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The study of the relationship between pore structure and photocatalysis of mesoporous TiO_2

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Abstract. Mesoporous titania was synthesized by a sol–gel method using the surfactants Span85 and X114 as the template. The pore structure was determined by the N_2 adsorption/desorption method below 73 K and calculated using the BJH model. TEM characterizations show that the pores are formed through particle accumulation. Two kinds of channels, straight channels made of cylindrical capillaries and curved channels made of slit-shaped pores, exist in the bulk materials. The influence of the pore structure of mesoporous TiO_2 on its photocatalytic performance was studied. The sample with higher porosity, better textural properties and straight channels are good for photocatalytic performance.

Keywords. Mesoporous TiO_2; pore structure; photocatalytic performance.

1. Introduction

TiO_2 is an effective catalytic material and has been intensively studied for sensors,[1,2] as a photocatalyst,[3] in solar cells,[4] lithium-ion cells[5] and many others. Many studies have reported that the surface properties of TiO_2, including grain size, crystallization, morphology, specific surface area, surface state, and porosity clearly influence its photocatalytic activity.[6–8]

Mesoporous TiO_2 has better properties in many respects than ordinary TiO_2 because of its high specific surface area and uniform pore diameter. Mesoporous TiO_2 was first synthesized through modified sol–gel routes in the presence of alklyphosphate surfactant templates in 1995.[9] Since then, researchers have adopted different routes to the synthesis of TiO_2 with the mesoporous structure such as the hydrothermal process using cetyltrimethylammonium bromide (CTAB) as a template agent,[10] the ultrasonic irradiation method,[11] the use of block copolymers,[12] the hydrolysis of $TiOCl_2$ aqueous solution at low temperature using octyl polyethylene oxide as the template agent,[13] and so on. Though this mesoporous TiO_2 has proved to have excellent performance as a photocatalyst there has been little investigation of the relationship between the pore structure and photocatalysis. In this paper, mesoporous TiO_2 was synthesized by the sol–gel method using tetrabutyl titanate as the precursor and Span85 or X114 as the surfactant. The pore structure of mesoporous TiO_2 was characterized by N_2 adsorption/desorption isotherms, X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) methods. The influence of the pore structure of mesoporous TiO_2 on its photocatalytic performance was studied. The results show that the catalytic activity has a close relationship with the pore structure.

2. Experimental

2.1 *Synthesis of mesoporous TiO_2*

Mesoporous TiO_2 was synthesized by the sol–gel method. Span85($C_{60}H_{108}O_8$) and X114(*t*-Oct-C_6H_4-$(OCH_2CH_2)_xOH$, x = 7–8) were chosen as the surfactants respectively. A homogeneous solution was obtained by stirring a mixture of 50 ml ethanol and surfactant. The dosage of Span85 and X114 are

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0.006 mol and 0.025 mol. 17 g tetrabutyl titanate was dropped into the above solution and then allowed to react at 60°C overnight. The resulting sol solution was gelled at 80°C in air for 7 days. Mesoporous TiO_2 was obtained by calcination of the gel at 500°C for 6 h in air to remove the surfactant species. The samples were designated as TiO_2-X114 and TiO_2-Span85 in this paper depending on the surfactant. TiO_2 is the nano-titania as purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2 *Photocatalytic performance*

Photocatalytic performance was tested by a study of the photo-degradation of acetone. The content of produced CO_2 was analysed by a gas chromatograph GC112 equipped with a thermal conductivity detector (TCD) using TDX-101 as the chromatogram column.

2.3 *Characterization*

The N_2 adsorption/desorption isotherms of mesoporous titania were measured on a Micromeritics ASAP 2020 instrument at a temperature below 73 K. The sample was treated at 300°C before measurement. Surface areas of the samples were calculated from the adsorption isotherms by the BET method and the pore size distributions determined from desorption isotherms by the Barrett–Joiner–Halenda (BJH) method. The average pore size was calculated from the *t*-plot method.

XRD patterns of the samples were obtained on a Thermo ARL SCINTAG X'TRA X diffractometer (using CuKα radiation, $\lambda = 0{\cdot}15406$ nm, scan range $2\theta = 15°{\sim}80°$, scan rate = 0.02 s^{-1}).

TEM was conducted on a JEM2010 (HR) instrument. SEM was conducted on a Hitachi S-4700 instrument.

