

*Communication*

# Preparation of Monolithic Ti-incorporated Mesoporous Silica Materials *via* Tartaric Acid Templated Sol-gel Process

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Monolithic and transparent Ti-incorporated mesoporous silica materials of large size (*e. g.* 2 mm) in dimension have been prepared with tartaric acid (TA) as template *via* sol-gel reactions of tetraethyl orthosilicate (TEOS) and tetrabutyl titanate (TBT). The materials are characterized by infrared (IR), nitrogen adsorption-desorption isotherms, powder X-ray diffraction (XRD) and transmission electron microscopy (TEM). The results indicate that the monolithic materials exhibit large specific surface areas (*ca.* 1200 m<sup>2</sup>/g) and pore volumes (*ca.* 0.900 cm<sup>3</sup>/g).

**Keywords** Ti-incorporated mesoporous silica, monolithic, tartaric acid, nonsurfactant template, sol-gel process

## Introduction

The synthesis and application<sup>1,2</sup> of mesoporous materials have attracted researchers much attention in recent years due to their unique physicochemical properties and potential uses in catalysis, and separation technologies. Titanium silicalite<sup>3</sup> is an effective molecular sieve catalyst for the selective oxidation of alkanes, the hydroxylation of phenol and the epoxidation of alkenes in the presence of H<sub>2</sub>O<sub>2</sub>. However, the range of organic compounds that can be oxidized is greatly limited due to the relatively small pore size of the molecular sieve. Therefore, titanium-containing mesoporous materials Ti-MCM41,<sup>4,6</sup> Ti-HMS,<sup>6</sup> Ti-MSU<sup>7</sup> have already been prepared *via* surfactant templated pathway, and these materials show ex-

cellent catalytic activity and selectivity when bulky substrates are involved.<sup>4-6</sup> It is noticeable that most of these materials are in powder form owing to the uncontrollable precipitation procedure.

Recently nonsurfactant compounds have been employed as template to prepare silica,<sup>8-12</sup> titania<sup>13</sup> and alumina<sup>14</sup> mesoporous materials with randomly interconnecting worm-like pores. This new and facile method makes it possible to prepare monolithic and transparent mesoporous materials.<sup>10</sup> In the current report we describe the preparation of monolithic and transparent Ti-incorporated mesoporous silica materials. These materials might facilitate their application as catalysts due to the easy separation from the reaction system, and the three-dimensional pore structure might have significant benefits in practical catalytic applications by reducing the probability of pore blockage.<sup>7</sup>

## Experimental

### *Synthesis of mesoporous materials*

The synthetic procedures were similar to that given in our previous literature,<sup>10</sup> except that tetrabutyl titanate (TBT, Aldrich, 99%) was employed. In a typical synthesis (*e. g.* TA60-ST40), 10 cm<sup>3</sup> of tetraethyl orthosilicate (TEOS, Acros Organics, 98%) was prehy-

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drolyzed with deionized H<sub>2</sub>O in ethanol using HCl as catalyst (at TEOS:HCl:H<sub>2</sub>O:EtOH molar ratios of 1:0.01:4:3) at about 345 K for 5 h. Upon being cooled to room temperature, the prehydrolyzed solution was added a designed amount (*e. g.* 9 cm<sup>3</sup>) of 0.45 g/cm<sup>3</sup> aqueous solution of tartaric acid (TA) under stirring to afford homogeneous solution. Then, a calculated amount (*e. g.* 3.9 cm<sup>3</sup>) of 10% (V/V) TBT ethanol solution was added dropwise to the above mixture in a beaker. After stirring for about 10 m, the beaker was sealed with a cellophane film containing several pinholes to allow for slow evaporation of the solvent and reaction by-products. The transparent template-containing disks were obtained after gelling and drying for over two months at room temperature. The dried disks showed slight yellowish when the Si/Ti molar ratio was less than 40. The silica disks were broken into small pieces instead of being ground into fine powders<sup>8,9,11,12</sup> and extracted with ethanol for 3 d in a Soxhlet apparatus under ambient pressure. Upon being dried in a vacuum oven at about 353 K for *ca.* 3 h, the monolithic porous silica materials were obtained.

