Assembly of nanosized mesostructured aluminosilicates by in situ hydrolysis of inorganic precursors

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Abstract

This work emphasizes the influence of the addition of inorganic aluminum salt on the macroscopic properties of mesoporous aluminosilicates. It was found that upon the addition of an optimal amount of aluminum salt followed by a basic catalyst into the system, mesoporous aluminosilicate nanoparticles could be obtained, an observation that had barely been mentioned before. The assembly of nanosized mesostructures was explained by the separate control of silica hydrolysis and condensation in the system, each of which can be effectively manipulated by the aluminum salt and basic catalyst, respectively.

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1. Introduction

The discovery of the newest family of mesoporous molecular sieves, designated as the M41S family, is of considerable interest for heterogeneous catalysis [1]. However, their neutral silica frameworks are of limited use for various catalytic applications. The ability to control the chemical composition of these materials is an important topic in catalysis research. Depending on the nature and the number of trivalent framework cations, both the strength and density of the acid sites can be adjusted to meet the requirements for various processes. For instance, the incorporation of trivalent atoms (Al, Fe or Ga) into the silica walls creates Brønsted acidic sites and allows the preparation of materials possessing different catalytic and adsorptive properties [2]. Among them, Al-substituted ones have received much more attention due to the availability of reagents and the presence of relatively stronger and more stable active sites.

It has been noted that the principal feature of AlMCM-41 and related solids, namely their ordered unimodal porous structures, does not offer specific advantages in some determined applications, such as catalysis, especially when bulky molecules are involved [3]. Furthermore, owing to its long channels, unimodal AlMCM-41 could suffer from poor accessibility to active sites and quick deactivation [3]. Indeed, it has been proven that the site accessibility in unimodal MCM-41-like materials can be effectively enhanced by miniaturization of their particle size. It was reported that, for instance, an ultra-small AlHMS catalyst showed a much higher activity for the alkylation of bulky 2,4-di-tert-butylphenol with cinnamyl alcohol than typical AlMCM-41 [4], clearly revealing the importance of the “nano” effect in reactions.

Recently, various types of nanosized mesostructures have been reported [5–14]. However, most of the investigations are only focused on the pure silicas, although the ability to endow nanosized mesostructures with diverse functionalities can increase their application range significantly. This may be associated with the difficult-to-handle conditions for heteroatom-modified nanosized mesoporous species [8–14]. Amorós and co-workers reported various metal-incorporated MCM-41-like nanocatalysts using an atrane complexing method [8,9]; one of them, TiUVM-7, exhibited excellent performance in olefin epoxidation [8]. Lin and co-workers synthesized nanosized AlMCM-41 by a two-step process and the catalyst showed higher activity in cumene cracking than typical AlMCM-41 [10]. A microwave-hydrothermal route to nanoscale mesoporous aluminosilicates with strong Brønsted acidity has been recently

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reported [11]. Also, Zhai et al. reported the synthesis of nano-sized mesoporous aluminosilicates with superior activity in bulky trisopropylbenzene cracking [12,13]; more interestingly, these catalysts still showed high activity after severe steam treatment [13].

Following our previous work, we recently succeeded in synthesizing another kind of nanosized Al-containing mesostructure using dual surfactants [14]. In the experiment, however, we did find that, even without co-surfactant of PEG-4000, nanosized mesoporous aluminosilicates could still be obtained. In this work, a more detailed study on the one-pot surfactant-assisted procedure was presented, which not only allowed us to prepare materials in this growing family but also to revisit the well-known classical “silica chemistry”.

2. Experiment

2.1. Synthesis

The basic concept behind the present synthesis is the control of hydrolysis and condensation of the inorganic precursors. Firstly, a corrected amount of cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS) and aluminum salt was mixed and stirred at room temperature for a period of 60 min. Next, a fast co-condensation reaction resulting from the entirely or partly hydrolyzed inorganic species was achieved with the addition of aqueous ammonia and keeping the pH value of the system at 9–10. After further stirring for 48 h at room temperature, the products were collected by filtration, dried and calcined in air. The gel molar composition was 1.0TEOS:0.2CTAB:(0.0–0.4)Al(NO3)3:200H2O, and three samples with Si/Al ratios of 5, 40 and ∞ are denoted as AlM(5), AlM(40) and AlM(∞), respectively.

2.2. Characterization

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were measured on a JEOL JSM 6400 and Tecnai on F20 microscope, respectively. X-ray diffraction (XRD) was monitored by a Rigaku RAD-C system with Cu Kα radiation. N2 sorption was analyzed on a Micromeritics TriStar 3000. 27Al MAS NMR was obtained with a Bruker DRX 300 spectrometer. Elemental analysis was determined by inductively coupled plasma (ICP) on a Plasma 400 spectrometer.

3. Results and discussion

Typical EM micrographs of the samples with various amounts of aluminum salt are shown in Figs. 1 and 2. Noticeably, significant difference in grain size distribution among the three materials can be distinctly observed in the SEM images. AlM(5), the sample prepared with the highest aluminum salt amount, is typical of nanomaterial composed of nanoparticles with a sharp distribution and definite dispersity, a property that is almost entirely similar to that of the nanosized mesostructures reported before [5–14]. In contrast, AlM(40), which was prepared with a medium aluminum salt amount, exhibits a relatively wider particle size distribution, though half of the particles are similar to AlM(5). As for AlM(∞), which had no aluminum salt in the system, much bigger particles than either AlM(5) or AlM(40) were found. Clearly, the amount of aluminum salt has an important effect on the morphology of the products and...
under optimal conditions the formation of nanosized materials is feasible.

