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Formation of mesoporous Co_3O_4 replicas of different mesostructures with different pore sizes

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ABSTRACT

Mesoporous metal oxides Co_3O_4 are prepared via hard templating synthesis method by using various mesoporous silicas with different pore size as templates. The pore size of the mesoporous silicas with the symmetry of two-dimensional (2d)-hexagonal *p6mm*, bicontinuous cubic $Ia\bar{3}d$ and $Pn\bar{3}m$ have been controlled in the range of 6.6–10.7, 4.2–7.5 and 5.1–6.7 nm, respectively, by choosing different surfactants and co-surfactants and by adjusting either the aging temperature or the ionization degree of the surfactant. The pore size of the silica template has been considered to be an important factor that determines the mesostructure of the resulting metal oxides. It has been found that for *p6mm*, it is easier to replicate the mesoporous symmetry at large size of mesopores. For $Ia\bar{3}d$, at large-pore size two sets of bicontinuous meso-channels are replicated into mesoporous Co_3O_4, while small-pore $Ia\bar{3}d$ leads to replication of both one set and two sets of meso-channels. Co_3O_4 can replicate both one set and two sets of bicontinuous $Pn\bar{3}m$ meso-channels at all pore sizes that can be obtained (5.1–6.7 nm), indicating the existence of ordered complementary micropores within the silica walls.

1. Introduction

Mesoporous metal oxides are of great interest for applications in catalysis since they can be regarded as self-supported catalysts with large specific surface areas and shape selective properties, which find utilities in areas of catalysis, chemical sensing, superconductivity, colossal magneto-resistance, piezoelectricity, etc. [1–4]. Their nano-sized forms differ greatly in many properties from the bulk materials [5]. These materials can be synthesized by using either organic soft templates [6], similar to the synthesis of mesoporous silica, or mesoporous silica as a hard template [7–10]. While soft templating normally results in amorphous materials, compared to silica, the surfactant/oxide composite precursors are often more susceptible to suffer from lack of condensation, redox reaction, and phase transitions accompanied by thermal breakdown of the structural integrity [6,11]. The hard templating method was firstly introduced by Ryoo and co-workers for synthesizing mesoporous carbon [7,12–14], and several mesoporous metals [15,16], metal sulfides [17], nitride [18] and oxides [19–21] have been fabricated, although the wall of most of these materials was still disordered and the formation mechanisms of these new materials were not discussed extensively. Recently, researchers reported the synthesis of mesoporous metal oxides by using hard templating method, some of which are in single crystalline state [22–29].

Mesoporous cobalt oxide Co_3O_4 is one of the metal oxides that have been studied extensively. Zhao et al. and Schüth et al. prepared mesoporous Co_3O_4 with functional mesoporous silicas as hard templates by using impregnating method [20,23]. Zhou et al. prepared mesoporous Co_3O_4 by using a solid–liquid route, and products were maintained to be single crystal [25]. The formation mechanism of mesoporous Co_3O_4 has been studied, and the factors determining the porous structure of replica are considered to be crystallization conditions, pore size of template, interconnectivity between mesopores and precursor loading levels [22,27]. Recently, Schüth et al. visualized the pore topology of mesoporous Co_3O_4 by high-resolution scanning electron microscopy [28].

Various mesoporous silicas can be used as hard template for synthesizing mesoporous metals or metal oxides. Two typical examples are mesoporous silica SBA-15 with hexagonally close-packed straight mesopores connected by some smaller channels and micropores [30], and KIT-6 with $Ia\bar{3}d$ symmetry containing three-dimensional (3d) bicontinuous meso-channel networks [31]. Typically, such methods employ mesoporous silicas as the hard templates, into which a solution-based precursor of the desired metal or metal oxide is introduced, followed by heating or hydrogenation to form the desired metal oxide or metal and silica

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composites [10]. The silica template is dissolved away to leave a replica mesoporous structure of the target compound. The hard templating route has opened a way to great varieties of mesoporous transition metal oxides.