#### Characterization of mesoporous materials

The FT-IR spectra of the samples before and after solvent extraction were measured in the form of KBr powder-pressed pellets on a Bruker Vector 22 FT-IR spectrometer. The surface area, pore volume, pore diameter and pore size distribution of the silica samples as small pieces after the solvent extraction were determined by nitrogen adsorption-desorption isotherms at 77 K on a Micromeritics ASAP2010 analyzer. Before each measurement, the sample was degassed at 473 K and below 1.33 Pa for more than 3 h. The powder X-ray diffraction (XRD) pattern was recorded on a Rigaku DMAX2400 instrument using Cu K<sub>α</sub> radiation ( $\lambda = 0.15418$  nm, 40 kV, 100 mA) at scanning rates of 1°/min in the 2 $\theta$  range of 0.6–10° and of 8°/min in the range of 10–40°. Morphologies of the porous samples were examined on a JEOL JEM-200CX transmission electron microscope (TEM) operating at an accelerating voltage of 200 kV. The samples for TEM were prepared by dipping an ethanol suspension of finely ground sample powders onto a Cu grid coated with a holey C film.

## Results and discussion

The FT-IR spectra of the monolithic sample TA60-ST40 before and after ethanol extraction are given in Fig. 1. It can be seen that the absorption band at about 1738 cm<sup>-1</sup> (see curve a), which is assigned to the C=O stretching vibration of TA molecules, disappears (see curve b) after the samples are extracted with ethanol, indicating the complete removal of the template. It is noted that the absorption band at 1636 cm<sup>-1</sup> is attributable to the O—H vibration of H<sub>2</sub>O molecules adsorbed into the samples and KBr substrate. The spectrum of the mesoporous sample after the removal of template closely resembles that of Ti-MCM41.<sup>5</sup> The band observed around 960 cm<sup>-1</sup> can be attributable to the Si—O—Ti group and Si—OH group.<sup>5</sup>

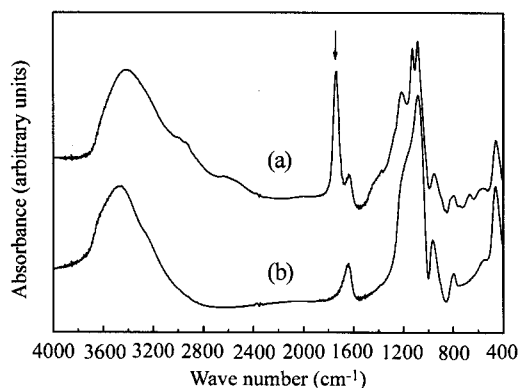


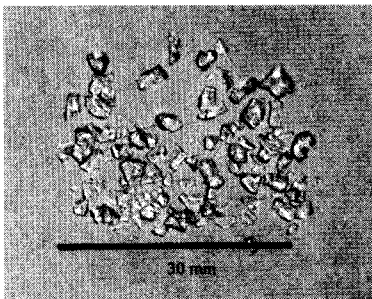
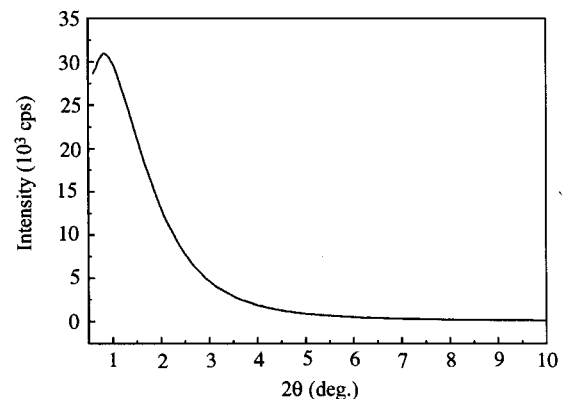
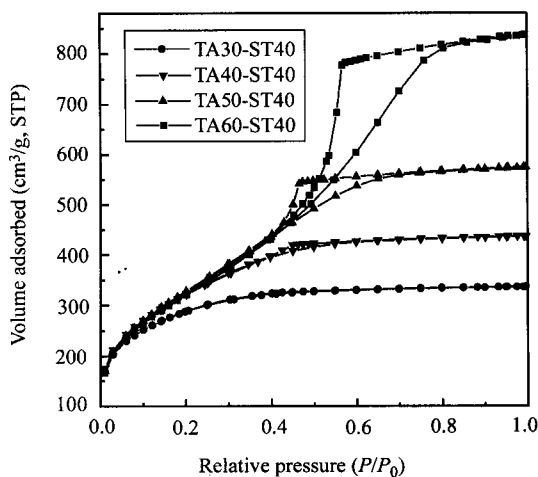
Fig. 1 FT-IR spectra for the monolithic sample TA60-ST40 before (a) and after (b) extraction with ethanol.

