



Synthesis of nanoporous metal oxides through the self-assembly of phloroglucinol–formaldehyde resol and tri-block copolymer

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ABSTRACT

A versatile route to synthesize nanoporous crystalline metal oxides has been developed through the self-assembly of phloroglucinol–formaldehyde resol and tri-block copolymer templates. Materials were characterized by a complementary combination of X-ray diffraction, nitrogen sorption, and transmission electron microscopy. Metal oxides synthesized using this route have remarkably high surface area when compared with the commercial samples. The surface area of metal oxides decreased upon calcination at higher temperatures. However, the surface area was still much higher when compared with the commercial samples. TEM investigation reveals that upon calcination at higher temperature, the size of the crystal increased but the short range order was merely disturbed. The analyses show that the present method is suitable as a direct route to synthesize crystalline nanoporous metal oxides. Hydrogen bonding plays a key role in the preferential arrangement of porous metal–carbon structure in the domain of tri-block copolymer. The nanoporous metal oxides with ordered mesoporous structure, high surface area, and crystalline framework are expected to show significant improvement in catalysis and nano-technology.

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1. Introduction

Last decade is witnessed for the development of nanoporous materials for their numerous potential applications. Porous materials have attracted considerable attention of chemists and material scientists because of their commercial applications in chemical separation, heterogeneous catalysis and as host matrixes for bio-technological applications. The nanostructure materials are generally synthesized by the synergistic self-assembly of surfactant micelles and inorganic species to form mesoporous ordered materials [1,2]. Since the discovery of mesoporous silica materials [3], increasing attention has been focused on the synthesis of siliceous and non-siliceous mesoporous materials. It was demonstrated that the method for the preparation of M41S materials can be extended to the preparation of non-siliceous nanoporous materials such as metal oxides [4–7]. Since the chemistry of nanoporous metal oxide is more versatile than that of the classical mesoporous silica materials, the potential of the metal oxide compositions seems to be higher than that of the silica materials. Nanoporous metal oxides are of great importance in many applications including catalysis, electronics, and sensor technology [8–13]. These materials have interesting electric, magnetic and thermal

properties. Nanoporous metal oxides with ordered mesoporous structure, high surface area and crystalline framework structures are expected to show significant improvement in catalysis and nano-technology.

It may be noted that the silica and aluminosilicates are stable materials under different synthesis and calcination condition, whereas non-silica precursors are often more susceptible to hydrolysis, redox reaction or phase transitions accompanied by thermal breakdown of the structural integrity. These factors make the preparation of non-siliceous mesoporous material difficult. Unlike mesoporous silica, mesoporous metal oxides with long range ordered pore, generally suffer from poor thermal stability because of their amorphous natures. The pores of the amorphous mesoporous metal oxide may collapse upon extended heating, resulting in damaged pore structure and diminished surface area, thus posing serious threat to its applications [14–16]. The absence of crystal lattice to hold on the pore walls is likely to be the main reason for structural collapse [17]. Hence, a rational way to improve the thermal stability of the mesoporous metal oxide is to have crystalline mesoporous structures [18], or to embed nanocrystalline particles as structural bricks into the amorphous walls [19]. Antonelli et al. [6] and Ciesla et al. [7,20] first reported the mesoporous framework of TiO₂ and ZrO₂, respectively. Then, many papers related to non-siliceous materials appeared in the literature, and a few reviews have been published [4,21–25]. Mesoporous metal oxides can be synthesized using soft templates as well as hard

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templates. The majority of soft template routes utilize organic precursor species which allow the formation of liquid crystals, such as molecular surfactants or block copolymers. Using soft templates, two general phenomena may occur: (i) the composite forms cooperatively from the species present in solution, which are not in a liquid–crystalline state prior to mixing of the precursors and (ii) a liquid–crystalline precursor phase is used which is infiltrated with the inorganic species (true liquid crystal templating). Large-scale nanorods of crystalline cerium oxide have been prepared by a simple surfactant-assisted hydrothermal process in the presence of the cationic surfactant cetyltrimethyl ammonium bromide [26]. Several other soft templates such as octadecylamine, ethyleneglycol and citric/tartaric acid have also been utilized for the synthesis of metal oxides [27–29]. Hard template mediated synthesis of mesoporous metal oxides has been reported in the recent past [30–34]. For the preparation of ordered nanostructure array, a hard template has some advantages over soft template, especially in its specific topological stability, accuracy, uniformity and controllability. Mesoporous silica having large surface area and pore volume makes it a perfect candidate to serve as a hard template. The space of the regular channels in mesoporous silica materials has been used as a nanoreactor for producing mesoporous composites [35,36] and as hard templates for crystal growth of porous metal oxides [30–34]. The general route for producing the porous crystals of oxides using mesoporous silica as template is to introduce a metal-containing precursor into the silica pores, allowing the precursor to decompose followed by crystal growth of metal oxides inside the pores during thermal treatment. Mesoporous carbon, obtained from the mesoporous silica by nanocasting route, can be reversibly used as a hard template for ordered mesoporous silica materials [35–40]. Recently, mesoporous metal oxides have been prepared via non-replication technique using mesoporous carbon (CMK-3) as a hard template [41].

