

Effects of Template Contents on the Physicochemical Sorption Properties of Zr-Incorporated Mesoporous Titania Materials

ZHENG, Jin-Yu^a(郑金玉) QIU, Kun-Yuan*^a(丘坤元) WEI, Yan*^b(危岩)

^a Department of Polymer Science and Engineering, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

^b Department of Chemistry, Drexel University, Philadelphia, PA 19104, USA

Zr-Incorporated mesoporous titania materials were prepared via nonsurfactant templated sol-gel process of zirconium (IV) butoxide (ZBT) and titanium (IV) butoxide (TBT) in the presence of urea molecules as template or pore forming agent. The effects of template contents on the pore parameters of the materials synthesized with fixed Zr incorporation contents were investigated by nitrogen adsorption-desorption measurements, powder X-ray diffraction (XRD) study and transmission electron microscopy (TEM). The changes of template contents play significant roles on the pore parameters at low incorporation content of Zr. The pore diameters display a clear increase tendency with the increase of template contents. When high Zr incorporation content is used, the template contents have less effect on the pore diameters that almost keep unchanged with the increase of template contents. All the materials possess type IV isotherms with H₂ hysteresis loops suggesting the formation of mesophase. The materials with low Zr incorporation content have anatase structures; however, it can not be found in the materials with high Zr incorporation content. TEM images show that some accumulated inter-particulate pores and well-distributed worm-like pores are present in the Zr-incorporated materials.

Keywords Zr-incorporated mesoporous titania, nonsurfactant template, urea, sol-gel

Introduction

As a breakthrough of new material, mesoporous material is attracting more and more attention since its first synthesis achieved by Mobil Company in 1992.^{1,2} The re-

searchers employed ionic surfactants as templates and hydrothermal synthesis method to accomplish the preparation of mesoporous silica and aluminosilicate materials. The surfactant micelles formed through the self-assembling of surfactants direct the formation of mesopores. The pore diameters in the range of 2—10 nm can be adjusted by changing the carbon chain length of surfactant molecules or adding additional compounds to enlarge the micelles. Ionic and neutral as well as special group modified surfactants, block copolymers and nonsurfactant small organic molecules have been widely used as template or pore forming agent in the synthesis of mesoporous materials.³⁻¹⁹ Besides the hydrothermal synthesis method, typical sol-gel method or modified sol-gel method was also widely exploited in the preparation of mesoporous materials, especially for mesoporous metal oxides.¹¹ A lot of research groups focus their work onto the practical applications of mesoporous materials, such as used as separation agents, matrix of catalysts and catalysts, mainly due to the controlled pore sizes and special structures of mesoporous materials.

Metal oxides possess many useful properties especially the catalytic properties on organic reactions. Many works have been processed on the synthesis of metal incorporated mesoporous silica and metal oxides. Al, Ti, Zr, Mn, Sn, *etc.* have been introduced into the skeleton of mesoporous silica, moreover, mesoporous alumina, titania and zirconia have also been obtained.^{8,9,11,12} The

* E-mail: kyqiu@chem.pku.edu.cn; weiyen@drexel.edu

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modified sol-gel method is always employed in the synthesis of metal oxides because some metal oxides are not stable at high temperature that is necessary for hydrothermal synthesis method. Many organic reactions have been investigated deeply by using these porous metal oxides.

Surfactant molecules are the most general molecules widely used as templates or pore forming agents. As we know, some surfactants are expensive or noxious; moreover, high temperature must be used in the elimination of surfactants that always results in the collapse of pore walls and affects the properties of the porous materials. In 1998,^{18,19} Wei's group reported the synthesis of mesoporous silica materials by using nonsurfactant small organic molecules, such as *D*-glucose and *D*-Maltose, via typical sol-gel reactions of ethyl orthosilicate. The nonsurfactant molecules can be easily removed out from the composite materials by solvent extraction. Urea,²⁰ hydroxyacetic acid derivatives²¹ and poly-multi-acids²² have been successfully used in the preparation of silica via this nonsurfactant route. Benefited from the low-temperature synthesis of sol-gel route and extraction of solvent, mesoporous titania materials are also obtained at ambient temperature in the presence of small organic molecules, *e.g.* urea,²³ glycerol²⁴ and mixture of urea and β -cyclodextrin.²⁵ Based on the special catalytic properties of binary metal oxides, Zr-incorporated mesoporous titania materials with different incorporation contents of Zr were synthesized.

