

## A Novel Synthesis of Titania-silica Mixed Oxide with Mesoporous Structure

Wei Ping HUANG\*, Hong LI, Bao Qing LI, Feng GAO,  
Xiu Chen ZHENG, Shou Min ZHANG, Shi Hua WU

Department of Chemistry, Nankai University, Tianjin 300071

**Abstract:** Mixture formed from sonicating  $\text{TiCl}_4$  and  $\text{Si}(\text{OEt})_4$  in the absence of water is used as precursor and hydrolyzed by using a long-chain organic ammonium bromide as a structure-directing agent. The product, titania-silica, is of mesoporous structure and characterized with SEM, FT-IR, BET, XRD and so on.

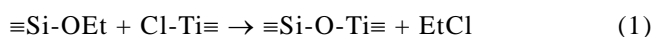
**Keywords:** Titania-silica, mixed oxide, sonication, mesoporous structure.

Due to growing public concerns on the harmfulness of water containing various pollutants, many researchers have focused on the detoxification of water polluted by organic compounds. Heterogeneous photocatalytic process for the water empoisoned by organic compounds is regarded as promising technique because the process does not produce the secondary environmental problem such as landfill and is achieved by using the extensive light energy and inorganic semiconductor. Titanium dioxide, *n*-type semiconductor, has been known as a good photocatalyst for elimination of relatively recalcitrant organic compounds in water. However, the small adsorption coefficient of visible light and the low quantum efficiency of the pristine  $\text{TiO}_2$  limit its wide use. As a result, many efforts using size-quantized and doped  $\text{TiO}_2$ <sup>1</sup> have been made in order to increase the quantum efficiency of  $\text{TiO}_2$  and extend the light absorbed by  $\text{TiO}_2$  to the visible region. Titania-silica, a doped  $\text{TiO}_2$ , has attracted many attentions during the last decade<sup>2</sup>, not only due to its good photocatalytic activity<sup>3</sup>, but also its interesting catalytic properties in selective oxidation reaction. Therefore many researchers have prepared titania-silica mixed oxide by various methods, for example, Khomane and cooperators synthesized TS-1 in micellar media<sup>4</sup>; Jung and Park prepared silica-embedded titania particles by sol-gel process<sup>3</sup>. The highly dispersed Ti and Si, is related to the Ti-O-Si species. In this paper we report on a novel method for preparation of titania-silica mixed oxide which has mesoporous structure, and in which the Ti and Si are highly dispersed. The raw materials used were  $\text{TiCl}_4$  and  $\text{Si}(\text{OEt})_4$ . The key procedure is to produce a precursor containing Si-O-Ti structure in the absence of water, and then the precursor was hydrolyzed by using a long-chain organic ammonium bromide as a

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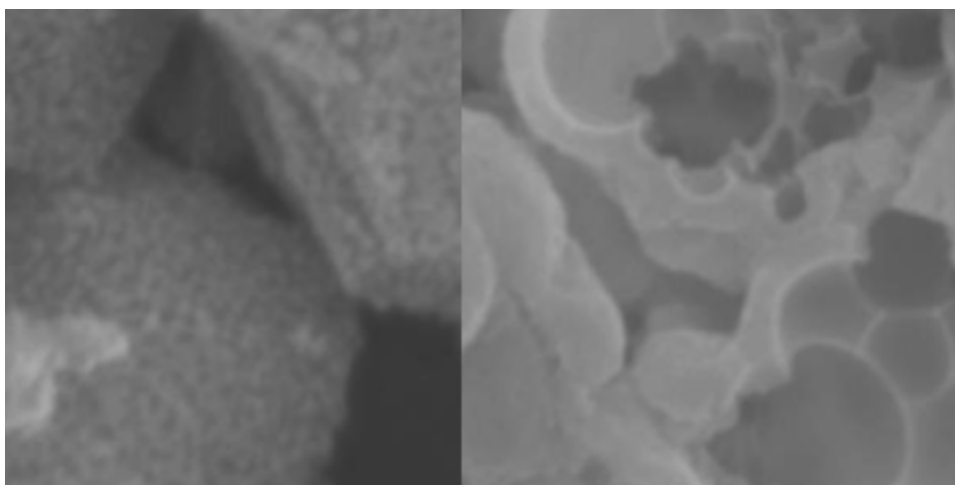
\* E-mail:huangw@eyou.com

structure-directing agent. It is well known that the elements Ti and Si are “oxyphilic, the bond energies of Si-O (185 Kcal/mol) and Ti-O (156 Kcal/mol) are higher than that of O-C (90 Kcal/mol) and Ti-Cl (87 Kcal/mol)<sup>5</sup>. If the precursor formed from TiCl<sub>4</sub> and Si(OEt)<sub>4</sub> contains Si-O-Ti species this structure would not be broken while the precursor was hydrolyzed in the sol-gel process and the formed product should have high dispersity of Ti and Si. Experimental details are described in the experimental section. The precursor containing Si-O-Ti structure was obtained by ultrasound irradiation of Si(OEt)<sub>4</sub> and TiCl<sub>4</sub> in the absence of water. Sonication in liquid creates acoustic cavitation that produces intense, short lifetime local heating or hot spots and high heating and cooling rates (about 10<sup>10</sup>K/s)<sup>6</sup>. The temperature of the hot spots may reach about 5000 °C. It is the hot spot that drives the reaction (1), by which the Si-O-Ti species form.



