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Synthesis and formation mechanism of TS-1@mesosilica core–shell materials templated by triblock copolymer surfactant

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ABSTRACT

Micro-/mesoporous composite materials that possessed core–shell structure were prepared through oriented assembly of mesoporous silica on premade titanosilicate zeolite TS-1 using triblock copolymer surfactant P123 as template in an acid-free system. When the pH value of P123/NaCl/H_2O/EtOH/TEOS/TS-1 synthetic system was controlled in the range of 3.5–5.5, the crystalline particles of TS-1 were negatively charged, whereas P123 micelles were partially protonated. Thus induced an electrostatic interaction between inorganic zeolite and organic micelles probably via enhanced hydrogen bonding, and made an oriented assembly of silica oligomer or silica-micelle composite on the surface of P123/TS-1 and further condensation. Otherwise, the silica was self-assembled in a phase separation manner, or failed to form a mesophase. The mesopores in silica shell were of wormhole-like and interconnected with the micropores in TS-1. When as-synthesized core/shell composites were hydrothermally post-treated, the pore volume, specific surface area and pore size of shell increased with increasing temperature. The average shell thickness and particle size were conveniently adjusted in the range of 30–90 nm and 350–500 nm, respectively, by changing the synthesis time, temperature, and amount of silica source added.

1. Introduction

Core–shell materials with ordered porous structures are attractive for their promising applications in many areas including adsorption and separation [1,2], drug delivery [3–6], catalysis [7–16], etc. In general, core–shell structured porous materials are classified into two types of structures, that is, a solid core with a porous shell [9,11,12,17–22,8,23] and a porous core coated by a secondary porous shell [23–30]. Dimodal core–shell materials might provide opportunities to prepare bi-functional or multi-functional catalysts with different types of active sites located independently in porous core and shell [31].

To fabricate a core–shell material containing a mesoporous shell, the most important step is to introduce an oriented mesophase shell onto the core surface. Several techniques have been developed to reach the goal. Ge et al. reported the preparation of Fe_3O_4@mesoporous silica core–shell material via a “surface-protected etching” method to create the mesopore shell [11]. This core–shell nanocatalyst exhibited high catalytic activities for ethylene hydrogenation and CO oxidation. This convenient technique is widely used, but encounters the difficulty in controlling the etching process precisely. In the case of silicalite-1 core–mesoporous shell materials, the synthesis was carried out using octadecyltrimethoxysilane (C_{18}-TMS) as mesopore-directing agent and with silica precursor of tetraethoxysilane (TEOS) for mesophase derivation [27]. The mesopores produced by these conventional methods show nonuniform size distribution and disordered array. A Pt nanoparticle/mesoporous silica material has been successfully prepared by tetradecyltrimethylammonium bromide (TTAB) as template for high-temperature reactions [12]. Deng et al. [19] and Yoon et al. [21] reported almost at the same time a kind of new material spherical solid core/mesoporous silica shell. The shell that was formed using cation-type surfactant cetyltrimethylammonium bromide (CTAB) as template possessed a structure very similar to MCM-41 mesoporous silica. These materials showed an important feature that the mesopore channels in shell were perpendicular to the core. This would permit the molecules to penetrate the shell reaching the core. Similarly, the material of zeolite core mesoporous silica shell was prepared using CTAB as pore-directing agent but without addition of silica source [23]. The mesoporous silica shell was self-assembled from the silica species partially dissolved from the zeolite crystals in strong basic media. In addition, a novel material with solid core and periodic mesoporous organosilica (PMO) shell was also prepared by CTAB as template [18].

Above literature survey indicates that cationic surfactant CTAB is prior to orient a mesoporous silica shell aligned on silica-based

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cores in basic media. However, the pore size of resultant mesopores is usually below 5 nm. In order to obtain large-pore silica shell to extend its application variety, it is preferable to use block copolymer as template, which is usually employed to synthesize mesoporous silica with larger ordered pore (>5 nm). The adsorption of template micelle or oligomer/micelle composite on core surface is critical for introducing an oriented assembly of silica shell. In basic system, the metal oxide cores are mostly negatively charged, thus, cationic surfactant (e.g., CTAB, TTAB) can be adsorbed onto the outer surface of core materials via electrostatic interaction. However, the isoelectric point of nonionic block copolymer such as Pluronic P123 is nearly neutral and has a weak or even a repulsive interaction with core materials either in strong basic media or in acidic system. Thus, copolymer molecules are difficult to adsorb on the outer surface of cores. An alternative strategy is to use CTAB as a co-surfactant. When a solid silica core was modified with CTAB in advance, a mesoporous silica shell templated by triblock copolymer was successfully obtained in strong acidic system [32]. The mesopore shell was formed by the nanorods adsorbing or arranging around the core of CTAB/silica composite. The mesochannels of the shell were shown to run parallel to the surface of core silica spheres. It is still a challenge to make large-pore mesoporous silica shell self-assemble on zeolite crystals.

In contrast to strong acidic conditions usually adopted, large pore mesoporous silica was possibly synthesized using P123 as template in acid-free system [33], pH value of the system was ca. 4.4–5.1, allowing P123 micelles partially protonated. The zeolite crystals introduced into above synthetic system would be negatively charged on surface because the isoelectric point (IEP) of most siliceous zeolites is usually below 4. The interaction or adsorption of P123 micelle with zeolite core is expected to be enhanced. This kind of inter-surface electronic matching may be useful for the synthesis of zeolite/mesoporous silica core–shell material using P123 solely.

