, the aluminum ions are thus anchored on those PVA chains by P-O-Al bond. After the substitution of P by Si, the framework of SAPO-11 is formed. The silicoaluminophosphate crystals continuously grow along those cross-linked polymers molecules, until the growth process is completed. The encapsulated PVA molecules occupy corresponding spaces in mesoscopic scale, thereby, tremendous mesopores within the molecular sieves crystal are exposed after their removal by calcination. During the crystallization, those phosphor atoms connected to the polymer chains are bonded into the crystalline frameworks, therefore, those mesopores are of intracrystal but not intercrystal. Figure 4 schematically illustrates the templating effect of polyvinyl alcohol in the case that only two chains are cross-linked.

As a matter of fact, the cross-link of PVA chains is much complicated. More than two polymer chains can be connected by P-O bonds to form a three-dimensional spatial network macromolecule with cross-linked structure. In this case, they occupy more spaces, leading to the formation of intracrystal mesopores with wider diameters, as observed in HR-TEM. On the other hand, those unhydrolyzed ethyl groups of PVA are
hydrophobic, promoting those polar species forming SAPO-11 to react preferentially around the hydrophilic hydroxyls and thus inducing the mesoscopic ordered structure to occur, as found in the formation of ordered silica porous materials [18]. Both factors, mesoporous templating and directing effects, function together to generate the intracrystal mesopores in the currently reported hierarchical material.

5. Summary and conclusions

Hierarchical micro- and mesoporous SAPO-11 has been successfully prepared with PVA as mesoporous template. The prepared materials are separately characterized by N2 adsorption /desorption, XDR, SEM and HR-TEM. It turns out that the prepared hierarchical SAPO-11 has a high mesoporous surface area and regular mesopore size distribution. HR-TEM, combining with adsorption analysis, demonstrates that regular intracrystal mesopores are formed in H-SAPO-11. Due to hierarchical architecture, the hydroisomerization catalyst with it as support, improves the selectivity in isomerization reaction of n-hexane. This work provides a very promising mesoporous templating agent for efficient preparations of hierarchical SAPO-11 molecular sieves with intracrystal mesopores. Also, it might also be used to synthesize zeolites with specific pore structure.

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