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Ordered mesoporous silicalite-1 zeolite assembled from colloidal nanocrystalline precursors

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ABSTRACT

A series of ordered mesoporous silicalite-1 zeolites has been synthesized by the self-assembly of nanosized zeolite silicalite-1 seeds with different sizes using a two-step procedure. The nanosized silicalite-1 seeds were prepared with an alkali precursor solution that was heated for different periods, and then assembled into ordered mesoporous materials under strongly acidic conditions, similar to that of mesoporous silica SBA-15 which has well ordered hexagonal mesopores and amorphous walls. A significant change in synthesis conditions prevents the continued growth of zeolite seeds and induces assemblage into ordered mesoporous materials templated by triblock copolymers. The samples assembled by zeolite nanoclusters were investigated by X-ray diffraction, electron microscopy, infrared spectroscopy, and N₂ adsorption-desorption isotherms. This "bottom-up" approach yields porous materials that contain ordered micro- and mesopores. The mesoporous zeolite has a large surface area (> 730 m²/g).

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1. Introduction

Zeolites are known for their molecular size- and shape-selective applications in catalysis, oil refining, sorption, and separation processes, and their use as ion-exchangers, volatile organic compound adsorbents, photoelectric devices, sensors, and drug encapsulators [1]. However, the small pore size of zeolites excludes bulky molecules from diffusing into the internal zeolite surface. The diffusion limitations and slow mass transport to and away from the catalytic center inside the zeolite crystals lead to more secondary reactions, coke formation, and catalyst deactivation [2,3]. On the other hand, external and pore mouth acid sites on the outer zeolite crystal surfaces are believed to be active sites for chemistry related to bulky molecules [4]. While for micro-sized zeolite crystals, their external surfaces are negligible compared with the large surface area in

the internal micropores [5]. Therefore the large external surface of nanosized zeolite particles is appealing. The zeolitic mesoporous materials combine the advantage of a large pore volume and mesoporous structure surface area and strong micropore acidity, and therefore exhibit improved catalytic properties such as selectivity and activity by shortening the diffusion length and exposing more acid sites compared with conventional micro-sized crystals [6,7].

Several strategies have been developed to synthesize mesoporous zeolites, including soft templating methods using conventional surfactants, macromolecular polymers, amphiphilic surfactant derivatives or large silylating agents [8–11], hard-templating methods using carbon or other solids [12–15], multifunctional templating methods [16–18], dry gel conversion to transform the preformed solid precursor into zeolite [19–21], and removal of framework Si or Al atoms by acid or

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alkali leaching treatments [22,23]. However, most of these methods are costly and time-consuming.

The surfactant-mediated assembly of zeolite seeds into mesoporous structures has been reported [24–26]. X-ray studies have shown that the amorphous zeolite gel precursors have an intermediate structure between true zeolites and completely amorphous materials [6,27–30]. However, phase separation between meso- and micro-phases is difficult to avoid when cetyl trimethylammonium bromide is used as a mesopore template [31,32]. Xiao's group [33–36] reported the synthesis of various ordered mesoporous silicate materials using clear zeolite solutions and a Pluronic P123 triblock copolymer template. Shantz' group [26] synthesized ordered mesoporous materials at low temperature and different acidities. Qiu's group [37] synthesized high aluminum-content mesoporous aluminosilicates using zeolite X as precursor. These materials were generally assembled from zeolitic nanoclusters below five nanometers [29,38], so they had no typical zeolite X-ray diffraction (XRD) pattern, and lacked long-range ordered micropores. To obtain materials with true zeolite units, the zeolite seed crystal size should be larger than 5 nm. Xiao's group [39] reported that it was difficult to achieve self-assembly of silica species larger than 20 nm because of the lack of strong interaction between the silica species and surfactant micelles.

In this study, we synthesized a series of ordered mesoporous silicalite-1 zeolites using different sizes of nanoclustered zeolite silicalite-1 seeds as precursors. The zeolites were produced by controlling the heating time at low temperature, and using conventional triblock copolymer P123 as surfactant. This "bottom-up" approach yields materials that contain ordered micro- and mesopores with no phase separation at a large zeolite nanocrystal precursor size range. This seeding assembly method may even be used to synthesize mesoporous zeolites assembled by large zeolite nanoclusters (~200 nm). All mesoporous zeolites exhibit a large surface area (> 700 m²/g) and large mesopore volume.

2. Experimental

2.1. Reagents

Tetrapropylammonium hydroxide (TPAOH, 25 wt%) was purchased from Acros. Pluronic P123 (M_{av} = 5800), EO20PO70EO20 was purchased from Aldrich. Tetraethyl orthosilicate (TEOS), hydrochloric acid (36.5%) and NaOH (99.6%) were purchased from Beijing Chemical Company. All chemicals were used without further purification.

