Porous nanoballs formed through an in situ generated “framework” template

Fei Teng, Li Wang, Yongfa Zhu *

Department of Chemistry, Tsinghua University, Beijing
100084, China

Received 23 February 2007; received in revised form 10 June 2007; accepted 14 June 2007
Available online 19 June 2007

Abstract

The unique hierarchic porous nanoballs were constructed through a controllable hydrolysis process in 40–60 vol.% ethanol aqueous solution. The effects of ethanol concentration, hydrolysis duration, solvent, heating way on the formation of the porous structures have been investigated. The samples were characterized by TEM, EDX, SEM, XRD, TG, and pH apparatus, etc. An in situ generated “framework” template was proposed to explain the formation of porous structure. The results showed that ethanol molecules enclosed in the “framework” played an important role in the formation of the porous structures. Importantly, the formation process of such nanoballs is useful for the structure control of porous materials. © 2007 Elsevier B.V. All rights reserved.

Keywords: Porous; Nanoballs; Framework template; In situ

1. Introduction

Recently, great progress has been made in research on hollow nanostructures, which could be applied as biomaterials [1], nano-reactors [2], and lubricates [3]. Particularly, mesoporous filter and nano-reactor play important roles in biologic chip [4], chemical detector [5], chemical sensor [6], and high-efficiency catalyst/support [7]. Consequently, nanoballs with mesopores will be the good candidates for manufacturing a variety of nanodevices. In all of the methods reported, mesoporous structure and nanoballs cannot be obtained simultaneously. There is no good way to prepare porous nanoballs using general templates, since the templates with secondary structure are hard to be found so far as we know. Fortunately, the work performed by Mann and co-workers [8–11] provides us with some ideas to design a new way to fabricate the mesoporous structure. In their works, the porous structure was obtained using foams as templates: the pore size of the obtained sample was larger than 50 nm [8]. Nevertheless, it is difficult to accurately control the pore size. As a result, understanding the formation process of the pores is important to control the pore structure effectively.

Herein, we reported, for the first time, a facile synthesis of MAI₄O₇ (M = Sr, Ba) nanoballs with porous structures through an in situ generated “framework” template. The nanoballs with unique hierarchic nanopores were constructed by the controllable hydrolysis of MAI₂O₄ (M = Sr, Ba) spinel powders in 40–60 vol.% ethanol aqueous solution, in which the pore sizes were handily controlled in the range of 10–30 nm. The effects of ethanol concentration, hydrolysis duration, drying ways and the intensity of electron beam on the pore structures were investigated. Besides, the annular arrangement of pores with a diameter of 10 nm resulted in hierarchic porous nanoballs. Most importantly, a “framework” template generated in situ was proposed to explain the formation of the porous structures, which is significantly different from the typical template process. The idea would provide an important contribution to the structure control for the porous structures.

2. Experimental section

2.1. Preparation of spinel SrAl₂O₄ and BaAl₂O₄ powders

The SrAl₂O₄ and BaAl₂O₄ spinels were prepared by a non-crystalline route, as reported in our previous research [12,13]. Typically, the fresh Al(OH)₃ colloid was prepared by dropping NH₃·H₂O into an Al(NO₃)₃ solution, followed by washing for...
several times. Then H$_5$DTPA solution was mixed with fresh Al(OH)$_3$ and SrCO$_3$ in a calculated molar ratio, heated and stirred with a magnetic stirrer to promote the formation of heteronucleus complexes. After the solution became transparent, it was dried at 60–80°C to yield the precursor. X-ray diffraction (XRD) patterns illustrated that the precursor was amorphous. Nano-sized spinel SrAl$_2$O$_4$ was synthesized by calcining the precursor at 600°C for 3 h in air. A slow heating rate (5°C min$^{-1}$) was used to increase temperature to various pre-set temperatures and maintained for a defined period of time to promote the formation of SrAl$_2$O$_4$ with spinel structure. BaAl$_2$O$_4$ spinel was also prepared by the similar method.

### 2.2. Preparation of porous nanoballs

The spinel-structured SrAl$_2$O$_4$ powder was dispersed in 40–60 vol.% ethanol aqueous solution, in which the molar ratio of SrAl$_2$O$_4$ to the mixture solvents was controlled above 1:40; and then the mixture system was sonicated for 10 min to promote the hydrolysis of SrAl$_2$O$_4$. The solids in the suspension were removed by centrifuging at 500 r min$^{-1}$. After the recovered topper solution was exposed to air for 60 min, the solids was recovered by high-speeded centrifugation (5000 r min$^{-1}$) and then dried naturally in air. BaAl$_2$O$_4$ spinel was used to prepare the porous counterpart.

