One-pot pseudomorphic crystallization of mesoporous porous silica to hierarchical porous zeolites

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ABSTRACT

Hierarchically porous silica with mesopore and zeolitic micropore was synthesized via pseudomorphic crystallization under high-temperature hydrothermal treatment in the presence of cetyltrimethylammonium tosylate and tetrapropylammonium ions. A combined characterization using small-angle X-ray diffraction (XRD), nitrogen adsorption, high-resolution transmission electron microscopy (TEM), thermogravimetric analysis (TG), and elemental analysis showed that dual templates, CTA^+ and TPA^+ molecules, can work in a cooperative manner to synthesize mesoporous zeolite in a one-pot system by precisely tuning the reaction conditions, such as reaction time and temperature, and type and amount of heterometal atoms. It is found that the presence of Ti precursor is critical to the successful synthesis of such nanostructure. It not only retards the nucleation and growth of crystalline MFI domains, but also acts as nano-binder or nano-glue to favor the assembly of zeolite nanoblocks.

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1. Introduction

It is well-known that zeolites show unique shape selectivity in various reactions due to molecular-sized microporosity, but suffer diffusion limitations on reactions due to the small size of the channels (less than ~0.8 nm) and cavities (typically <1.5 nm) [1,2]. The development of ordered mesoporous materials has ever shed light on the reactions involving large molecules [3]. However, the relatively low reactivity and hydrothermal stability of mesoporous aluminosilicates limit their potential applications as catalysts in petroleum refining and fine chemical synthesis. Much effort has therefore been devoted to synthesize new materials with the combined advantages of both mesoporous materials and crystalline microporous zeolites. One means is to synthesize hierarchical zeolites, i.e., to generate mesopore into the zeolitic crystals via hard-casting template techniques, the assembly of zeolite nanoparticles, steaming treatment and chemical leaching approaches (desilication and dealumination) [4]. The other is to introduce zeolite-like order into the mesopore walls, where the amorphous walls of

mesoporous silicates (e.g., MCM-41 or SBA-15) are converted to a partially zeolitic product [5–14].

To obtain hierarchical micro- and mesoporous materials with well-controlled textual properties, the borderline between the zeolite crystal growth and the preservation of mesopore should be emphasized and well controlled [15]. The surfactant or polymer generating the mesopore and small structure-directing agent (SDAs) leading to the micropore in the crystalline zeolite framework must work in a cooperative rather than a competitive manner in order to avoid the formation of the physical mixtures of amorphous mesoporous material and bulky zeolite, when dual templates were used [16–20].

Zeolite nucleation could be defined as a phase transition whereby a critical volume of a semi-ordered gel network is transformed into a well-ordered structure from which the crystal lattice can propagate [21]. This process can be generalized as 'solution mediated' mechanism. Consequently, an internal, bond-switching rearrangement from amorphous to crystalline material accompanies a morphological change. Recently, Ryoo and coworkers synthesized a hierarchically meso-/microporous BEA zeolite using a cyclic ammonium as SDA, which led to pseudomorphic crystallization of the zeolite by suppressing the mobility of silicates during crystallization [22–24]. In this mechanism, the mobility of the dissolved silicate species is very low, and it is immediately captured by a SDA to form a zeolite crystal. Thus, the morphology of the initial gel is maintained in the final product. This limiting case was traditionally described as 'solid-state' crystallization, i.e., pseudomorphic crystallization [22].

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Here, we reported that the amorphous pore walls of well-formed Ti-containing MCM-41 materials could be partially transferred into crystalline-like MFI zeolite domains via pseudomorphic crystallization, where the morphology of the initial mesoporous materials was maintained in the final hierarchical product. More importantly, the mesostructure was well kept after high temperature hydrothermal treatment at 175 °C for 48 h, while no physical mixture of mesoporous materials and zeolites was observed.

2. Experimental

2.1. Synthesis

The hierarchically porous silica was synthesized based on the previous literature with some modifications using CTATos and TPABr as dual templates [25–30]. In a typical synthesis procedure, 7.40 g of cetyltrimethylammonium tosylate (CTATos, Merck) was dissolved in 120 ml of water and stirred for 1 h at 60 °C. 63 ml of 1.0 M tetra-propylammonium hydroxide (TPAOH) aqueous solution was added into 107 ml of water, followed by addition of 10.78 g of fumed silica under vigorous agitation. After stirring for 1 h at 60 °C, the silicate solution was cooled to ice temperature, and 0.68 g pre-hydrolyzed titania nanoparticles (79.0% TiO_2, calculated by thermogravimetric analysis) using Titanium(IV) ethoxide as a precursor under air atmosphere were added slowly. The solution was stirred continuously for 30 min at 0 °C, and then it was heated to 60 °C, and stirred for 10 min. The above obtained solution was added into a CTATos solution dropwise. The collected gel composition was 1 SiO_2:0.037Ti:0.09 CTATos:0.35 TPAOH:79.9 H_2O. The mixture was stirred continuously for 2 h at 60 °C and then loaded into a 250 ml Teflon-lined steel autoclave where the gel mixture was pre-aged for 48 h at 35 °C to stabilize the pore framework, and finally heated in an autoclave under static condition at 175 °C for 48 h. It is important to note that the molar ratio of TPA^+/CTA^+ in a current gel composition was close to 4.0, which is much larger than that reported by literatures [31–33]. The final products were collected by filtration, washed, and dried. To remove the templates, the products were heated under air ventilation for 6 h at 550 °C. The molar ratio of Si/Ti in the final powder measured by elemental analysis is 18.6, less than 26.7 in gel composition, indicating that the silica is not fully utilized in the crystallization of zeolites at high concentration of TPAOH.