3. Results and discussion

3.1 *Structure characterization*

The XRD patterns of TiO_2-X114 and TiO_2-Span85 are shown in figure 1. The diffraction peaks at 25.28°, 37.80° and 48.05° are consistent with the (101), (004) and (200) peaks of anatase TiO_2. The XRD results suggest that the samples prepared in this work have good anatase crystallization and the kind of surfactant has little influence on the nature of crystal formation.

Figure 2 shows the N_2 adsorption/desorption isotherms of TiO_2-X114, TiO_2-Span85 and TiO_2. The isotherms of TiO_2-X114 and TiO_2-Span85 are of type.[14] and that of TiO_2 is of type II. During the process of adsorption, single molecular layer adsorption occurred at relatively low pressure and then multi-molecular layer adsorption occurred at higher pressure. The larger are the sample pore sizes, the higher the pressure of capillary cohesion that occurred.[14] As shown in figure 2, the capillary cohesion of TiO_2 occurred at the highest pressure and that of TiO_2-Span85 occurred at the lowest pressure. It suggests that the sample TiO_2 had the largest pore size and TiO_2-Span85 had the smallest pore size. The hysteresis loop of TiO_2-X114 is the H1 type,[14] which can originate from independent cylindrical capillaries. The hysteresis of nanometer TiO_2 is H3,[14] which suggested that the sample has slit-

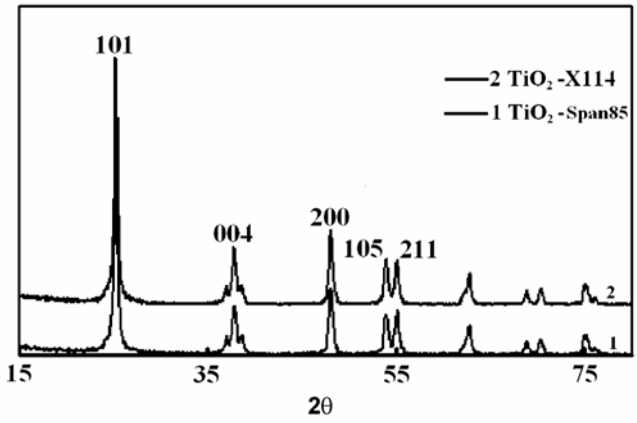


Figure 1. X-ray patterns of sample TiO_2-X114 and TiO_2-Span85.

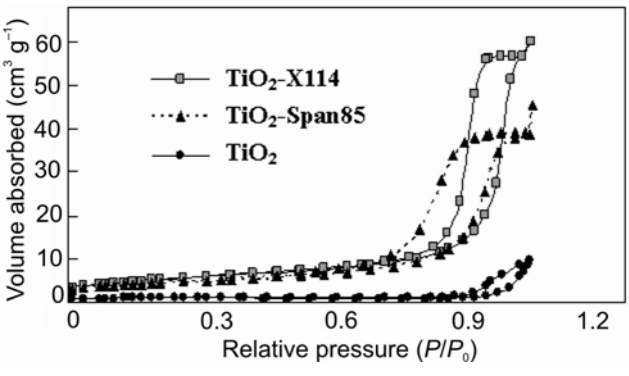


Figure 2. N_2 adsorption/desorption isotherms of TiO_2-X114, TiO_2-Span85 and TiO_2.

shaped pores. The hysteresis loop of TiO_2-Span85 is the H1 + H3 type, which indicated that this sample has some slit-shaped pores. Figure 3 is the pore size distribution of sample derived from the desorption branch of the N_2 adsorption/desorption isotherm. Samples TiO_2-Span85 and TiO_2-X114 have a narrow pore size distribution and most of the pore diameters are in the range of 10–20 nm. The sample TiO_2 has a wide pore size distribution with most of the pore diameters in the range of 10–30 nm. The surface area, pore volume and the average pore size of samples

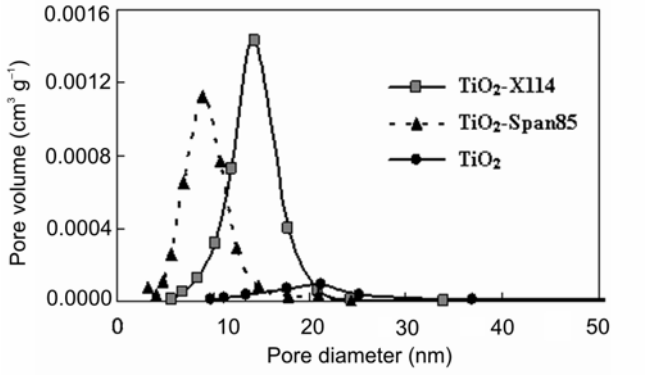


Figure 3. Pore size distributions of TiO_2-X114, TiO_2-Span85 and TiO_2 derived from desorption branches of N_2 adsorption/desorption isotherms.

