

## Preparation and Photocatalytic Characterization of Nanoporous TiO<sub>2</sub>

Xue Ping LI\*, Jing Bo ZHANG, Fen YIN, Yuan LIN, Xu Rui XIAO

Laboratory of Photochemistry, Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080

**Abstract:** Nanoporous TiO<sub>2</sub> photocatalysts were prepared by use of controlled drying method with surfactants. The surface area and porous properties are dependent on the chain length of incorporated surfactant cation. The TiO<sub>2</sub> materials prepared in the presence of surfactant molecules during the gel formation exhibit much higher photocatalytic activity than that prepared in the absence of surfactants.

**Keywords:** Nanoporous, TiO<sub>2</sub>, photocatalysis.

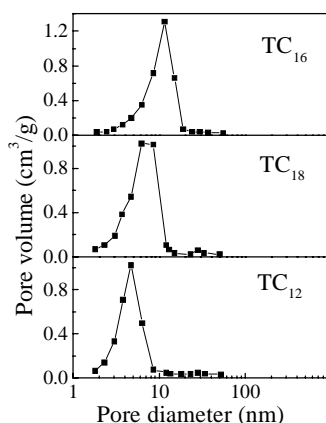
The sol-gel technique has been a very effective method for preparing nanometer TiO<sub>2</sub> photocatalysts<sup>1</sup>. But, there is a problem that when a hydrous titanium (IV) oxide gel is dried, the surface tension of solvents (usually water and /or alcohol ) contained in the pores within the Ti-O-Ti network leads to the shrinkage and collapse of the pores, reducing the surface area and destroying the microstructure of the dried gel. In order to obtain nanoporous TiO<sub>2</sub> with high surface area the collapse of the network structure has been overcome by supercritical drying of the hydrous TiO<sub>2</sub> gel<sup>2</sup>. In this work we report the preparation of nanoporous TiO<sub>2</sub> by a simple and effective method – controlled drying method with surfactants and the study of the photocatalytic degradation of dichloroacetic acid (DCA).

Nanoporous TiO<sub>2</sub> photocatalysts were prepared by a sol-gel synthesized from the combined solution of the TiOCl<sub>2</sub> precursor and surfactants (alkyltrimethylammonium halide) under basic condition and subsequent controlled drying with surfactants and calcination. The surface area and porous properties of materials were determined on a Micromeritics ASAP 2000 instrument. The photocatalytic experiments were performed in a Pyrex cell with aqueous solution of DCA irradiated by high pressure Hg lamp.

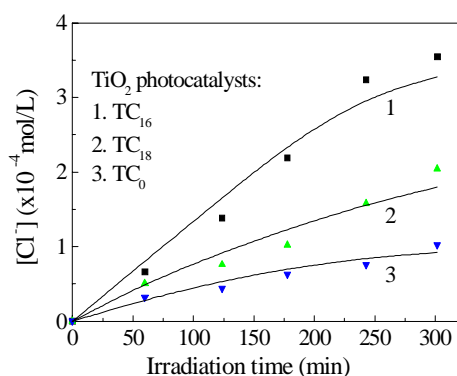
**Figure 1** gives pore size distributions calculated from the desorption isotherms for three samples: TC<sub>12</sub>, TC<sub>16</sub> and TC<sub>18</sub>. These TiO<sub>2</sub> materials are nanoporous with narrower pore size distribution and generally increasing the chain length of incorporated surfactant cation (C<sub>12</sub> –C<sub>18</sub>) results in apparent shift in the pore diameter distribution to larger size. The detailed data of surface area and porosities were listed in **Table 1**. Very significant increase in S<sub>BET</sub> and V<sub>TP</sub> was observed for TC<sub>12</sub>, TC<sub>16</sub> and TC<sub>18</sub>, as compared to TC<sub>0</sub> without surfactant molecules during the formation of the gel. The

variation of  $S_{\text{BET}}$ ,  $V_{\text{TP}}$  and the average pore diameter are dependent on the chain length of incorporated surfactant cation.

**Figure 1** Pore size distribution for three  $\text{TiO}_2$  samples calcined at  $450^\circ\text{C}$



**Figure 2** Change of  $[\text{Cl}^-]$  with irradiation time



**Figure 2** compares the concentration change of  $\text{Cl}^-$  produced in photocatalytic degradation of DCA with irradiation time on different samples.  $\text{TC}_{16}$  and  $\text{TC}_{18}$  exhibit much higher photocatalytic activity than  $\text{TC}_0$ . The apparent constants for  $\text{Cl}^-$  production,  $K_{\text{Cl}^-}$  are  $3.75 \times 10^{-3}$ ,  $1.6 \times 10^{-3}$  and  $7.0 \times 10^{-4} \text{ min}^{-1}$ , respectively. The larger pore size (10.2 nm) for  $\text{TC}_{16}$  sample may be favorable to the diffusion of organic molecules from the solution to the  $\text{TiO}_2$  surface and reducing the recombination of holes and electrons, thus leading to higher photocatalytic activity than  $\text{TC}_{18}$ .

**Table 1** BET surface area ( $S_{\text{BET}}$ ), total pore volume ( $V_{\text{TP}}$ ) and average pore diameter for samples calcined at  $450^\circ\text{C}$

Material	$S_{\text{BET}}$ ( $\text{m}^2\text{g}^{-1}$ )	$V_{\text{TP}}$ ( $\text{cm}^3\text{g}^{-1}$ )	Average pore diameter (nm)
$\text{TC}_0$	0.0005	0.0055	/
$\text{TC}_{12}$	237	0.3402	5.7
$\text{TC}_{16}$	169	0.4295	10.2
$\text{TC}_{18}$	252	0.4316	6.9

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 29877025).

### References

1. O. Yutaka, S. Hisao, *et al.*, *J. Am. Ceram. Soc.*, **1996**, 79, 825.
2. G. Dagan, M. Tomkiewicz, *J. Phys. Chem.*, **1993**, 97, 12652.

Received 30 November, 2001