The relationship between the pore size of the silica template and that of the obtained metal oxide replicas is an interesting topic. Here, the mesostructures including 2d-hexagonal *p6mm*, cubic *Ia*$\bar{3}$*d* and *Pn*$\bar{3}$*m* that possess rod-type pore system have been selected for studying the relationship, because, in the case of cage-type mesoporous silica, it is well known that the small apertures make it difficult for the precursors to completely fill the cages and to form rigid carbon or metal oxide bridges between their nanoparticles prepared in silica cages. Here, we present a report on the study of the effect of pore size and pore symmetry on the formation of mesoporous Co_3O_4 by preparing the mesoporous cobalt oxide Co_3O_4 (*Fd*$\bar{3}$*m* crystal structure) using mesoporous silicas SBA-15 (2d-hexagonal *p6mm*), KIT-6 (bicontinuous cubic *Ia*$\bar{3}$*d*) and AMS-10 (bicontinuous *Pn*$\bar{3}$*m*) with different pore size as hard templates. The dependence of the structure of replica on pore size and symmetry of the silica template will be discussed in details. Different from earlier literatures, in this study, we will show that solely the pore size of silica template cannot determine the replication extent, and the discussion is valid only when considering the mesopore symmetry. Structural properties of the mesoporous silicas, especially newly developed AMS-10, are also derived from inverse replication.

2. Experimental section

2.1. Synthesis

2.1.1. Synthesis of mesoporous silica

The mesoporous silica templates SBA-15 [23], KIT-6 [24], and AMS-10 [32] were prepared according to the procedure described previously.

2.1.1.1. Synthesis of 2d-hexagonal p6mm structured mesoporous silica (SBA-15) with different pore size. SBA-15 mesoporous silica was synthesized by using the triblock copolymer Pluronic P123 (EO_{20}-$PO_{70}EO_{20}$, BASF) as surfactant and tetraethoxylsilicon (TEOS) as silica source. In a typical synthesis experiment, TEOS (20.8 g) was added to a mixture of P123 (10 g), HCl (62.57 g, 35 wt.%), and deionized water (319 g) under stirring at 35 °C. After the mixture was stirred for 24 h, the mesostructured products thus formed were aged at 100 °C for additional 24 h. The products were filtered, dried without washing, and calcined at 550 °C. The pore size was controlled by adjusting aging temperature in the range of 40–100 °C. The samples with three pore sizes have been synthesized at aging temperature of 40, 80 and 100 °C. These samples were denoted as SBA-15-40, SBA-15-80, and SBA-15-100, respectively.

2.1.1.2. Synthesis of bicontinuous Ia$\bar{3}$*d structured mesoporous silica (KIT-6) with different pore size.* The large-pore cubic *Ia*$\bar{3}$*d* mesoporous silica KIT-6 was synthesized by using triblock copolymer Pluronic P123 as surfactant and TEOS as silica source. In a typical synthesis, 6 g of P123 was dissolved in 217 g of distilled water and 11.8 g of HCl (35 wt.%). To this, 6 g of butanol was added under stirring at 35 °C. After stirring for 1 h, 12.9 g of TEOS was added at 35 °C (TEOS:P123:HCl:H_2O:BuOH = 1:0.017:1.83:195:1.31 mol ratio). The mixture was left under stirring for 24 h at 35 °C, and subsequently aged for 24 h at 100 °C under static conditions in a closed polypropylene bottle. The products were filtered, dried without washing, and calcined at 550 °C. In the similar manner of SBA-15, the pore size was controlled by adjusting aging temperature in the range of 40–100 °C. The samples with three pore sizes have been synthesized at different aging temperature of 40, 80, and 100 °C. These samples were denoted as KIT-6-40, KIT-6-80, and KIT-6-100, respectively.