### 2.3. Characterization

The morphology of the sample was characterized with a TEM (Japan Hitachi H-800, accelerating voltage of 200 kV) equipped with a Link ISIS EDX analyzer. The same instrument was involved in the recording of X-ray maps. The acceleration voltage in all cases was 15 keV and the current was 1.2 nA. In the recording of X-ray maps the current of 6.7 nA was used. The powders were dispersed in ethanol ultrasonically, and then the samples were deposited on a thin amorphous carbon film supported by copper grids. The morphology and compositional distribution of the sample in the samples was determined by use of a SEM (Hitachi S-450). TG curve was performed on Pyris 1 TGA thermogravimeter (U.S. Perkin-Elmer Co.), and the temperature rises from room temperature to 600°C at a rate of 10°C min$^{-1}$. pH values of the solution were determined with pH apparatus (PHS-25CW, Shanghai LIDA Instrument Co.) at 25°C.

![Fig. 1. The hollow sample prepared by the hydrolysis of SrAl$_2$O$_4$ powders in 50 vol.% ethanol aqueous solution for 60 min: (a) TEM images; (b) EDX spectra; (c) top images of SEM; (d) side images of SEM.](image-url)
3. Results and discussion

3.1. Effect of ethanol concentration on the porous nanoballs

The hydrolysis of SrAl₂O₄ powders was carried out in 40–60 vol.% ethanol aqueous solution at room temperatures to synthesize the hierarchic porous nanostructures (See supporting information of experimental section). Fig. 1a gives the typical TEM images of the obtained nanoballs in 50 vol.% ethanol aqueous solution. It is clear that the nanoballs of 80 nm in diameter are well uniform. A clair-obscure contrast between the centre and outer regions of the nanoballs can be observed clearly, confirming that the interesting nanostructures with hollow interiors of about 10 nm in size. The sample compositions were further characterized by EDX analysis, as shown in Fig. 1b. The analysis results show that the sample is comprised of Al and Sr, and the atomic ratio of Sr to Al is 1:4, since Cu signals resulted from copper grid. The sample was further characterized by SEM (Fig. 1c and d). The top and side SEM images of the sample show the formation of three-dimensional ball-like structures with smooth surface. Since the C, O and H elements cannot be detected by EDX spectra, TG analysis was performed to determine the sample compositions, as shown in Fig. 2. In the range of 30–600 °C, two peaks of weight loss in TG curve can be observed. In the range of 30–250 °C, the weight loss (14 wt.%) of the sample can be ascribed to the removal of water, ethanol, and part of hydroxyls; in the range of 250–600 °C, the weight loss (7 wt.%) of the sample can be caused by the removal of hydroxyls. By calculation, the sample is comprised of Sr₄Al₄O₉(OH)₃ and contains 14 wt.% ethanol. The molar ratio (1:4) of Sr to Al is consisted with the analysis result of EDX above. Combing with the preparation and the used chemicals, we could deduce that the sample may have the structure very similar to Sr₄Al₁₂O₃₇, which is a long afterglow phosphor [14]. This could also be confirmed by XRD patterns (See supporting information of Fig. S1).

Fig. 2. TG curves of the sample prepared in 50 vol.% ethanol aqueous solution for 60 min.

The porous structures of the sample can be handily adjusted by controlling ethanol concentration, as typically shown in Fig. 3. The smooth and uniform mesoporous nanoballs (100 nm in diameter) were obtained in 40 vol.% ethanol aqueous solution (Fig. 3a). After the sample was exposed to electron beam for about 8 min, a large number of tiny pores less than 5 nm in size were formed. It is interestingly that the pores in the fringe parts are larger than those in the centre region (the insert of Fig. 3a). These porous nanostructures show higher stability under exposed electron beam than those formed in 50 vol.% ethanol aqueous solution. This probably means that there were less solvents enclosed within the nanostructures. In 50 vol.% ethanol aqueous solution, the sizes of the formed nanoballs are 80 nm; after being exposed to electron beam for 2 min, the large pores have the diameters of about 15 nm and the shell thickness is about 5 nm (Fig. 3b); it is interesting that the multi-shelled struc-
tures were formed (the insert of Fig. 3b). When the volume ratio of ethanol to water was increased to 60 vol.%, the formed hollow nanostructures immediately deformed to some extent even under exposed to electron beam for 2 min. Differing from those formed in 40 vol.% ethanol aqueous solution, the small hollow balls connected with one another, whose average diameters and thickness of shells are about 50 and 5 nm, respectively. This may be ascribed to the high concentration of ethanol in the mixture. However, only very fewer of hollow nanostructures contained the tiny pores (Fig. 3c).