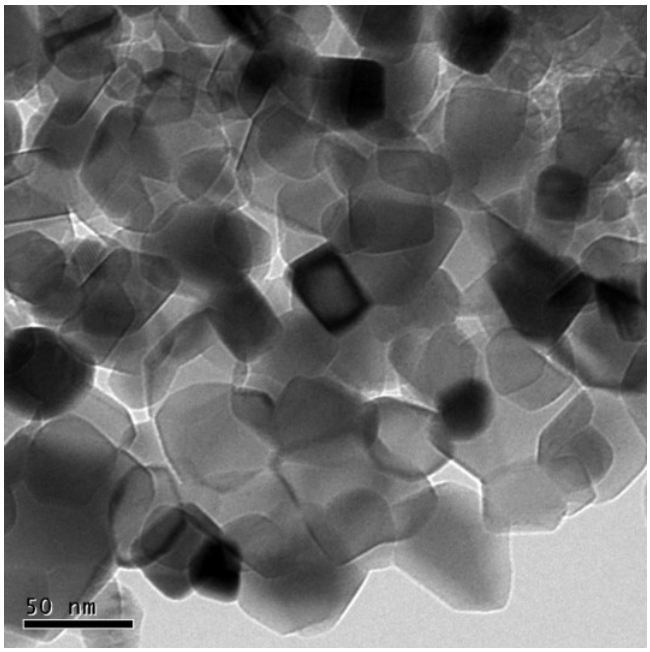
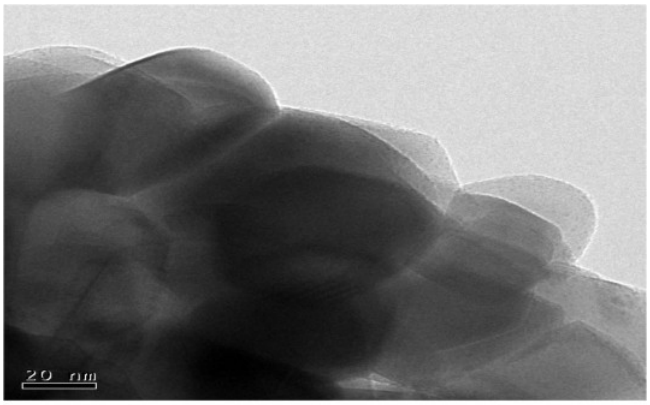


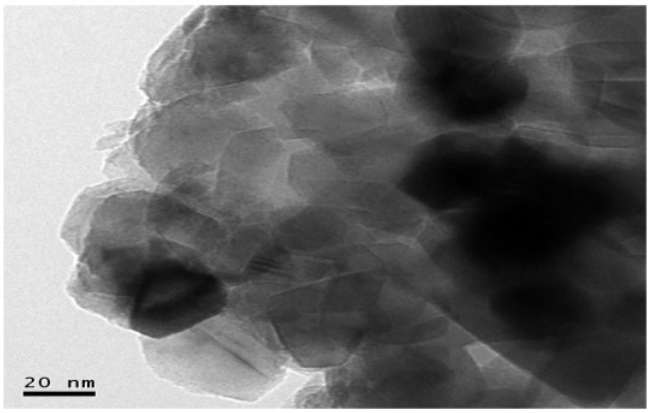
Figure 4. TEM image of sample TiO_2-X114.

Table 1. The specific surface area, pore volume and the average pore size of samples.