2.1.1.3. Synthesis of bicontinuous Pn$\bar{3}$*m structured mesoporous silica (AMS-10) with different pore size.* The bicontinuous cubic *Pn*$\bar{3}$*m* mesoporous silica (AMS-10) was synthesized by using *N*-myristoyl-L-glutamic acid sodium salt (C_{14}GluAS, one of the carboxylic acid groups of the glutamic acid was neutralized by sodium hydroxide) as surfactant, *N*-trimethoxylsilylpropyl-*N*,*N*,*N*-trimehylammonium chloride (TMAPS) as co-structure-directing agent (CSDA) and TEOS as silica source. In a typical synthesis experiment, HCl (0.417 g of 1 mol L^{-1} solution) was added to a solution of C_{14}GluAS (0.379 g, 1 mmol) in deionized water (36 g) under stirring at 80 °C. After the solution became homogeneous, a mixture of TMAPS (0.773 g, 50 wt.% in methanol, 1.5 mmol) and TEOS (3.12 g, 15 mmol) was added, and the mixture was stirred at 80 °C for 10 min. The molar composition of the final gel was C_{14}GluAS/TMAPS/TEOS/H_2O/HCl = 1:1.5:15:2000:0.42. The precipitate was then aged at 80 °C for 2 days, filtered, and calcined at 550 °C for 6 h to remove the surfactants. The pore size of AMS-10 was controlled by adjusting the HCl/C_{14}GluAS molar ratio in the range of 0.42–0.48. The samples with four pore sizes were synthesized with different HCl/C_{14}GluAS molar ratios of 0.42, 0.44, 0.45 and 0.48. They were denoted as AMS-10-0.42, AMS-10-0.44, AMS-10-0.45 and AMS-10-0.48, respectively.

2.1.2. Synthesis of mesoporous Co_3O_4 replica

In a typical synthesis of mesoporous Co_3O_4, 0.75 g of $Co(NO_3)_2{\cdot}6H_2O$ (98% Aldrich) was dissolved in 16 mL of ethanol followed by addition of 0.5 g of mesoporous silica templates. The mixture was stirred at room temperature until nearly dry powder had been obtained; the sample was then heated slowly to 300 °C and calcined at the same temperature for 3 h to pyrolyze the nitrate. The impregnation procedure was repeated twice with 0.4 g of $Co(NO_3)_2{\cdot}6H_2O$ and 0.25 g $Co(NO_3)_2{\cdot}6H_2O$ dissolved in 16 mL ethanol, followed by calcination at 550 °C for 5 h with a ramp 1 °C min^{-1} for metal oxide to crystallize. The resulting samples were treated with 10% HF to remove the silica template, centrifuged, washed with water and ethanol, and then dried at 60 °C in air. They were denoted as Co_3O_4-SBA-15-X, Co_3O_4-KIT-6-X and Co_3O_4-AMS-10-Y (X: aging temperature of silica template in °C; Y: molar ratio of HCl/C_{14}GluAS in the synthesis of AMS-10).

2.2. Characterizations

X-ray diffraction (XRD) patterns were recorded on a Rigaku RINT 2000/PC Multiplex instrument using Cu Kα radiation (λ = 0.15406 nm), operated at 40 kV and 20 mA (0.8 kW) at the rate of 1.0° min^{-1} over the range of 0.8–6.0° (2θ).

N_2 adsorption–desorption isotherms were measured at −196 °C on a Quantachrome Nova 4200e volumetric adsorption analyzer. Before the adsorption measurements, all samples were outgassed at 200 °C in the port of the adsorption analyzer for 4 h. Specific surface areas were calculated via the Brunauer–Emmett–Teller (BET) model in regions applicable to the derivation of the model between P/P_0 values of 0.05–0.3. The total pore volume was determined from the uptake of nitrogen at a relative pressure of $P/P_0 \sim 0.99$. Pore size distribution curves were obtained from the adsorption branch by using the Barrett–Joyner–Halenda (BJH) method.

Scanning electron microscopy (SEM) features of all the samples were observed by SEM (JEOL JSM-7401F). The samples were observed without any metal coating. High-resolution transmission electron microscopy (HRTEM) images were taken from thin edges of particles supported on a porous carbon grid, using JEOL JEM-3010 electron microscope (point resolution 1.7 Å, Cs = 0.6 mm)