3.2. Effect of hydrolysis duration on the porous nanoballs

The effect of hydrolysis duration on the prepared sample in 50 vol.% ethanol aqueous solution was further investigated (Fig. 4). After hydrolysis for 10 min, the morphology of the obtained sample is similar to that of SrAl2O4 powders, probably because little hydrolysis has taken placed (Fig. 4a); after hydrolysis for 60 min, the obtained sample was composed of the regular nanoballs, which were much different from the original SrAl2O4 sample (Fig. 4b); in the range of 80–120 min, it was found that the number of the regular nanoballs decreased significantly and some nanowires were formed; after 120 min, SrCO3 nanowires with the diameters of about 20 nm and the lengths of about 3–5 μm were obtained (Fig. 4c); after 300 min, the orthogonal SrCO3 nanorods were formed (Fig. 4d). On base of our previous study [15], SrAl2O4 hydrolyzed in pure water to form the mixture of Al(OH)3 and SrCO3, where SrCO3 resulted from the reaction between Sr(OH)2 and CO2 in air. The colloidal Al(OH)3 agglomerated severely to precipitate out of the solution; therefore, it could be inferred that the hydrolysis of SrAl2O4 powders have completed after 120 min. It could also be concluded that the hydrolysis of SrAl2O4 in 50 vol.% ethanol aqueous solution was much slower than that in pure water.
water, and the formed nanoballs may be an intermediate in the process.

3.3. Effect of solvent on the formation of the porous nanoballs

The above results showed that ethanol played an important role in the formation of the nanoballs. To research the solvent effect, the solvent was varied from ethanol to acetone and glycol. However, in acetone–water or glycol–water, we have not obtained the uniform nanoballs with hollow interiors. (See supporting information of Figs. S2 and S3), suggesting that the formation of the hollow nanostructures may be correlated to the properties of the solvents. Considering their similar polarities, we suggested that ethanol molecules stabilized the intermediate structure. While Sr dissolved and entered the solution, some “holes” or vacant sites” were formed. Ethanol molecules may adsorb on and/or fill into these “holes or vacant sites”, and the intermediate could exist stably for enough time. As a result, ethanol could effectively stabilize the Al-enriched framework. For glycol or acetone molecule, it was probable that they cannot adsorb on or fill into the “holes or vacant sites” due to their stereo effects (their large molecule sizes). As a result, the intermediate was unstable and the Al-enriched framework collapsed. The proof is needed to research further. The above results have shown that the mixture compositions and the hydrolysis duration have significant influences on the formation of the porous nanostructures.

3.4. Effect of heating way on the formation of the porous nanoballs

In this work, an interesting phenomenon was also observed while the hollow nanostructures were exposed to electron beams with TEM. Fig. 5 shows the TEM images of the mesoporous nanoballs, which were prepared by the hydrolysis of spinel SrAl₂O₄ powders in 50 vol.% ethanol aqueous solution. The TEM sample was then exposed to electron beam for different durations. After exposed for 2 min, the nanostructures are highly dispersed, while the bare surfaces kept smooth (Fig. 5a). The TEM micrograph with a high magnification of single nanoball is shown in the insert of Fig. 5a, indicating that the nanoball has the multi-shelled structure. There are many tiny pores with the diameters of less than 10 nm near the wall of the nanoball, as well as the connected shells with the thickness less than 5 nm. While being exposed for 5 and 10 min (Fig. 5b and c), the sizes of the pores within the nanoballs increased to about 40 nm; the neighbouring nanoballs merged into one another, probably indicating that the more ethanol molecules remained in nanoballs were released. As mentioned above, the release of volatile molecules could be attributed to thermal effect by electron beams. While electron beams irradiated the sample, the tiny pores immediately merged together and the shapes of nanoballs deformed significantly. At a low electron beam intensity (i.e. ×50,000 magnification), the surfaces of nanostructures are smooth and clean-cut; at a high electron beam intensity (i.e. ×100,000 magnification), the nanostructures deformed obviously. After being exposed to electron beams, the tiny pores within the ball inner firstly emerged, then merged and grew bigger with the duration gradually. As a result, the mesoporous nanostructures were finally formed. It was found that while the intensity of electron beam was lowed, the deformation process would become slow and then stopped; but the process took place again while the intensity of electron beam increased again. This can be ascribed to the heating effect caused by electron beam. The deformation process of nanostructures under electron beam led to a new concept for controlling porous structures. Summarily, the pore structures in nanoballs could be controlled by the exposure duration of electron beam.