Herein, we reported the effects of template contents on the pore parameters and crystal phases as well as morphologies of the materials obtained at fixed incorporation content of Zr and different template contents.

Experimental

Synthesis

The preparation of the Zr-incorporated mesoporous titania materials is similar to our previous articles,²³ in which the template content was fixed at 10 wt% in the final composites with the assumption that $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and $\text{Zr}(\text{OC}_4\text{H}_9)_4$ were completely converted to TiO_2 and ZrO_2 , respectively. The only difference is that in this article the Zr/Ti molar ratio was fixed at 1/20 (system A) and 1/4 (system B), and the template contents were adjusted from 5 wt% to 60 wt%. For instance, 0.21 g of ZBT (80 wt% solution in 1-butanol, Aldrich) was added into 24.1

g of TBT (97%, Aldrich) ethanol solution directly based on the designed molar ratio of Zr/Ti (1/20). Then 0.008 mL of HCl ($12 \text{ mol} \cdot \text{L}^{-1}$) and 0.33 mL of HCl ($0.28 \text{ mol} \cdot \text{L}^{-1}$) aqueous solution were dropped into the mixed solution to catalyze the sol-gel reactions. Finally 0.591 g of template solutions (mixed solution of urea-ethanol- H_2O) were put into the hydrolyzed transparent sol solutions with designed template contents (10 wt%) in the final inorganic composites under vigorous stirring and then kept stirring for another 2 h. The transparent urea-containing Zr-incorporated titania materials were obtained after gelling and aging for 20–30 d under ambient temperature. The dried materials were grounded into fine powder to be extracted by water for 3 d in order to remove the template molecules and then dried at 100 °C for one day to obtain porous materials.

Characterization

The removal of the template molecules from the incorporated samples after water extraction was confirmed on a Bruker Vector22 FT-IR spectrometer. Nitrogen adsorption-desorption measurements of the Zr-incorporated titania materials were performed on a Micromeritics AS-AP2010 analyzer via 69 points full analysis. The sorption and pore parameters were collected automatically at 77 K by the analyzer. The extracted samples were degassed at 110 °C for 4 h under 1 Pa before measurements. The pore size distributions were calculated from the desorption branches of the isotherms using Barrett-Joyner-Halenda (BJH) method. A Rigaku DMAX2400 X-Ray Diffractometer was exploited to characterize the crystal phases of the obtained materials before and after extraction by exploiting Cu $K\alpha$ radiation ($\lambda = 0.15418 \text{ nm}$, 40 kV, 100 mA). The samples were scanned in the ranges of 2θ value of 0.6° – 8° and 8° – 60° at scan rates of $1^\circ/\text{min}$ and $8^\circ/\text{min}$, respectively. The morphologies of the Zr-incorporated porous materials with different template contents were characterized by a JEOL JEM-200CX transmission electron microscopy (TEM) with an accelerate voltage of 200 kV.

Results and discussion

The Zr-incorporated mesoporous titania materials with fixed incorporation contents of Zr and various template contents were easily obtained at room temperature

via HCl-catalyzed sol-gel reactions of TBT and ZBT, in conjunction with nonsurfactant organic molecules-urea acting as template or pore-forming agent. In the gelling and aging process at room temperature, some white crystals came out from the composite materials prepared with high template contents (> 40 wt%). It is ascribed to that some of the urea molecules separated out from the materials and did not serve as templates any more. The separation of urea is further confirmed by large-angle XRD patterns measured on the samples before extraction demonstrating that some diffraction peaks corresponding to urea crystals appeared.

