SHORT PAPER

Photocatalytic activity of TiO$_2$ synthesised by the sol-gel method[†]

Suzuko Yamazaki* and Tomoko Hayashi

Department of Chemistry, Faculty of Science, Yamaguchi University, Yamaguchi 753-8512, Japan

The effects of alkoxides, solvents, and the peptization and dialysis procedures in the sol-gel synthesis of TiO$_2$ on the degradation rates of ethylene were investigated.

Keywords: photocatalyst, titanium dioxide, sol-gel method, anatase, rutile

Much attention has been focused on the photocatalytic degradation of organic pollutants mediated by TiO$_2$ particles. A lot of work has demonstrated that this method is an effective approach towards the degradation or mineralisation of a wide variety of harmful/toxic organic pollutants.[1] The TiO$_2$ powders are commercially available but the powder form is not appropriate for practical use. Various researchers have investigated the synthesis of TiO$_2$ pellets or tried to immobilise TiO$_2$ particles in a thin film form by the sol-gel process.[2-9] The sol-gel synthesis involves hydrolysis of metal alkoxides by water, producing metal oxides or hydrated oxides. The hydrolysis conditions such as water/alkoxide ratio, solvent, catalyst, reaction temperature, and alkyl groups in the alkoxide are well known to affect the kinetics of hydrolysis reaction and in turn to modify the structural and physical characteristics of oxide materials obtained by sintering.[10] In this paper, we study the photocatalytic activity of the TiO$_2$ which was synthesised by sol-gel techniques under various conditions.

The TiO$_2$ was prepared as follows. When 15ml of [Ti(OC$_2$H$_5$)$_4$], [Ti(OC$_3$H$_7$)$_4$] or [Ti(OC$_4$H$_9$)$_4$] was hydrolysed in 180 ml H$_2$O containing 1.3 ml HNO$_3$, precipitation occurred immediately. The precipitates were stirred continuously at room temperature to form a highly dispersed sol. In this peptisation process, which is a common method for preparing stable colloidal solutions from bulk matter, the time required to obtain the dispersed sol varied depending on the alkoxides: 7 days for [Ti(OC$_2$H$_5$)$_4$], 5 days for [Ti(OC$_3$H$_7$)$_4$] and 2 days for [Ti(OC$_4$H$_9$)$_4$]. This sol was then dialysed in a cleaned molecularly porous dialysis tube (Spectra/Por, molecular cut-off 3500) until a value of approximately pH 4 was obtained. The sol was concentrated by a factor of five in a rotary evaporator and was dried in an oven at 40 – 50 °C for 2 days. The resulting gel was sintered at 100 – 500 °C. Table 1 shows that the specific surface area and mean pore radius for the obtained TiO$_2$ pellets were not influenced by the nature of the alkoxides. The X-ray diffraction patterns of the synthesised TiO$_2$ at various firing temperatures were not affected by the starting alkoxides: with increasing firing temperatures, anatase crystals grow continuously until they start to convert into rutile at 300°C. This phase transition was almost complete at 500 °C.[9]

The photodegradation experiments of ethylene were performed to examine the photocatalytic activity of the synthesised TiO$_2$. In this paper, the TiO$_2$ samples synthesised under various conditions were ground into powders with a mortar and pestle and the photocatalytic activities were compared using the powder form. A 0.2 gram sample of a TiO$_2$ powder was packed in a tubular photoreactor (inner diameter: 2.2 mm, catalyst bed: 9 cm) which was surrounded by four 4 W fluorescence black light bulbs (Matsushita, FL 4BL-B). The gas stream containing 160 ppmv ethylene, 2.2 × 10^5 ppmv O$_2$ and 1.9 × 10^3 ppmv water vapor was passed through the TiO$_2$ in a single pass mode at a flowrate of 88 ml min^{-1}. The photodegradation of ethylene did not proceed in the absence of either TiO$_2$ or the light irradiation. However, when the gas stream flowed through the TiO$_2$ under irradiation, ethylene was degraded to CO$_2$. The experiments were conducted with irradiation period of 2 h, in which no deterioration of the degradation rate of ethylene was observed, *i.e.* the photocatalytic activity of the catalyst was not changed. The stoichiometric ratio of the concentration of CO$_2$ in the outlet gas to that of ethylene degraded was estimated to be 1.96 ±0.02 under any condition in the present experiments, which suggests ethylene was completely mineralised. Fig. 1 shows that the degradation rate of ethylene decreased in the following order: [Ti(OC$_2$H$_5$)$_4$] > [Ti(OC$_3$H$_7$)$_4$] > [Ti(OC$_4$H$_9$)$_4$]. The degradation rate on the TiO$_2$ synthesised from [Ti(OC$_2$H$_5$)$_4$] was higher by a factor of 1.4 than that from [Ti(OC$_4$H$_9$)$_4$]. However, the physical properties such as specific surface area, pore radius and XRD data were independent of the starting alkoxides. More work is required to clarify other factors controlling the degradation rates. Fig.1 also indicated that the reaction rate decreased with an increase in firing temperature, which is due to a decrease in specific surface area as seen in Table 1.