Though several synthetic pathways are reported to date for the synthesis of mesoporous metal oxides, however, a general one-step synthetic strategy to prepare crystalline nanoporous metal oxides is still desired. In this manuscript, a direct, one step synthetic protocol to synthesize nanoporous metal oxides has been reported. The essence of this method is the direct use of the self-assembly of block copolymers as templates for generation of porous metal–carbon structures, without the extra step of generating templating silica structures. Mesoporous metal oxides were synthesized using tri-block copolymer (structure-directing agent), a mixture of phloroglucinol and formaldehyde (carbon source) and metal nitrates (metal source) under mild acidic condition.

2. Experimental

2.1. Materials

Cerium nitrate hexahydrate, zirconyl nitrate hydrate, phloroglucinol, and phenol were obtained from Aldrich. Surfactants were commercially available from Aldrich and BASF and were used as received. Surfactant include $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{106}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{106}\text{H}$ (designated $\text{EO}_{106}\text{PO}_{70}\text{EO}_{106}$, BASF, Pluronic F-127), $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$ (designated $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$, Aldrich, Pluronic P-123), Polyoxyethylene lauryl ether (designated Brij-35, Aldrich), Poly(ethylene glycol) methyl ether (average $M_n = 2000$, Aldrich).

2.2. Sample preparation

Mesoporous metal oxides were synthesized using polymer (structure-directing agent), a mixture of phloroglucinol and formaldehyde (carbon source) and metal nitrates (metal source)

under mild acidic condition. The optimized molar composition of the mixture was phloroglucinol/metal nitrates/formaldehyde/ethanol/ $\text{HNO}_3 = 1/1/2/30/0.13$; phloroglucinol/polymer = 1/3 (weight ratio).

In a typical synthesis, (10 mmol, 1.62 g) phloroglucinol and 4.86 g surfactant (polymer) were dissolved in 25 ml of absolute ethanol. After dissolving the solid, metal nitrate (10 mmol) was added and stirred at room temperature till complete dissolution. 0.15 g of 65% HNO_3 was added to the above reaction mixture. The resultant solution was stirred at room temperature until a light pink color appeared. Subsequently, 1.6 g of 37% formaldehyde was added to the above solution. The reaction mixture was stirred for further 4 h at room temperature and then transferred to a petri dish and ethanol was evaporated at room temperature. It was then cured at 373 K for 24 h before carbonization. Materials were carbonized at 1073 K under nitrogen atmosphere via heating ramp of 1 deg/min and kept at 1073 K for 3 h. The resultant carbon–metal composite was further calcined at a desired temperature (in the range of 723–1273 K) for 4 h. Elemental analysis confirms that no carbon impurity was present in the sample after calcination (723–1273 K).

2.3. Instruments

X-ray diffraction (XRD) patterns were recorded on a Rigaku Multiplex instrument operated at 1.5 kW (using $\text{Cu K}\alpha$ radiation, graphite monochromator). Diffractograms were recorded between 0.5° and 80° with a step of 0.02° (2θ). N_2 adsorption/desorption at 77 K was performed by NOVA 1000 series Quantachrome Instruments volumetric adsorption analyzer. Before the measurements, samples were degassed under vacuum for 6 h at 623 K. The Brunauer–Emmett–Teller (BET) equation was used to calculate the apparent surface area from adsorption data obtained at P/P_0 between 0.1 and 0.3. The pore size distributions (PSD) were calculated by analyzing the adsorption branch of the N_2 sorption isotherm using the Barret–Joyner–Halenda (BJH) method. Transmission electron microscope (TEM) images were taken from thin edges of particles supported on a porous carbon grid by using Hitachi H-88 Tecnai transmission electron microscope operated at 200 kV.

3. Result and discussion

Nanoporous metal oxides were synthesized using tri-block copolymer (structure-directing agent), a mixture of phloroglucinol and formaldehyde (carbon source) and metal nitrates (metal source) in absolute ethanol. CeO_2 is one of the most important rare earth metal oxide widely used in emerging technologies for environmental and energy related applications due to its ability to store and release oxygen. It is widely used as a promoter in three-way catalyst for the elimination of toxic auto-exhaust gases, fuel cells, oxygen sensor and low temperature water–gas shift reaction. Nanocrystalline CeO_2 with high surface area and open mesoporous structure is desired for the above application due to kinetic advantages. For many such applications, it is desirable to prepare CeO_2 samples with large surface area. In this study, main focus was given for the synthesis of nanoporous CeO_2 . Preliminary study was devoted to obtain optimized synthesis condition to prepare high quality CeO_2 . CeO_2 was synthesized using phloroglucinol, formaldehyde and cerium nitrate hexahydrate $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (metal source) in absolute ethanol.

The nanocrystalline nature of the CeO_2 samples was confirmed by powder XRD. Metal oxide exists in the crystalline structure only after carbonization and calcination. Wide-angle XRD pattern reveals that the material is crystalline and the reflections

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