The sorption properties and pore parameters of the samples in system A prepared with various template contents and 1/20 Zr/Ti molar ratio are listed in Table 1. Similar to mesoporous titania we reported earlier, even the template content is lower to 5 wt%, the template molecules can still direct the formation of mesopores. The pore diameters increase significantly up to 6.4 nm (BJH) with the increase of template contents. However, at high tem-

plate contents, such as 60 wt%, only part of urea molecules serve as template due to the crystallization of some urea molecules and result in the decrease of pore diameter. The surface areas show a relative decrease tendency with the changes of pore diameters. The pore volumes almost unchanged as the template content is increased, because the numbers of the pores decrease with the increased template contents, even the pore diameters increase. At this relative low Zr incorporation content, the change of template contents plays important roles in the adjusting of pore diameters.

Table 2 is the pore parameters of system B samples obtained by different template contents and fixed 20 mol% incorporation content of Zr. Seen from the table, the pore diameters hardly change as the increase of template contents. The surface areas and pore volumes decrease a little bit first and then go up again, it is proposed that the increased template molecules were used to form more pores not to form larger pores. Due to the crystallization of urea molecules, only some urea molecules

Table 1 Physicochemical sorption properties and pore parameters for the samples prepared at Zr/Ti molar ratio of 1/20 and different template contents

Sample code ^a	Template content (wt%)	Surface area (m ² ·g ⁻¹)		Pore volume (cm ³ ·g ⁻¹)		Pore diameter (nm)	
		BET	BJH	SP ^b	Total ^c	BET ^d	BJH ^e
ZT-A-5	5	334	409	0.31	0.33	3.7	3.5
ZT-A-10	10	230	305	0.38	0.31	6.6	5.7
ZT-A-30	30	200	272	0.35	0.35	6.9	5.9
ZT-A-40	40	187	252	0.35	0.35	7.5	6.4
ZT-A-60	60	215	296	0.34	0.35	6.3	5.4

^a A means system A with the Zr/Ti molar ratio of 1/20 and the number indicates the designed template content. ^b The single point (SP) pore volume was obtained at $p/p_0 \approx 1$. ^c The total pore volume was calculated based on BJH method. ^d The BET pore diameter was calculated from $4V/A$ in which V is the SP pore volume and A is the BET surface area. ^e The BJH pore diameter was obtained from the adsorption branches of isotherms.

Table 2 Physicochemical sorption properties and pore parameters for the samples prepared with 20 mol% Zr incorporation content and different template contents

Sample code ^a	Template content (wt%)	Surface area (m ² ·g ⁻¹)		Pore volume (cm ³ ·g ⁻¹)		Pore diameter (nm)	
		BET	BJH	SP ^b	BJH ^c	BET ^d	BJH ^e
ZT-B-5	5	641	630	0.44	0.41	2.7	2.8
ZT-B-10	10	633	672	0.41	0.49	2.6	2.8
ZT-B-30	30	553	614	0.37	0.45	2.7	2.8
ZT-B-40	40	614	646	0.40	0.47	2.6	3.0
ZT-B-50	50	635	676	0.44	0.49	2.8	3.1
ZT-B-60	60	623	662	0.43	0.48	2.7	3.0

^a B means system B with the Zr/Ti molar ratio of 1/4 and the number indicates the designed template content. ^{b, c, d, e} see Table 1.

play template roles. So there is only a slight increase of surface areas and pore volumes. In this situation, no obvious effect of template contents was observed.

Comparing these two systems, the dispersion of Zr in the titania skeleton and the high hydrolysis and condensation rates of $Zr(OC_4H_9)_4$ play roles at the same time and lead to the above results. At low incorporation content of Zr, the high hydrolysis and condensation rates of $Zr(OC_4H_9)_4$ have less effect on the whole process, which makes the urea molecules have enough time to form large aggregates at high template contents. However, when Zr incorporation content is increased to 20 mol%, the high hydrolysis and condensation rates of $Zr(OC_4H_9)_4$ become main force. The formation of the Zr-O-Ti networks is too quickly to wrap large urea aggregates that can not be formed in such a short time. As a result, the pore diameters almost can not be tuned by the changes of template contents.