The first titanosilicate TS-1 is a highly efficient liquid-phase catalyst which has been applied in various oxidation reactions [34,35]. It is desirable to obtain multi-functional catalysts through modifying TS-1 with metal or metal oxide particles. This study was carried out to synthesize a bimodal porous material by coating TS-1 with mesoporous silica shell directly using triblock copolymer P123 as template. With the mesochannels in shell not always parallel to the surface of TS-1 core, and the oxidation active sites in core still available to the molecules from outside, this novel composite material might be potentially useful for designing promising bifunctional catalysts by introducing secondary active sites into the mesoporous silica shell. In present study, we have investigated the synthesis procedures, post hydrothermal treatment, tuning of shell thickness and formation mechanism of micro/meso-structured TS-1@mesosilica materials assisted by P123 template.

2. Experimental

2.1. Synthesis of TS-1 Particles

TS-1 was hydrothermally synthesized using Tetrapropylammonium hydroxide (TPAOH, 25 wt.% aqueous solution) as structure-directing agent (SDA) from the gels with a molar composition of 1.0 SiO_2:0.025TiO_2:0.18TPAOH:18H_2O at 443 K for 48 h according to conventional procedures reported by EniChem [36]. TS-1 particles were collected by centrifugation, washed by deionized water, dried at 363 K overnight, and finally calcined in air at 823 K for 10 h.

2.2. Synthesis of TS-1@MS core–shell materials

TS-1@mesosilica (denoted as TS-1@MS) materials were synthesized by using triblock copolymer P123 ($EO_{20}PO_{70}EO_{20}$, $M_w = 5800$, Sigma–Aldrich) as template and TEOS ($SiO_2 \geqslant 28.4$ wt.%, Sinopharm Chemical Reagent Co. Ltd.) as silica source. In a typical synthesis, 2.5 g of P123 and 2.92 g of NaCl (99.5 wt.%, Sinopharm Chemical Reagent Co. Ltd.) were dissolved in 199 g of deionized water and 76.0 g of absolutely ethanol (EtOH) at room temperature. After stirring for 2 h, 1.0 g of TS-1 was added into the above solution, stirred vigorously for 30 min and ultrasonicated for another 30 min. Thereafter, 2.1 g of TEOS (10 mmol) was added dropwise into the mixture and mechanically stirred (ca. 500 rpm) at 303 K for 48 h. The molar composition in liquid-phase was 0.043P123:5NaCl:1100H_2O:165EtOH:1.0TEOS. To investigate the effects of hydrothermal treatment on silica shell formation, the temperature of reaction mixture was raised to 343 K or 373 K for another 24 h. The reaction mixture premade at 303 K was also adjusted to reach 1.0 M HCl using 37 wt.% HCl, and then heated at 373 K for 24 h in autoclave under stirring. The white solid precipitate was separated by filtration, washed with deionized water for three times, and dried at 363 K overnight. The samples were calcined to remove organic species at 823 K in air for 6 h. The shell thickness was tuned by changing the amount of added TEOS. The samples were denoted as TS-1@MS-*x*, where *x* represents the mole-to-weight ratio of TEOS to TS-1 in mmol g^{-1}. In the case of TS-1@MS-10, the as-synthesized sample amounted 1.76 g. Assuming TS-1 remained unchanged during self-assembling of mesophase silica shell, the proportion of TS-1 core was calculated to be 56.8 wt.% in as-synthesized composite. After removal of organic species by calcination, the amount of solid product turned to be 1.51 g, corresponding to 94.4% yield.

To study the formation mechanism of the core–shell materials assisted by nonionic surfactant P123, the pH value of the composition mixture was monitored at different synthesis time. The zeta potentials of TS-1 suspension and P123 solution at different pH values were measured at 298 K on a Malvern Zetasizer instrument.

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Rigaku Ultima IV X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5405$ Å) at 30 kV and 25 mA. The pore structures of core–shell materials were analyzed by nitrogen adsorption/desorption at 77 K on a BELSORP-MAX instrument after activated at 573 K under vacuum for at least 10 h. Specific surface areas were calculated using Brunauer–Emmett–Teller (BET) method in the P/P_0 range of 0.05–0.2. The pore size distribution of micro/mesoporous core–shell materials calculated by HK and BJH methods for micropores and mesopores, respectively. The pore sizes were obtained from the peak positions of distribution curves. Total pore volume was accumulated at relative pressure $P/P_0 = 0.975$, and that of micropore volume was obtained by *t*-plot method.

The SEM images and Energy Dispersed X-ray (EDX) emission spectra were taken on a Hitachi S-4800 field emission scanning electron microscope. The TEM images were taken on a JEOL-JEM-2100 transmission electron microscope. Thermogravimetry (TG) and derivative thermogravity (DTG) analyses were carried out on a Mettler TGA/SDTA 851^e instrument with a ramping rate of 10 K min^{-1} in an air flow of 40 mL min^{-1}. The amount of Si, Ti and Na was quantified by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo IRIS Intrepid II XSP atomic emission spectrometer.

2.4. Liquid-phase epoxidation of 1-hexene with H_2O_2

The epoxidation of 1-hexene with H_2O_2 was adopted as a probe reaction to evaluate the catalytic availability of the active sites inside core particles of TS-1. The reaction was carried out under vigorous stirring in a 50 mL glass flask connected to a cooling