2.2. Materials synthesis

Synthesis of the silicalite-1 colloidal precursor solutions was carried out following methods in literature with some modifications [40]. 10-mL TPAOH aqueous solution, 31.67 mL of NaOH dilute aqueous solution (containing 32.8-mg NaOH), and 21.34 mL of TEOS were mixed and stirred at room temperature for 24 h to ensure complete TEOS hydrolysis to form a clear solution (1 TEOS:0.12 TPAOH:0.008 NaOH:19.2 H₂O). The mix-

ture was aged at 60 °C for different periods until a white precipitation was visible. This colloidal solution was the precursor solution for the next step. 0.4-g Pluronic P123 was dissolved in 3-mL water mixed with 12-mL HCl (2 mol/L), followed by the addition of 2.51 g of precursor solution obtained in the above procedure. The mixture was stirred at 40 °C for 20 h and then transferred into an autoclave at 100 °C for 24 h. The products were filtered, washed with water and ethanol, dried in air, and calcined at 550 °C for 8 h to remove the organic template. The final samples were labeled MS-Dx, where Dx refers to the number of days that the silicalite-1 precursor solutions were heated at 60 °C.

For comparison, ordered mesoporous silica SBA-15 which has well ordered hexagonal mesopores and amorphous walls was prepared under identical conditions, except that the amount of silica contained in the precursor solution was replaced by a corresponding amount of TEOS. Large-sized silicalite-1 was obtained from the precursor solution aged at 60 °C for 26 d.

2.3. Characterization

The morphology and size of the resultant powder were characterized by a field-emission scanning electron microscope (FESEM JEOL-6701F). Transmission electron microscopy (TEM) images were taken using a JEM-2100F (JEOL) operated at 200 kV. Power XRD patterns were collected on a Rigaku-2500 in the 2 θ range of 0.5°–6° and 5°–55°. Fourier transform infrared (FTIR) spectra were recorded on a Nicolet iN10-iZ10 infrared spectrophotometer from 4000–400 cm⁻¹ using a KBr pellet containing 3 wt% sample. N₂ adsorption isotherms were measured at -196 °C on a Quantachrome Autosorb AS-1 instrument, and samples were outgassed at 120 °C for 12 h prior to testing. Pore size distributions were evaluated from the adsorption isotherms using the Barret-Joyner-Halenda (BJH) formula and the microporous volume was evaluated by nonlocal density functional theory. ²⁹Si solid-state cross polarization magic angle spinning nuclear magnetic resonance (CP/MAS NMR) spectra were measured on a 400-MHz Bruker Avance III spectrometer equipped with a 4-mm MAS NMR probe. The ²⁹Si frequency of 79.3 MHz had a recycle delay of 2 s, and the spinning speed was 12 kHz.

3. Results and discussion

The colloidal silicalite-1 mixture precursor was a clear solution at the initial heating stage. With a prolonged heating time, it turned pale blue after 10 d, white on day 14, and then formed a white precipitate after 26 d. Although the nucleation and growth mechanism of zeolites is complicated, it is generally accepted that colloidal silicalite-1 formed from clear solution involves a self-assembly of primary zeolitic building units (nanoslabs and nanotablets with a silicalite-1-type connectivity), which were aggregated into intermediate small fractions at elevated temperatures, and finally integrated into silicalite-1 particles that exhibit crystallinity detected by XRD [29,41–43]. The formation of a zeolite particle at relatively low temperature

Fig. 1. Wide-angle (a) and small-angle (b) XRD patterns for mesoporous silicalite-1 zeolites. (1) MS-D0.5; (2) MS-D2; (3) MS-D6; (4) MS-D10; (5) MS-D14; (6) MS-D18; (7) MS-D22; (8) MS-D26.

is a slow process. In this study, the preformed colloidal zeolite mixture was heated continually at a relatively low temperature of 60 °C, during which the nanoparticles in the precursor gradually grew from primal nanoslabs and nanotablets into silicalite-1 nanoparticles.