The nitrogen adsorption-desorption isotherms for both synthetic systems are presented in Fig. 1. For system A, shown in Fig. 1(a), all the samples have type IV isotherms with H_2 hysteresis loops, special for mesoporous materials. When the template content is lower to 5 wt%, the adsorbed volumes are lower than the others and the relative pressure corresponding to the hysteresis loop is around <0.5 that indicate the obtained pore diameter is about 3–4 nm. With the increase of template contents, the hysteresis loops shift to high values suggesting the increase of pore diameters. As seen from Fig. 1(b) for system B, at low template contents, the isotherm plots look like type I reversible isotherms typical for micropores because of their small hysteresis loops. When the template content is increased up to 40 wt%, the characteristic of type IV isotherms becomes obvious. However, the values of hysteresis loops hardly shift to high values with the template contents, which identify the similarity of pore diameters and slight effect of template contents on the pore diameters.

The BJH pore size distribution plots obtained from the desorption-branches of the isotherms are shown in Fig. 2. The sample with 5 wt% template content displays narrow pore size distribution and the average pore size is in the range of 3–4 nm. At high template contents, the peak pore diameter increases up to about 7.5 nm but the width of the distributions becomes very broad, which suggests the significant effects of template contents on the pore diameters. As for system B shown in Fig. 2

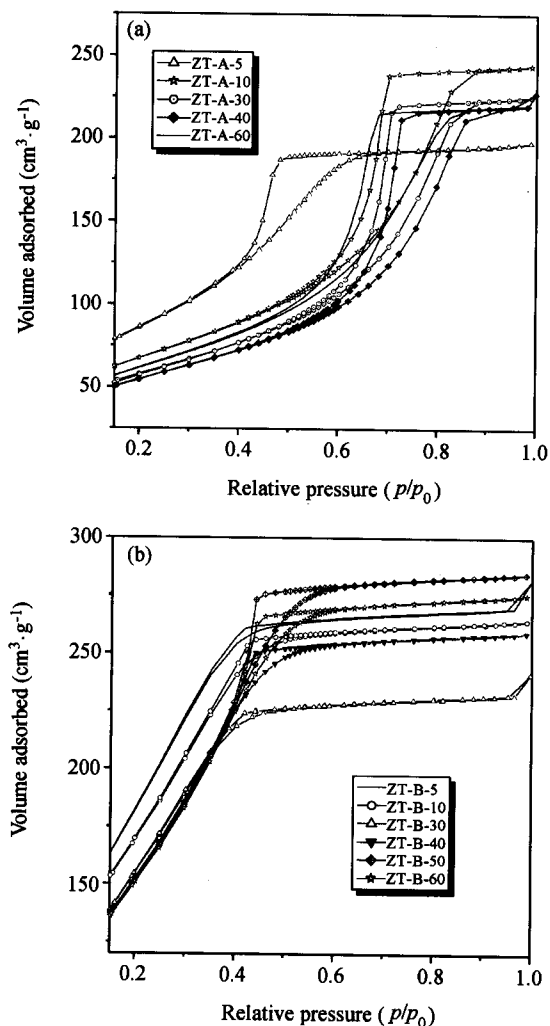


Fig. 1 Nitrogen adsorption-desorption isotherms for system A (a) and system B (b).

(b), no distribution peaks are found at low template contents. When the template content is increased to 40 wt% or higher, the distribution peaks come out indicating the formation of more pores in meso-range; moreover, the average pore sizes almost unchanged with the increased template contents. Different from system A, the widths of the peaks become more and more narrow with the increased template contents.