The physicochemical characteristics of the monolithic and transparent Ti-incorporated mesoporous silica samples (*e. g.* TA50-ST100 shown in Fig. 2) are presented in Table 1. The monolithic mesoporous materials with different Si/Ti molar ratios, *e. g.* 100, 80, 40, 20, were obtained. The samples prepared with template content higher than  $w = 50$  % show large specific surface areas (*ca.* 1200 m<sup>2</sup>/g), pore volumes (*ca.* 0.900 cm<sup>3</sup>/g) as well as pore diameters of *ca.* 3.0–4.0 nm. At a fixed Si/Ti molar ratio the pore volume and pore diameter tend to increase with the TA content. From the t-plot analysis the contributions from micropores to the measured surface areas and pore volumes are negligible

**Table 1** Physicochemical properties of the monolithic Ti-incorporated mesoporous silica materials with different Si/Ti molar ratios

Sample code	TA content <sup>a</sup> (w/%)	Si/Ti molar ratio <sup>b</sup>	Specific surface area (m <sup>2</sup> /g)	Total pore volume <sup>c</sup> (cm <sup>3</sup> /g)	Pore diameter <sup>d</sup> (nm)	Micropore <sup>e</sup>	
						Surface area (m <sup>2</sup> /g)	Pore volume (cm <sup>3</sup> /g)
TA50-ST100	50	100	1202	0.957	3.5	–	–
TA50-ST80	50	80	1212	0.945	3.5	–	–
TA30-ST40	30	40	1030	0.521	2.6	249	0.104
TA40-ST40	40	40	1172	0.676	2.7	47	0.005
TA50-ST40	50	40	1204	0.889	3.2	–	–
TA60-ST40	60	40	1181	1.300	4.2	–	–
TA50-ST20	50	20	1248	0.919	3.2	–	–
TA60-ST20	60	20	1214	1.287	4.1	–	–

<sup>a</sup>TA = tartaric acid, the designed template content is calculated from TA/(SiO<sub>2</sub> + TA) based on the feed composition under the assumption that TEOS is completely transformed into SiO<sub>2</sub>; <sup>b</sup> Designed Si/Ti molar ratio as calculated from the feed composition; <sup>c</sup> Single point total pore volume at the relative pressure of *ca.* 0.995; <sup>d</sup> Average pore diameter calculated by BJH analysis from the adsorption isotherm; <sup>e</sup> The surface area and pore volume of micropores were obtained by t-plot analysis using Harkins-Jura equation.

**Fig. 2** Appearance picture of the monolithic and transparent sample TA50-ST100.**Fig. 4** Powder XRD pattern for the sample TA60-ST40.**Fig. 3** Nitrogen adsorption-desorption isotherms for samples TA30-ST40, TA40-ST40, TA50-ST40 and TA60-ST40.

at template content higher than  $w = 50\%$ .

Fig. 3 shows the nitrogen adsorption-desorption isotherms for the samples with Si/Ti molar ratios of 40 and different template contents. The samples prepared with template content of  $w = 50\%$  or  $w = 60\%$  exhibit type IV-like isotherms with type H2 hysteresis,<sup>15</sup> which are similar to that of the reported mesoporous materials.<sup>8-12</sup> However, the samples TA30-ST40, TA40-ST40 show reversible type I isotherms.<sup>15</sup>

The powder XRD patterns of the samples generally show a diffraction peak at the small-angle range, as shown in Fig. 4. The XRD pattern of the sample TA60-ST40 contains a diffraction peak at  $2\theta$  value of  $0.880^\circ$ , which corresponding to a  $d$ -spacing of 10.0 nm, which are similar to the XRD patterns of the mesoporous materials prepared by surfactant<sup>16</sup> or nonsurfactant<sup>8,11,12</sup> tem-

plate pathway. The broadness of the single peak and the absence of additional higher degree peaks suggest that these samples lack long range ordering of the structure.<sup>16</sup> There is a typical amorphous halo around the  $2\theta$  value of  $23^\circ$ , indicating the amorphous nature of the sol-gel Silica matrix.<sup>8</sup>



Fig. 5 TEM image for the sample TA60-ST40.

Fig. 5 shows the TEM image of the mesoporous sample TA60-ST40 after the removal of template. The TEM image shows numerous wormlike interconnected channels or pores that are disordered in arrangements. The framework-confined mesoporosity is clearly revealed. The pore diameters are mostly about 4.5 nm, which is comparable to the average pore diameter obtained from nitrogen sorption measurements.

The Ti-incorporated mesoporous silica materials in powder form have also been synthesized. Further studies are in progress in our laboratory to determine the catalytic activity and selectivity for the Ti-incorporated mesoporous silica materials on some organic reactions.

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