2.2. Characterization techniques

The X-ray diffraction (XRD) patterns were collected on a Bruker D8 ADVANCE instrument using Cu-Kα radiation (λ = 1.5418 Å) at 40 kV and 40 mA. Nitrogen adsorption–desorption isotherms were recorded at 77 K on a Quantachrome Autosorb-3B instrument after activating the sample under a vacuum at 473 K for at least 10 h. The specific surface areas were evaluated using Brunauer–Emmett–Teller (BET) method, and the total pore volumes were determined from the amount adsorbed at a relative pressure of about 0.99. The pore size distribution curves were calculated from the analysis of the desorption branch of the isotherms using Barret–Jovner–Halenda (BJH) algorithm. The SEM images were taken using Hitachi S-4800 microscope. TEM analysis was performed on a JEOL 2010F microscope equipped with a field emission gun and operating at 200 kV. Solid UV/vis spectra were recorded in the 200–500 nm range on UV2550 from an aluminum cell with quartz window. Elemental analysis was carried out at "Service Central d'Analyse de Solaize", CNRS. Thermogravimetric analysis (TG) was performed using a Perkin-Elmer TGA analyzer with a heating rate of 10 °C/min under air flow. The Ti content actually incorporated into the final titanosilicates was determined by inductively coupled plasma emission spectrometry (ICP) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer after the sample was dissolved in aqueous HF solution.

3. Results and discussion

Fig. 1 showed the evolution of mesoporous structure with crystallization time. If the crystallization lasted for 2 h, four peaks of MCM-41 silica are observed, indicating well-ordered hexagonal MCM-41 (Fig. 1a, left). However, when the crystallization was prolonged to 48 h, the calcined sample (Fig. 1b, left) exhibited three readily distinguished peaks of MCM-41, implying that the MCM-41 structure was maintained after high-temperature hydrothermal treatment. Correspondingly, d_{100} value shifted from 3.9 nm to a higher value of 5.6 nm, indicating that the pore size was expanded during the hydrothermal treatment [31–33]. To our best knowledge, this is the first example of MCM-41 that can be synthesized at high crystallization temperature up to 175 °C while using TPAOH as the base source. Recently, Xiao et al. have shown that the MCM-41 sample prepared at 160 °C only exhibits one peak with relatively low intensity [34]. More importantly, wide-angle XRD patterns showed completely different structure features. At a shorter crystallization time of 2 h, XRD pattern (Fig. 1a, right) only exhibited a 'halo' peak centered at around 23°, implying amorphous nature of pore wall of the MCM-41 silica [35]. If crystallization time was extended to 48 h, the unusually high intensity of the peaks labeled with a star in a wide-angle XRD pattern indicates the a,b-oriented growth of MFI structured zeolite (Figs. 1b, right and S1), confirming that small nanocrystals with MFI structure were formed. In general, only rare cases in literature showed the synthesis of a- and b-oriented MFI zeolites and most of them applied complex SDA or mixed templates to control the oriented growth of zeolite [36,37]. In our study, dual templates of CTATos and TPABr were used and the mesoporous structure was maintained during the whole hydrothermal treatment, which provided a confined environment for the nucleation and growth of zeolite nanocrystals, leading to a,b-oriented growth of MFI nanozeolites. The similar space-limited growth mechanism was proposed by Yan to elucidate the formation of b-oriented MFI zeolite film, where the zeolite crystals formed a continuous film on stainless steel foil [38].

The formation of a- and b-oriented nanozeolite in current mesoporous materials suggested that the amorphous pore walls could be partially transferred into MFI nanozeolite via pesudomorphic crystallization while well keeping the mesostructure. This hypothesis was further proven by direct observation of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

As shown in Fig. 2, some irregular amorphous materials disappeared with increasing crystallization time, which implied that high temperature hydrothermal treatment accelerated the dissolution and redeposition of small silica particles [39]. The redeposition of silica probably resulted in the increase of mesopore wall thickness and the dissolved silica provided the nutrients for nucleation and growth of nanozeolites in the mesophase. The increase in mesopore wall thickness was indirectly proven by the N_2 adsorption–desorption later. Furthermore, most elongated or rod-like mesoporous particles did not exhibit the distinct morphology change during the high-temperature post-synthesis treatment, indicating that the extensive restructuring did not happen. More importantly, both samples did not show the presence of separated MFI structured zeolites, implying that the dual templates functioned in a cooperative manner [16,17].

TEM has been proven to be a powerful technique for the investigation of genesis of nanozeolites in the mesoporous silica matrix [40,41]. As shown in Fig. 3, the boundary between two-dimensional channels could not be easily distinguished in the sample synthesized at 175 °C for 48 h, significantly differing from the sample prepared at a short crystallization time of 2 h which exhibited the typical MCM-41 2D channels with a pore size of ~3.0 nm (Fig. S2). High-resolution TEM image in Fig. 3c displayed that the mesoporous channels were plugged with zeolite nanoparticles with size between 2.0 and 4.0 nm. A close examination by TEM in panels b and d showed that some nanoparticles was in a core–shell structure, and the selected area electron diffraction (SAED)