Fig. 1 shows the wide- and small-angle XRD patterns of various mesoporous silicalite-1 samples synthesized using the colloidal silicalite-1 mixture source heated for different periods. In strong acidic media, the nanoparticle size in the preformed zeolite precursor and their X-ray crystallographic structure characteristics were maintained. Therefore the wide-angle XRD patterns of the assembled MS materials had characteristics of silicalite-1 nanoparticles. With increasing heating time, the zeolitic nanocluster sizes in the precursor gradually increased, and the intensity of their XRD peaks also increased (Fig. 1(a)). When the precursor solution was heated to 18 d, the MS-D18 sample started to exhibit typical diffraction peaks of silicalite-1 zeolite, which indicates the formation of relatively large zeolite nanoparticles. When the precursor was heated to 26 d, the resulting sample MS-D26 showed obvious XRD peaks of the MFI-type zeolite. During the heating period, maintaining a low temperature (60 °C) was critical to ensure homogenous growth of nanoparticles in the precursor. The samples heated for less than 18 d did not show obvious XRD signals from MFI zeolites, because the silicalite-1 nanocrystals are very small (less than 200 nm) and therefore do not have strong XRD signals [44]. However, the N₂ adsorption results support the presence of ordered zeolite micropores. The small-angle X-ray diffraction patterns (Fig. 1(b)) exhibit a narrow peak from the resulting sample MS-D0.5 to MS-D18, and reflect the formation of a worm-like ordered mesoporous phase similar to SBA-15. The pattern shows a two-dimensional hexagonal symmetry (*P6mm*) with three distinct peaks from 0.5° to 2.5° that can be indexed as the (100), (110), and (200) reflections of the SBA-15 sample. As the heating time increased to 18 d, the MS samples maintained a relatively narrow diffraction peak for the (100) lattice plane, the peak intensity decreased, and the peak broadened from the MS-D14 sample. For a later heating time, the disordered mesostructure increased gradually for the MS-D22 and

MS-D26 samples, which may be caused by the lack of strong interaction between the larger nanoparticles and the P123 surfactants with a limited charge density [39].

The MS-D22 sample was chosen to be representative to investigate the ²⁹Si CP/MAS NMR spectra (Fig. 2) since a disordered mesostructure began to appear on MS-D22 as indicated by the small-angle XRD patterns. Compared with SBA-15, the Q²/Q³ peak intensity ratio of the MS-D22 sample was weaker, which indicates that fewer Q² silanol groups existed in the mesoporous silicalite-1 zeolite. For the silicalite-1 sample collected from the precursor heated for 22 d, nearly no Q² signal existed but the highest Q⁴/Q³ intensity ratio was detected, which indicates that large amounts of crystallized Si-O-Si sites existed in the precursor of the MS-D22 sample. These results demonstrate that the disordered mesostructure was caused by the crystallized silicalite-1 nanoparticles in the precursor, which cannot provide sufficient silanol groups to interact strongly with the P123 surfactants.

The TEM images of these mesoporous silicalite-1 zeolites are shown in Fig. 3. At the initial heating period, the as-synthesized mesoporous materials assembled from the clear precursor solution exhibited an ordered hexagonal mesostruc-

Fig. 2. ²⁹Si CP/MAS NMR spectra of MS-D22, normal SBA-15 sample, and silicalite-1 sample collected from precursor heating for 22 d.

Fig. 3. TEM images of mesoporous silicalite-1 zeolites. (a) MS-D0.5; (b) MS-D2; (c) MS-D6; (d) MS-D10; (e) MS-D14; (f) MS-D18; (g) MS-D22; (h) MS-D26.

ture similar to SBA-15. All mesoporous zeolites showed a smaller mesopore size and thicker walls than those of the SBA-15 sample prepared under the same conditions. The wall thickness increased with increasing heating time, which indicates better thermal, hydrothermal, and mechanical stability than sole mesoporous silicates [45]. However at later heating periods, a disordered mesostructure appeared gradually, which is in agreement with the small-angle XRD results.

The N_2 adsorption-desorption isotherms are shown in Fig. 4 and the textual parameters are shown in Table 1, indicating that micro- and mesopores exist. For typical mesoporous zeolites in Fig. 4, each of the curves exhibits a typical type-IV isotherm at a relative pressure of $p/p_0 > 0.1$, whereas in the low relative pressure region ($p/p_0 < 0.1$), the curve exhibits type I properties. The type H1 hysteresis loops indicate the presence of uniformly sized mesopores. In the low relative pressure region ($p/p_0 < 0.001$), the isotherm slope is steep, and indicates the existence of micropores that are typical for zeolites [46,47]. All mesoporous zeolites have nearly the same mesopore size of ~ 3.8 nm as determined from the BJH model, which is much smaller than the normal SBA-15 (5.7 nm from Table 1). This

narrowing in pore size results from an increased wall thickness with zeolite nanoparticles embedded in the mesoporous silicate-1 material walls. All the mesoporous zeolites had a higher Brunauer-Emmett-Teller (BET) surface area and micropore volume than normal silicalite-1 zeolite ($391 \text{ m}^2/\text{g}$ and $0.089 \text{ cm}^3/\text{g}$, respectively) except for the MS-D0.5 sample. This confirms that a large microporosity volume exists in the MS samples. These results demonstrate the existence of zeolite MFI species in the mesoporous walls.