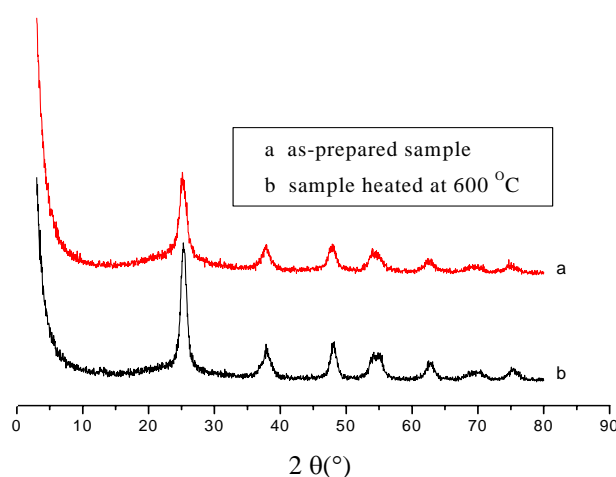
On the other hand, the boiling point of EtCl in reaction (1) is 13.1°C, and it leaves from the reaction system (ambient temperature) as soon as it forms, thereby also promoting the reaction (1). The similar reaction has been reported<sup>7</sup>, it confirmed that the reaction (1) really took place. The experimental result also proved this fact. After being sonicated and stored in refrigerator (-15 °C) for 10 h the precipitate appeared in the reaction cell, which is the product of reaction (1). We thought that the Si-Ti-O structure already exists in the precursor used for titania-silica and the Ti and Si are mixed atomically before the sol-gel process. The Ti/Si molar ratio of as-prepared sample determined by ICP is 0.409/0.338. According to the reference titania-silica mixed oxide with such ratio has good photocatalytic activity<sup>3</sup>, and the calcined sample has good photocatalytic activity for the decomposition of *p*-nitroaniline in water.

**Figure 1** SEM photographs of as-prepared (left) and calcined (right) samples



**Figure 1** shows the SEM photographs of as-prepared sample (left) and calcined sample (right) at 600 °C for 3 h. Clearly, a lot of pores (left) exist and the as-prepared sample has mesoporous structure, the pore size is between 4-5 nm. Sonochemistry has been used for the preparation of mesoporous titania, silica and TiO<sub>2</sub> with different crystalline state<sup>8</sup>, but it is very difficult to produce mixed oxide with mesoporous structure directly by sonication because of the different hydrolysis rate of various precursors. The sample calcined at 600 °C for 3 h has hollow sphere structure and the thickness of spherical wall is almost identical. Inside the sphere there is framework. Although there are many methodologies for synthesis of mesostructured materials<sup>9</sup> the approach reported here to mesostructured mixed oxide is relatively easy and effective. FT-IR spectra of the as-prepared and calcined samples are similar. The main peaks are 3300, 2926, 2855, 1620 1100 and 920 cm<sup>-1</sup> respectively. The peaks at about 1620 and 3300 cm<sup>-1</sup> are assigned to the OH bending and stretching of absorbed H<sub>2</sub>O. Compared with the FTIR spectrum of calcined sample the FTIR spectrum of as-prepared sample has peaks at 2926 and 2855 cm<sup>-1</sup>. They are assigned to vibration of organic residues, -CH<sub>2</sub>- and -CH<sub>3</sub>, and disappear after heating. The band present at 1100 cm<sup>-1</sup> corresponds to asymmetric stretching vibration of Si-O-Si and the band present at 920cm<sup>-1</sup> is assigned as Ti-O-Si vibration, which confirms the existence of Ti-O-Si species in samples. Any way it can varies slightly from the data in literature<sup>10</sup>.

**Figure 2** XRD patterns of samples



**Figure 2** shows X-ray diffraction patterns of as-prepared and calcined samples. The XRD patterns reveal that samples are of identical crystalline phase as pure anatase (JCPDS 21-1272). No significant peaks of rutile phase and no peaks of silica crystalline are observed for calcined sample at 600 °C for 3 h, which is consistent with literature that titania-silica shows only anatase crystalline phase even it is heated at high temperature<sup>3,10</sup>. The full adsorption-desorption isotherms and a pore distribution of as-prepared sample are determined by BET. Its specific surface area is 520.15 m<sup>2</sup>/g. The isotherms have a hysteresis loop which belongs to type IV isotherm<sup>11</sup>. This implies

that the as-prepared sample has mesoporous structure, which agrees with the result of SEM, because the type IV isotherms are associated with mesoporous materials. The pore size distribution is between 3-4 nm. The sample heated at 400 °C still keeps mesoporous structure.

### Experimental

5 g (C<sub>16</sub>H<sub>33</sub>)Me<sub>3</sub>NBr was dissolved in 220 mL H<sub>2</sub>O (I). 10 mL (0.044 mol) Si(OEt)<sub>4</sub> and 5 mL (0.046 mol) TiCl<sub>4</sub> were dissolved in 50 mL decalin (II). (II) was sonicated at ambient temperature for 4 h by a high-intensity ultrasonic probe (Sonics and Materials, VC-600, 20 kHz, 100 W/cm<sup>2</sup>). After sonication the sealed reaction cell was stored in refrigerator (-15 °C) for 10 h. A solid appeared and was separated by centrifugation. The solid, a precursor, was washed once with cooled decalin. It was added into the water solution of (C<sub>16</sub>H<sub>33</sub>)Me<sub>3</sub>NBr (I) with stirring, the precipitate was filtrated off, if it appears. The clear solution was kept in water-bath (60 °C) for 10 h. The precipitate sank and was separated by centrifugation, washed four times with water. The obtained precipitate was immersed in EtOH for 20 h, to extract (C<sub>16</sub>H<sub>33</sub>)Me<sub>3</sub>NBr, filtrated and washed three times with C<sub>2</sub>H<sub>5</sub>OH, dried overnight in vacuum.

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