To investigate the heating effect, the prepared samples were dried in oven at 60°C for 10 h and in microwave oven, respectively. The microwave drying was used to simulate the case of

Fig. 5. TEM micrographs of the samples prepared in 50 vol.% ethanol aqueous solution for 60 min but exposed to electron beam for different time: (a) 2 min; (b) 5 min; (c) 10 min.
fast heating by electron beam. As shown in Fig. 6a, the porous nanostructures were well dispersed and slightly deformed under microwave drying. Under fast heating, the volatile solvents would expand and release quickly, leading to the nanoballs. Shown in Fig. 6b, upon drying for 10 h, the nanoballs with large hollow interiors were obtained, which resulted from the merging of the tiny pores. It could also be found that the thick shell is loose and the outer surface is not smooth. It is clear that the drying way also has a significant effect on the pore structure of the sample.

3.5. The formation of porous BaAl4O7 nanoballs

Similarly, the hollow BaAl4O7 nanostructures were also prepared by the hydrolysis of BaAl2O4 in ethanol aqueous solution, as shown in Fig. 7. In 40 vol.% ethanol aqueous solution, the hollow nanostructures have the diameter of 100 nm and the hollow interior of 30 nm in size; in 50 vol.% ethanol aqueous solution, the majority of nanoballs with hierarchic nanopores have the diameter of 50 nm; and a few large balls with 100 nm in size can be also observed, which may result from the connection of the nanoballs to one another. EDX spectra also show the molar ratio of Ba to Al is 1:4. The result is similar to that of the prepared SrAl4O7.

3.6. The proposed formation mechanism of the porous nanoballs

To explore the formation mechanism of the nanoballs with hierarchic nanopores, the hydrolysis process of SrAl2O4 powders was followed basing on the variations of pH values of the solution with hydrolysis time, as shown in Fig. 8. In pure water, pH values of the system rapidly reached 12 at $t = 20$ min and kept constant at $t \geq 50$ min, indicating that the hydrolysis of SrAl2O4 in water was very fast and completed at 50 min. In 25 vol.% ethanol aqueous solution, pH values of the system increased continuously and reached 12 at $t = 70$ min and the hydrolysis of SrAl2O4 was completed at $t = 100$ min, meaning that the hydrolysis rate of SrAl2O4 decreased upon adding of ethanol. In 50 vol.% ethanol aqueous solution, it is interesting that two platforms of pH values appeared. At $t = 10$ min, pH value reached 11; in the range of 10–80 min, pH values nearly kept a constant of 11; with elongating the time from 80 to 110 min, pH value reached 12. The results probably indicate that a metastable intermediate may be formed in the process. After 24 h, the obtained sample is composed colloidal Al(OH)3 and wire-like SrCO3, signing that the hydrolysis reaction stopped. XRD patterns showed that the product was composed of crystalline SrCO3, Al(OH)3 and SrAl4O7, in which SrCO3 crystals resulted from the reaction of Sr(OH)2 with CO2 from air. (See supporting information of Fig. S4). It is important to note that SrAl4O7 was the main phase, but the peaks of SrCO3 and Al(OH)3 were weak. In 75 vol.% ethanol aqueous solution, pH values of the system varied very little from 8.2 to 8.5 within 180 min, indicating that the hydrolysis of SrAl2O4 have not almost taken place in the high-concentration ethanol aqueous solution. The effect of ethanol concentration on the pore structure of the product has been introduced above. The results showed that after hydrolysis for 60 min, the nanoballs with hierarchic nanopores could be prepared only in the range of 40–60 vol.% ethanol. At $x < 40$ vol.% ethanol, SrCO3 nanowires were formed, just as in pure water; at $x > 60$ vol.%, the samples were same as the original SrAl2O4, due to the very slow hydrolysis rate in the presence of the high-concentration ethanol. In the process, it may be that the hydrolysis of SrAl2O4 was fast in pure water, the Al-enriched framework could not be remained in the system, and but form Al(OH)3 precipitate before reconstructing to form SrAl4O7. As a result, reaction (1) may take place below. It is reasonable to believe that SrAl4O7 may exist as the
intermediate. In the presence of ethanol, the Al-enriched spinel framework may generate after part of Sr dissolved into the solution. The “holes” or “vacant sites” left by Sr would combine with ethanol molecules, so the Al-enriched spinel framework would exist for enough time. As a result, the Al-enriched framework and the remained Sr ions in the framework would reconstruct to form SrAl$_4$O$_7$. The ethanol molecules were enclosed in framework during reconstruction process, as shown in reaction (2) below:

$$\text{SrAl}_2\text{O}_4 + \text{H}_2\text{O} \rightarrow \text{Sr(OH)}_2 + \text{Al(OH)}_3$$ (1)

$$2\text{SrAl}_2\text{O}_4 + \text{H}_2\text{O} + x(\text{ethanol}) \rightarrow \text{Sr(OH)}_2 + (\text{ethanol})x\cdot\text{SrAl}_4\text{O}_7$$ (2)

Basing on the results above, a self-generated *in situ* “framework template” mechanism was proposed to explain the formation of porous hollow nanostructures. During the process, the presence of ethanol molecules reduced greatly the interaction between SrAl$_2$O$_4$ and water molecules. As a result, the complete hydrolysis of SrAl$_2$O$_4$ was refrained to some extent. While SrO units gradually left off from SrAl$_2$O$_4$ framework and dissolved into the solution under the attack by water; a very small amount of Al ions hydrolyzed to form Al(OH)$_3$ which would be precipitated out of the solution; but most of Al ions still retained in the framework due to the restrained hydrolysis by ethanol. As a result, some “holes” or “vacant sites” would generate in the framework because of the dissolution of Sr. The present ethanol molecules may prefer to adsorb on the “holes” and/or combine with the “vacant sites” in the framework; the Al-enriched framework was stabilized by ethanol.

![TEM photographs and EDX spectrum of BaAl$_4$O$_7$ hollow structures prepared at different ethanol concentrations in ethanol aqueous solution: (a) 40 vol.%; (b) 50 vol.%; (c) EDX spectrum of sample b.](image)
molecules. Then, the remained Sr and Al-enriched framework reconstructed to form the SrAl$_4$O$_7$ structure, in which the non-cracked framework acted as the template in situ. In the reorganization process, a large number of ethanol molecules were enwrapped into the nanostructures. While irradiated by electron beam with a low intensity or dried at mild condition, ethanol molecules were slowly released, and then a large number of tiny pores generated. Under bombed by high intensity of electron beam, ethanol molecules evaporated quickly and the tiny pores tended to expand and/or merged into the large pores. As a result, the nanoballs with hierarchic nanopores were formed. The formation process of such porous structure is useful for the structure control of porous nanoball, although more proofs are still needed.

4. Conclusions

The unique porous nanoballs were constructed by a facile and controllable hydrolysis route, which are mostly dependent on the intrinsic properties of the chemicals; the porous structures were formed through an in situ generated “framework” template. Importantly, this formation process of the porous nanoballs is useful for the structure control of porous materials.

5. Supporting information available

XRD patterns of the prepared sample by hydrolyzing of SrAl$_2$O$_4$ in 50 vol.% ethanol aqueous solution, TEM photographs of the prepared samples by the hydrolysis of SrAl$_2$O$_4$ in acetone–water, TEM photographs of the prepared samples by the hydrolysis of SrAl$_2$O$_4$ in glycerol–water (50:50 volume ratio) for different time and XRD patterns of the prepared sample by the hydrolysis of SrAl$_2$O$_4$ in 50 vol.% ethanol aqueous solution for 24 h. This material is available free of charge via the Internet at http://www.elsevier.com.

Acknowledgment

This work is supported by Chinese National Science Foundation (Nos. 20433010, 20571047).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.colsurfa.2007.06.021.

References