Fig. 5 shows SEM images of mesoporous samples assembled from different nanoclustered zeolite seeds. At the initial heating time of the precursor solution, the assembled mesoporous sample shows wormlike morphology similar to SBA-15. With increasing heating time, the wormlike morphology started to disappear. However, no phase separation was observed, although the average precursor nanoparticle size was greater than 200 nm (206, 217, and 229 nm for 18, 22, and 26 d, respectively, see Fig. 6). The silicalite-1 nanoparticles collected from the precursor heated for 10 d had an average size of 30 nm (Fig. 6(d)), which demonstrates that mesoporous zeolites can be obtained from the self-assembly of zeolite nanocrystal

Fig. 4. N_2 adsorption-desorption isotherms of typical mesoporous silicalite-1 zeolites. (a) MS-D0.5; (b) MS-D10; (c) MS-D18; (d) MS-D26.

Table 1

Textual parameters of SBA-15 and MS samples.

Sample	S_{BET} (m^2/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)	Mesopore size (nm)
MS-D0.5	892	0.076	1.380	3.823
MS-D2	784	0.095	1.001	3.823
MS-D6	757	0.102	0.953	3.813
MS-D10	885	0.100	0.966	3.817
MS-D14	735	0.099	0.969	3.848
MS-D18	770	0.100	1.075	3.821
MS-D22	793	0.120	1.094	3.841
MS-D26	749	0.119	0.877	3.850
SBA-15	664	0.063	0.836	5.669

precursors larger than 20 nm.

Fig. 7 compares the FTIR spectra of silicalite-1, SBA-15 and MS samples. Several reports attribute the strong peak at $\sim 550 \text{ cm}^{-1}$ to the presence of double five-membered silica rings. This IR spectral feature has been used as an indicator for the presence of MFI [12,48,49]. With increasing precursor heating time, the band peak intensity ratio of mesoporous silicalite-1 zeolite at 556 to 468 cm^{-1} also increased, which indicates that the mesoporous walls of the MS materials contain the primary units of MFI zeolite.

These results suggest that ordered mesopores and ordered micropores were obtained on these materials. However, even at low heating temperature, the zeolite nanocrystal growth was

Fig. 7. FTIR spectra of silicalite-1, SBA-15, and MS samples.

not uniform [44]. For a shorter heating time, only some of the silica source was consumed to produce silicalite-1 zeolite, and the other fraction may be a mixture of amorphous nanoparticles such as nanoslabs, nanotablets, and their intermediate aggregates, which can be more easily assembled into mesoporous structure. It is therefore more likely that the walls of mesoporous materials produced in this work are a homogeneous

Fig. 5. SEM images of mesoporous silicalite-1 zeolites. (a) MS-D0.5; (b) MS-D2; (c) MS-D6; (d) MS-D10; (e) MS-D14; (f) MS-D18; (g) MS-D22; (h) MS-D26. **Fig. 6.** SEM images of silicalite-1 nanoparticles collected from precursor heating for 18 d (a), 22 d (b), and 26 d (c) and TEM image for 10 d (d).

ous mixture of silicalite-1 nanocrystals and amorphous zeolitic nanoparticles. This mixture may help to hold the relatively large zeolite nanocrystals in the mesopore walls. In the mixture, the zeolite nanocrystals were not attached directly to each other, but rather, were surrounded by amorphous zeolitic nanoparticles. This structure may overcome the lack of strong interactions among zeolite crystals, and lead to ordered mesoporous zeolite materials.

4. Conclusions

We synthesized a series of mesoporous silicalite-1 zeolites with conventional triblock copolymer P123 using different sizes of nanoclustered zeolite silicalite-1 seeds as precursors by controlling the heating time at low temperature. This “bottom-up” approach yields materials that contain ordered micro- and meso-pores with no phase separation for a large zeolite nanocrystal precursor size range. All mesoporous zeolites have a large surface area and mesopore volume. This seeding assembly method can also be used to synthesize other mesoporous zeolites assembled by larger zeolite seeds (~200 nm).

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Graphical Abstract

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Ordered mesoporous silicalite-1 zeolite assembled from colloidal nanocrystalline precursors

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Ordered mesoporous zeolite with large surface area and pore volume is synthesized by nanosized silicalite-1 seed self-assembly and using commercial P123 triblock copolymer in acidic media.

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由纳米晶前驱体组装有序介孔silicalite-1分子筛

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摘要: 采用两步法将不同尺寸的silicalite-1分子筛纳米晶种通过自组装合成了一系列有序介孔silicalite-1分子筛. 首先将强碱性的silicalite-1前驱体分别加热不同时间得到纳米晶种, 然后在类似合成SBA-15的强酸性条件下组装成有序的介孔材料. 合成条件的剧烈变化阻止了分子筛晶种的继续长大, 并在三嵌段共聚物模板的诱导下组装成有序介孔材料. 这种“自下而上”的方法制备有序介孔分子筛同时包含微孔和介孔. 氮气吸脱附结果表明所制备的介孔分子筛材料均表现了很大的比表面积(730 m²/g以上).

关键词: 有序介孔; 分子筛; 自组装; 自下而上方法; 纳米晶种

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