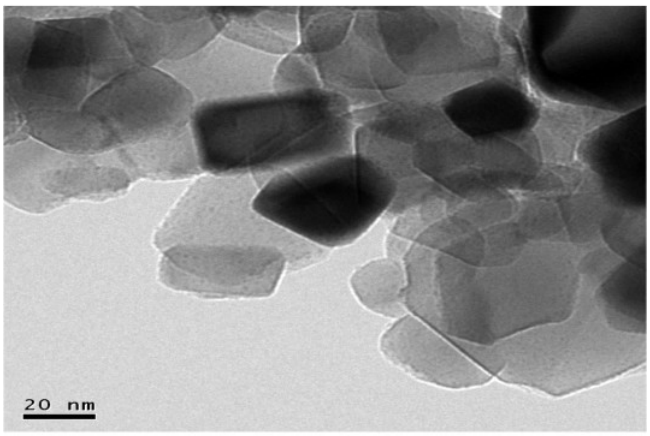
Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
TiO_2-X114	18·96	0·093	14·4
TiO_2-Span85	15·8	0·06	10·1
TiO_2	3·58	0·0094	24·38



TiO_2



TiO_2-Span85



TiO_2-X114

Figure 5. TEM images of TiO_2-X114, TiO_2-Span85 and TiO_2.

are summarized in table 1. Although the sample TiO_2 has the largest average pore size, its surface area and pore volume is smallest which indicated that the porosity is very low. The textural properties of TiO_2-X114 are greater than those of TiO_2-Span85.

Figure 4 shows the TEM image of TiO_2-X114. Nano-particles were packed randomly and pore channels were formed from the particle packing. The translucent region represents the straight channels and the gray region represents the curved channels. Figure 5 shows the TEM images of TiO_2-X114, TiO_2-Span85 and TiO_2. It is clear that TiO_2 has many shadow regions indicating that the nano-particles have agglomerated. TiO_2-X114 has much more translucent region than TiO_2-Span85 which suggests that TiO_2-X114 has many straight channels. TiO_2-Span85 has much more gray regions which suggest that many curved channels were formed. The results of the TEM accord well with that of the N_2 adsorption/desorption test. The H3 hysteresis loop of TiO_2 suggested that there are curved channels in the bulk. TiO_2-Span85 has many curved channels consisting mainly of slit-shaped pores. TiO_2-X114 has many straight channels consisting mainly of independent cylindrical capillaries.

Figure 6 shows the SEM images of TiO_2-X114, TiO_2-Span85 and TiO_2. It indicates that particles of TiO_2 congregate together so densely that few gaps exist between the pores. In contrast, the particles of TiO_2-X114 and TiO_2-Span85 congregate loosely. The particle size of TiO_2-X114 is slightly larger than that of TiO_2-Span85. The agglomeration of TiO_2 particles resulted in have low surface area and pore volume.