Table 1 Specific surface area (SSA) and mean pore radius (MPR) of the TiO$_2$ synthesised from various alkoxides

Firing temp. (°C)	Ethoxide		Propoxide		Butoxide	
	SSA(m^2/g)	MPR(Å)	SSA(m^2/g)	MPR(Å)	SSA(m^2/g)	MPR(Å)
100	288.6	15.1	244.9	18.6		
200	214.5	21.9	182.7	26.0	249.3	17.0
300	136.0	31.1	124.2	36.7		
400	82.7	37.1	80.4	46.5		
500	14.6	59.0	18.8	78.8	0.145	115.1

*To receive any correspondence. E-mail: yamazaki@yamaguchi-u.ac.jp
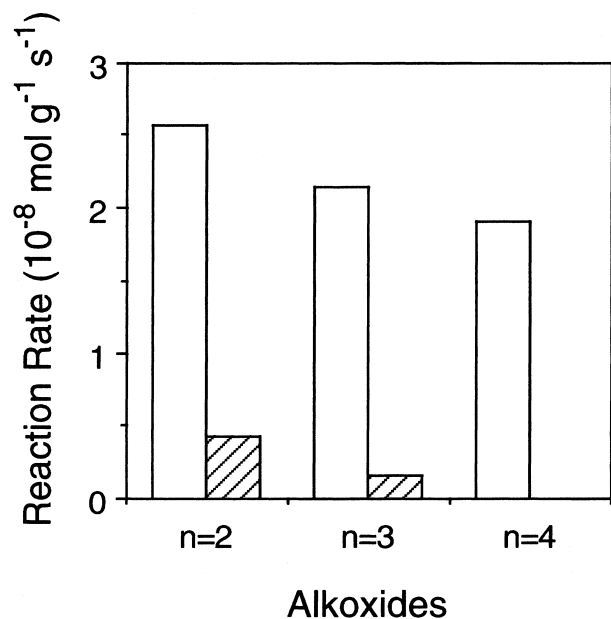[†]This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

Fig.1 Effect of alkoxides [Ti(OC$_n$H$_{2n+1}$)$_4$] as starting materials on the degradation rate of ethylene. TiO$_2$ was sintered at 200 °C (□) or 500 °C (▨).
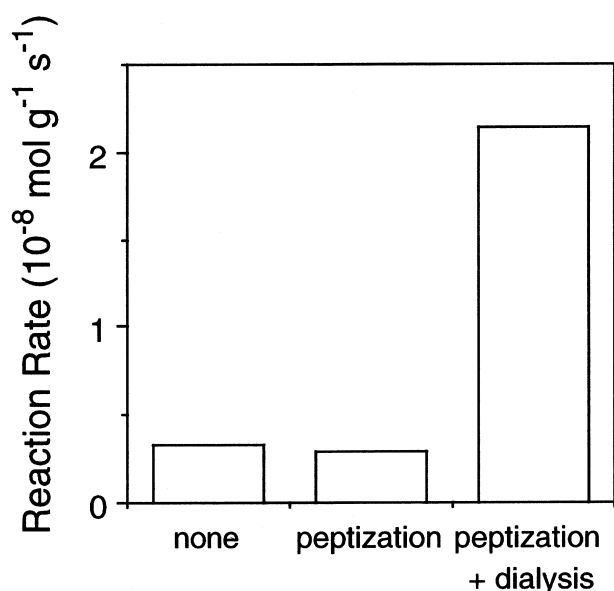

Fig.2 Effect of peptisation or dialysis procedure on the degradation rate of ethylene. TiO$_2$ was sintered at 200 °C.

Figure 2 depicts the effect of peptisation and dialysis on the degradation rate of ethylene. The reaction rate on the TiO$_2$ powder, ground after firing the white precipitates on hydrolysis, was estimated to be 3.27 x 10^{-9} mol/g/s, which was almost the same as that obtained from the dispersed sol after peptisation. However, a seven-fold increase in the rate was achieved by introducing a dialysis process. Since the pH of solutions inside the dialysis tubes changes slowly and uniformly, agglomerates are created in the sol, which will result in larger porosity. Indeed, a large pore, as much as 26 Å in radius, was formed only *via* dialysis. It is noted as listed in Table 2 that the specific surface area was not affected so much with or without peptisation or dialysis. Therefore, the higher catalytic activity with dialysis is due to the formation of the large pore.
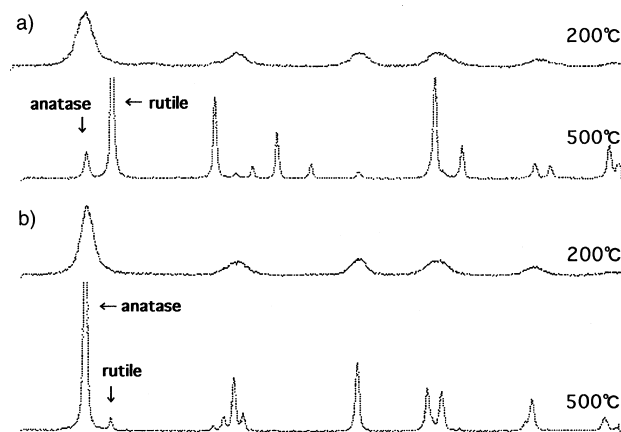

Fig.3 X-ray diffraction patterns of the TiO$_2$ prepared in (a) water or (b) a mixed solvent of water and ethanol (2 : 1).