Clearer evidence for the nanoscale material is further provided by the TEM technique. For instance, typical TEM images of AlM(5) are depicted in Fig. 2. Consistent with the SEM analysis, the sample is completely composed of nanoparticles ranging from 30 to 60 nm in diameter (see Fig. 2A). Another interesting phenomenon is that the present nanoparticles are well dispersed even though only the usual pretreatment for TEM experiment was used, which is different from the reported nanosized products [8,9]. In comparison with the silica ones, the preparation of well-ordered metal-incorporated mesoporous nanoparticles is much more difficult due to the sensitivity of the assembly process and the appearance of guest heteroatoms [9]; this is likely the reason why some authors have employed the so-called “atrane route” to prepare nanosized mesoporous catalysts [8,9]. In contrast, the present system is simpler.

Following the electron microscopy (EM) studies on the macroscopic properties, XRD and N2 sorption measurements were taken to investigate the porous characteristics, which are indispensable for porous materials. As shown in Fig. 3 (left), there is a significant difference in the XRD reflections among three samples. The AlM(5) exhibits a strong peak along with a discernible shoulder in the low angle region, which can be indexed to the (1 0 0) peak and the overlapping (1 1 0) and (2 0 0) reflections, respectively. As reported, this is characteristic of the class of nanoparticulated mesoporous solids prepared through surfactant-assisted procedures [8,9]. In any case, the XRD pattern can inform us about the relative order of the pore system in the nanoparticles, which is consistent with the TEM results. In contrast, the AlM(40) shows at least four peaks, i.e. (1 0 0), (1 1 0), (2 0 0) and (2 1 0) [1], clearly indicating a perfectly hexagonal mesostructure (TEM not shown). The apparent difference in the XRD analysis between AlM(5) and AlM(40) indicates that the primary particle size is not a determining factor for the XRD reflections, considering the fact that at least half the particles in AlM(40) are similar to AlM(5). However, for pure AlM(∞), the XRD pattern showing only a broad (1 0 0) peak seems unreasonable, and this may be closely associated to the specific self-assembling kinetics of TEOS and CTAB in the relatively mild basic solution (pH ~ 10). This also directly reveals that a small amount of aluminum salt can promote the formation of an ordered mesophase in the present system, consistent with our previous results [14].

The textural character of these samples is also illustrated by N2 sorption isotherms (Fig. 3, right). Clearly, the isotherms of both AlM(5) and AlM(40) reveal two well-defined adsorption steps, which is consistent with reported sorption results for nanoscale mesostructures [5–14]. The first step, performed at a low relative pressure (0.2 < P/P0 < 0.4), is characteristic of type IV isotherms and can be related to the capillary condensation of N2 inside the intra-particle mesopores [1]. The second one,
which is at high relative pressure ($P/P_0 > 0.8$), corresponds to the filling of the large pores among the primary nanoparticles, which is typical of nanosized objects [5–14]. However, the second step for AlM(5) is higher and steeper than that for AlM(40), clearly indicating that there is larger amount of textural porosity in the former, which can be attributed to its narrower grain size distributions; this is consistent with the EM micrographs (Figs. 1 and 2). In addition, the first step on the isotherms of AlM(40) is much sharper than that of AlM(5). This observation agrees well with the XRD results, confirming that the former is more ordered than the latter one [2]. In contrast to the similar sorption properties of AlM(5) and AlM(40), AlM($\infty$) has much more complicated isotherms. Besides a steep inflection point at a $P/P_0$ of 0.30–0.45, another irregular adsorption stage is displayed at $P/P_0 > 0.45$, possibly revealing that the particle dimension of AlM($\infty$) is between the boundary of nano- and microsized objects [10]. This is proved by its SEM analysis (see Fig. 1).

Table 1 shows the structural parameters of the samples. Clearly, all samples possess the typical advantages of the typical mesostructures, including high surface areas, pore volumes and narrow pore size distributions [11]. In contrast to others, the reduction of textural properties of AlM(5) should be another indication of the slight deformation of the framework pore structures caused by the presence of large amount of aluminum atoms, similar to those reported metal-modified nanoscale mesostructures [8,9].
The $^{27}$Al MAS NMR spectra for AlM(5) and AlM(40) with different chemical compositions are shown in Fig. 4. At first glance, both spectra display two intense deflections at about 51 and $-3$ ppm, which can be ascribed to the four- and six-coordinated units [12–14], respectively. For AlM(5), however, another peak at about 23 ppm is distinctly observed. This signal is associated with the five-coordinated atoms, though it is rarely observed for conventional AlMCM-41 even with high aluminum content. This has been proved in our previous work [14].

4. Conclusion

Mesoporous aluminosilicate nanoparticles have been prepared employing the synergistic effect of TEOS and aluminum salt, where the salt amount determines the hydrolysis degree of TEOS and thus the final macroscopic properties of the products. Based on this pathway, various metal-incorporated nanostructures, such as Sn-, Zr- and Fe-modified silicas or periodic mesoporous organosilicas (PMOs), are available and these results will be reported soon.

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