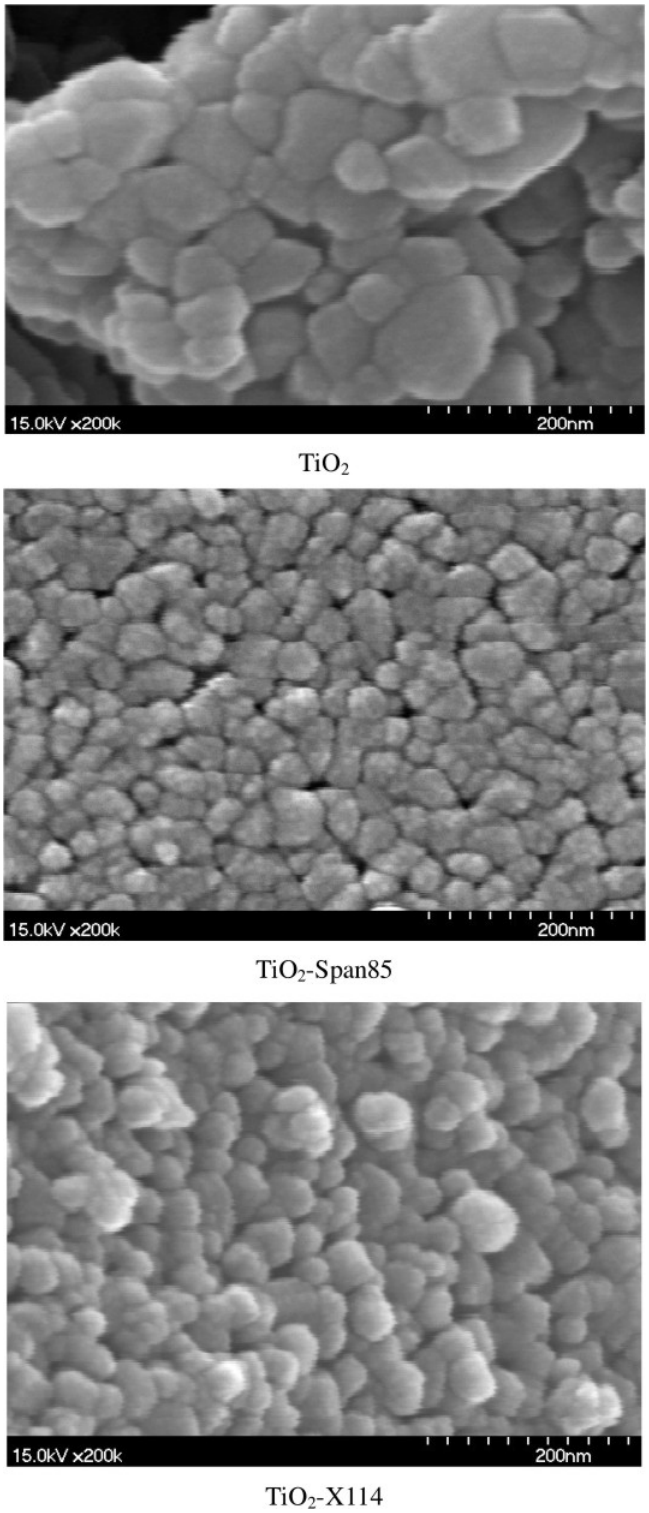


Figure 6. SEM images of TiO_2-X114, TiO_2-Span85 and TiO_2.

3.3 *Photocatalytic activity*

The pore-structure of mesoporous TiO_2 influences the adsorption of photoelectrons, reagents and prod-

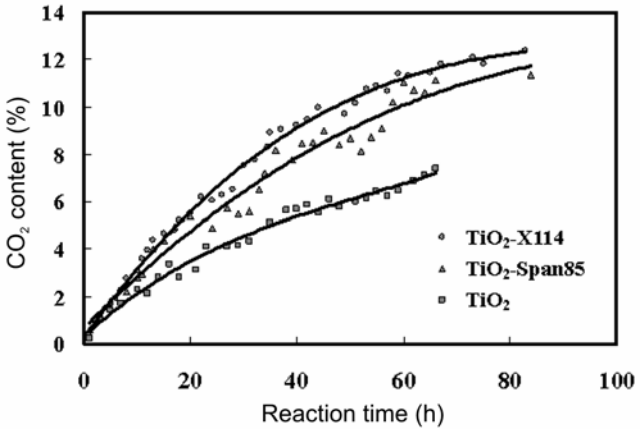


Figure 7. Photocatalytic performances of TiO_2-X114, TiO_2-Span85 and TiO_2.

ucts on the surface site. As a result, the photocatalytic activity of mesoporous TiO_2 will change with its pore structure. Figure 7 shows the dependence of the content of product CO_2 on the reaction time. The photocatalytic activity of nanometer TiO_2 is lower than that of mesoporous TiO_2-X114 and TiO_2-Span85. From the structure data, nanometer TiO_2 has many slit-gap pores with a H3 hysteresis loop and low porosity resulting in its small surface area and pore volume. Its structure is not suitable for the adsorption of photoelectrons and the diffusion of reagent and product. TiO_2-Span85 has many curved channels, a lower specific surface area, smaller pore volume and narrower pore diameter than TiO_2-X114, which limit the diffusion of reagent and product. As a result, TiO_2-Span85 has lower photocatalytic performance than that of TiO_2-X114.

4. Conclusions

In this paper, mesoporous TiO_2 was synthesized using the sol–gel method with surfactants Span85 and X114. The pore structures of the samples were determined by N_2 adsorption/desorption isotherms and TEM methods. Results indicated that the particles of mesoporous TiO_2 are arranged randomly and the pore channels are formed from the packing of particles. Two kinds of pore channels exist in the bulk samples. One is the curved channel composed mainly of slit-shaped pores. Another is the straight channel mainly formed by independent cylindrical capillaries. The photocatalytic activity of mesoporous TiO_2 has a close relationship to its pore structure. The sample with higher porosity, better textural properties and straight channel are good for photocatalytic performance. More detailed research into the dependence of pore structure on the photocatalytic activity is under investigation.

Acknowledgements

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