Table 2 Effect of peptisation and dialysis on specific surface area and mean pore radius of the TiO$_2$ fired at 200°C

	None	Peptisation	Peptisation + dialysis
SSA(m^2/g)	170.1	142.4	182.7
MPR(Å)	12.2	11.4	26.0

Table 3 Specific surface area (m^2/g) of the TiO$_2$ synthesised in the mixed solvent of water and ethanol (2:1)

Firing temp.(°C)	Ethoxide	Propoxide
100	351.2	
200	209.3	208.0
300	86.7	
400	46.2	
500	1.32	3.66
700	0.861	

The peptisation process was conducted in a mixed solvent of H$_2$O and ethanol (2:1) in order to examine the solvent effect. Even when stirring continued for 20 days, the white precipitates were not dispersed to a colloidal solution. Thus, after stirring only for 10 min, the precipitates were washed by repeating decantation to obtain pH 4, then filtered by aspirator, dried and fired. Comparison between Tables 1 and 3 reveals that the absence or presence of ethanol as a solvent did not alter the specific surface area of the TiO$_2$ which was fired at 200 °C. The XRD pattern was not influenced either as shown in Fig. 3 which presented broad anatase peaks. However, Fig. 4 showed that the degradation rate of ethylene on the TiO$_2$ prepared in the mixed solvent was lower by a factor of 2.5 than that in water. This might be due to a residual small quantity of ethanol, which was photodegraded competitively with ethylene. On the other hand, when firing temperatures above 300 °C were adopted, the specific surface areas of the TiO$_2$ synthesised in the mixed solvent were much lower than those in water. Fig. 3 indicated that their XRD patters were quite different at 500 °C. It is quite interesting that the anatase is dominant even at 500 °C when the mixed solvent was used. This means that the hydrolysis in the presence of ethanol prevents the crystal from converting to rutile. It is well known that photocatalytic activity of anatase is higher than that of rutile. However, the anatase form is usually produced at a lower sintering temperature than rutile and thus, the specific surface area of anatase is higher than that of rutile. Therefore, we can not determine whether the higher activity of the anatase form is due to the crystalline phase or to a higher specific surface area. Our results at
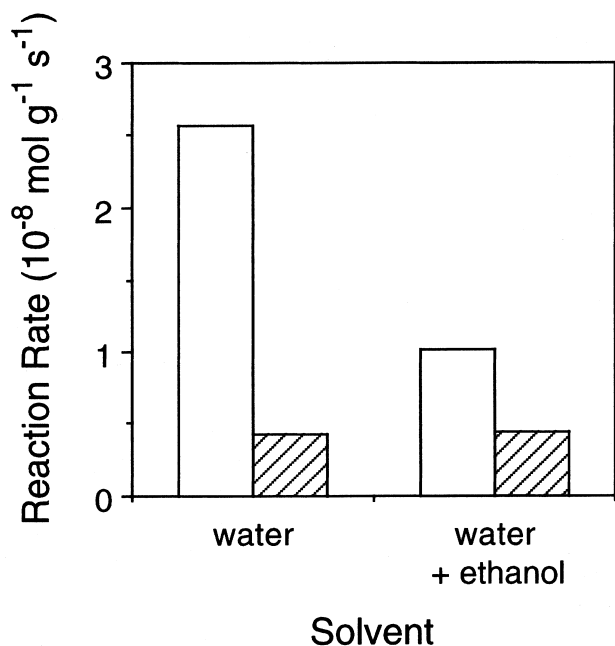
surface area is lower by a factor of 11.1 than that of rutile. On the other hand, the degradation rates of ethylene on both TiO_2 samples were estimated to be almost the same, *i.e.*, 4.28 x 10^{-9} mol/g/s for water and 4.49 x 10^{-9} mol/g/s for the mixed solvent as shown in Fig. 4. Therefore, we can conclude on the catalytic activity of crystalline phase that the anatase phase is more photoactive than the rutile phase.

Fig. 4 Effect of solvents on the degradation rate of ethylene. TiO_2 was sintered at 200 °C (☐) or 500 °C (▨).

500 °C show that rutile of 14.6 m²/g was produced in the case of water while anatase of 1.32 m²/g yielded when the mixed solvent was used. We produced an anatase whose specific

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