The small-angle (a) and large-angle (b, c) powder XRD figures are shown in Fig. 3. In Fig. 3(a) there is no any diffraction peak coming out at 2θ value of 0.6° – 8° indicating the disordered arrangements of the afforded porous materials. The materials with low Zr incorporation content show typical anatase structures with four specific diffraction peaks. The low Zr incorporation content and template contents almost have no effect on the crystal

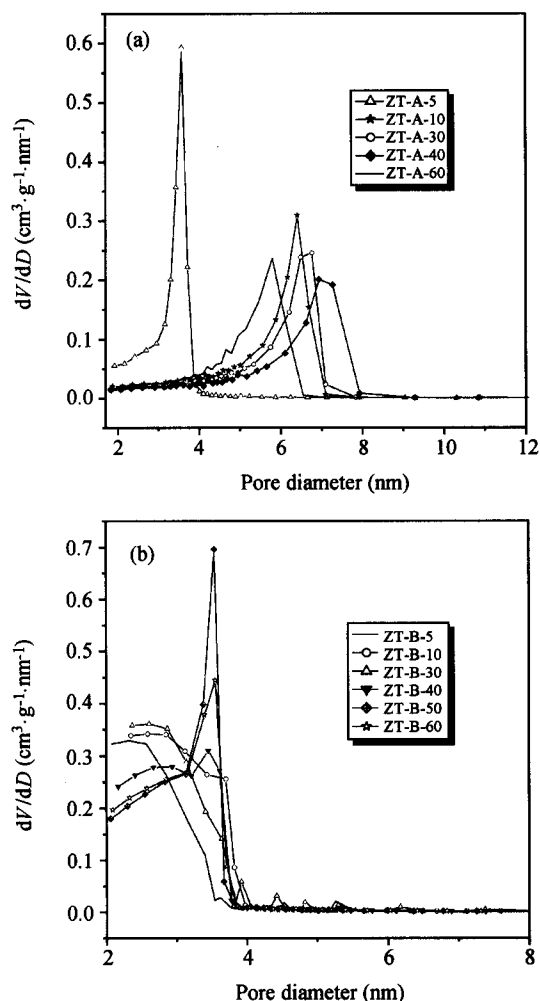


Fig. 2 BJH pore size distribution plots for system A (a) and system B (b).

phases of the materials. However, when the incorporation content of Zr is increased, the anatase structures disappear and there is only one wide diffraction peak appearing around 2θ value of 30° shown in Fig. 3(c). It is identified that the materials lost the anatase crystal phases at high Zr incorporation content, because the dispersion of Zr in titania disrupts the formation of continuous Ti-O-Ti structures and results in amorphous natures.

The transmission electron microscopy images of samples ZT-A-30 (a) and ZT-B-30 (b) are shown in Fig. 4. It can be seen that the characteristic of accumulated inter-particle pores is very clear for sample ZT-A-30 prepared with low incorporation content of Zr, which is similar to some pure titania materials reported earlier. In Fig. 4(b) the material displays well-distributed worm-like mesopores. No accumulated inter-particle pores

are found because the formation of mixed Ti-O-Zr structures is helpful for the formation of even-dispersed pores.

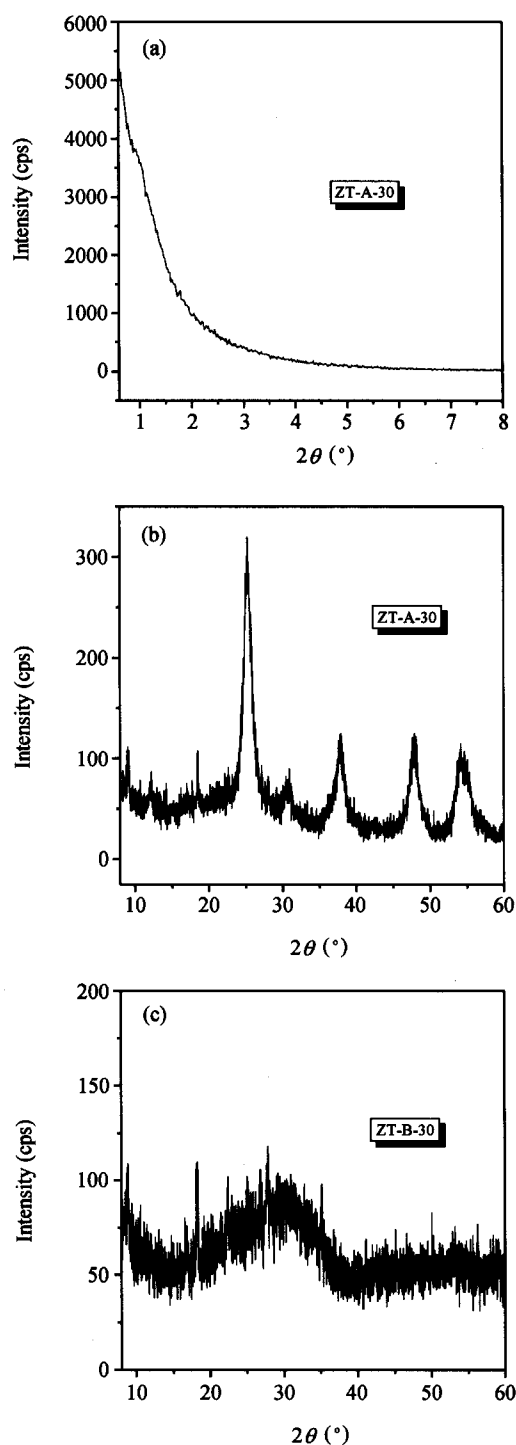


Fig. 3 Small-angle and large-angle powder X-ray diffraction patterns for samples ZT-A-30 (a, b) and ZT-B-30 (c).

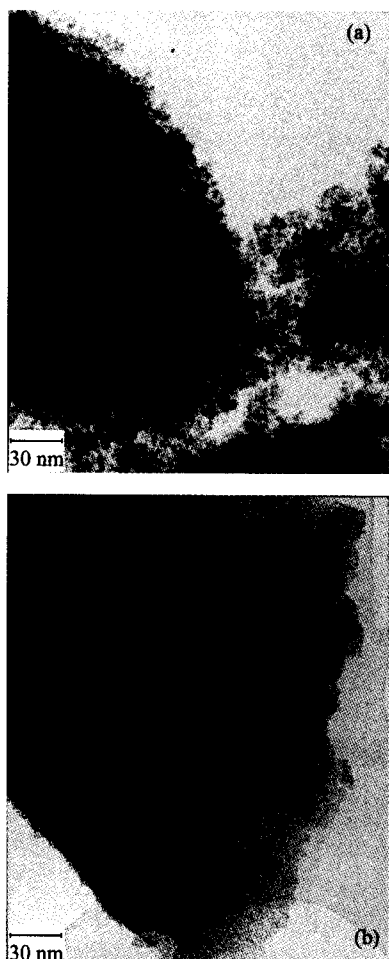


Fig. 4 TEM images for samples ZT-A-30 (a) and ZT-B-30 (b).

Conclusions

The Zr-incorporated mesoporous titania materials with fixed incorporation contents of Zr and various template contents have been synthesized by co-hydrolysis and co-condensation sol-gel reactions of $\text{Ti}(\text{OC}_4\text{H}_9)_4$ and $\text{Zr}(\text{OC}_4\text{H}_9)_4$ in the presence of urea molecules as nonsurfactant template. The resultant materials are typical mesoporous materials with pore diameters about 3.5–7.5 nm for low Zr-incorporated materials and 2.6–3.1 nm for high Zr-incorporated materials. The template contents have obvious effects on the pore parameters at low incorporation content of Zr; however, the pore parameters hardly change with the increased template contents when the incorporation content of Zr is high. The anatase structures are found in system A, but system B shows amorphous structures. Moreover, the crystal phases and mor-

phologies of the materials are mainly decided by the incorporation content of Zr and show less relationship with template contents. The well-distributed worm-like mesopores are formed at high incorporation content no matter how much the template contents used. The hydrogen bonding interactions of organic template molecules are still the important factor in the preparation of mesoporous materials via nonsurfactant templated sol-gel route.

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