Synthesis of thermally stable nanocrystalline anatase by high-temperature hydrolysis of titanium alkoxide with water dissolved in organic solvent from gas phase

H. KOMINAMI, Y. TAKADA, H. YAMAGIWA,* Y. KERA
Department of Applied Chemistry, Faculty of Science and Engineering and *Joint Research Centre, Kinki University, Kowakae, Higashiosaka 577, Japan

M. INOUE, T. INUI
Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01, Japan

Titania (TiO_2) is an important material as a photo-catalyst and is also an excellent support for many types of catalyst. It has been used as a support in commercial V_2O_5 catalyst for selective catalytic reduction of NO_x with NH_3 [1]. Inomata et al. [2] found that titania support exhibited a promoting effect on the selective oxidation of benzene to maleic anhydride. It was also reported that titania-supported molybdenum or cobalt–molybdenum catalyst showed a higher activity than alumina-supported catalyst in the hydrodesulphurization [1, 3].

Titania for catalytic use is usually prepared from $TiO(SO_4)$, $Ti(SO_4)_2$ or $TiCl_4$ by the precipitation (or hydrolysis) method. However, it is known that the counter anion of the starting titanium salt remains in the product [4] and affects the activity of the catalyst [5]. To avoid counter anion contamination, titanium alkoxides are used as the starting material for catalysts and catalyst supports. Hydrolysis of titanium alkoxide produces amorphous hydrated titania with a large surface area; however, its surface area drastically decreases due to the crystallization of anatase at about 400 °C [6].

Recently, nano-sized microcrystalline titania (nanocrystalline titania) was prepared by several methods [7–11] and was found to show a relatively high thermal stability even after calcination at 500–600 °C [9, 10]. Inoue et al. [9] found that thermal decomposition of titanium acetylacetonate in toluene at 250 °C yielded nanocrystalline anatase free from counter anion contamination, and that the sample calcined at 550 °C had relatively high surface area ($>50\,m^2\,g^{-1}$). Harle et al. [10] reported that nanocrystalline anatase prepared by the reaction of titanium oxysulphate with molten alkali-nitrate maintained a large surface area above $100\,m^2\,g^{-1}$, even after calcination at 600 °C, although the product was contaminated by a small amount of sulphate ion (0.1–0.5 wt%). The high thermal stability may be due to the sulphate ion in the product because sulphate ion occluded in titania particles was reported to increase the thermal stability of the titania sample [5].

Inoue et al. [12] also reported a novel method for synthesis of thermally stable monoclinic zirconia.

Hydrolysis of zirconium alkoxides at high temperatures with a limited amount of water dissolved in toluene from gas phase and simultaneous hydrothermal crystallization produced nanocrystalline monoclinic zirconia, which maintained a large surface area of $162\,m^2\,g^{-1}$ even after calcination at 500 °C. In this connection, we applied this method for titania synthesis and found that it yielded nanocrystalline anatase, which preserved large surface area even after calcination at 550 °C.

Titanium n-butoxide (TNB), 5 g, was dissolved in $70\,cm^3$ of an organic solvent in a test-tube, which was then set in a $200\,cm^3$ autoclave. In the gap between the test tube and the autoclave wall, $15\,cm^3$ of water were added. The autoclave was purged with nitrogen, heated to the desired temperature (125–300 °C) at a rate of $2.7\,°C\,min^{-1}$, and held at that temperature for 2 h under the autogenous pressure. After the autoclave was cooled, the resulting powders were washed repeatedly with acetone and air dried. The product was calcined for 1 h in a box furnace.

Powder X-ray diffraction (XRD) was determined using Ni-filtered CuK_α radiation. The crystallite size was calculated from the half-height width of the 101 diffraction peak of anatase using the Scherrer equation: the value of the shape factor, K, was arbitrary taken to be 0.9. The morphology of the product was observed on a Jeol JEM-3010 transmission electron microscope (TEM) operated at 300 kV. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) single-point method on the basis of nitrogen uptake measured at 78 K. Pore size distribution curves in the range 3–30 nm were calculated from the nitrogen adsorption isotherms by the Barrett–Joyner–Halenda method.

The XRD pattern of the product obtained by the reaction in hexanol at 300 °C is given in Fig. 1a, which shows that anatase was formed without contamination of other phases of titania. Addition of water to the supernatant after the reaction gave no precipitates, indicating that TNB was completely hydrolysed with water dissolved from the gas phase. Formation of the crystalline phase suggests that two successive processes, namely hydrolysis of TNB and

crystallization of anatase, took place during the reaction. The product showed 4.9% weight loss from 130 to 1000 °C; however, no exothermic peak was detected in the differential thermal analysis (DTA) profile of the product. This thermal behaviour is in contrast to that for the alkoxide-derived amorphous titania sample, which shows large weight loss and two exothermic peaks due to the combustion of organic moieties and crystallization of the anatase phase.

TEM observation showed that the product was composed of agglomerates of primary particles having an average diameter of 8.9 nm (Fig. 2). This value is in good agreement with the crystallite size (9.0 nm) calculated by the line-broadening technique, which suggests that each primary particle observed by TEM is a single crystal of anatase in nano scale.

The results obtained under the various reaction conditions are summarized in Table I. When the reaction was carried out at 125 °C, TNB was not hydrolysed. At temperatures higher than 150 °C, anatase was formed as the sole product. The crystallite size of the anatase formed gradually increased with increasing reaction temperature and prolonged reaction time. The reactions of TNB in other alcohols, toluene and xylene and the use of titanium isopropoxide instead of TNB also gave nanocrystalline anatase. As shown in Table I, solvent effect was observed in the crystallite size of the product, and the crystallite size of anatase can be controlled in the range from several nanometres to about 15 nm by reaction conditions and the choice of organic solvent. Removal of water from the present procedure gave no solid product and TNB remained in the solvent.

Kondo et al. [11] examined the hydrothermal treatment of alkoxide-derived amorphous titania particles and found that the crystallite size of

Figure 2 TEM photograph of the product. The synthesis conditions are described in Fig. 1.

anatase formed increased to 25 nm by the treatment at 250 °C. The crystallite size of the present anatase sample ($\sim$7 nm) was much smaller than that of the products obtained by the hydrothermal method. Smaller crystallite size can be explained by the limited solubility of titania in the organic solvent with a small portion of water under the autoclaving conditions.

The properties of the samples obtained by calcination of the present anatase at 550 °C are also summarized in Table I. Phases other than anatase were not observed in the calcined samples (Fig. 1b). Crystal growth of the present nanocrystalline anatase by calcination was relatively small, and the calcined samples showed crystallite sizes of 10–20 nm. Due to the small crystal growth, the calcined sample showed large surface areas of 80–120 m^2 g^{-1}. The thermal stability of the two amorphous titania samples prepared by the hydrolysis of titanium alkoxide was also examined (Table I). After calcination at 550 °C, surface areas of the amorphous titania samples decreased drastically due to crystallization of anatase and crystal growth. The nanocrystalline anatase samples also possessed pore volumes in the range of 0.16–0.51 cm^3 g^{-1}, which was much larger than that of a commercial titania sample (JRC-TIO-4, Catalysis Society for Japan) (0.07 cm^3 g^{-1}).

The pore size distribution and the mode pore diameter of the samples calcined at 550 °C are shown in Fig. 3 and Table I, respectively. The calcined samples had a relatively sharp distribution peak and the mode pore diameter increased with
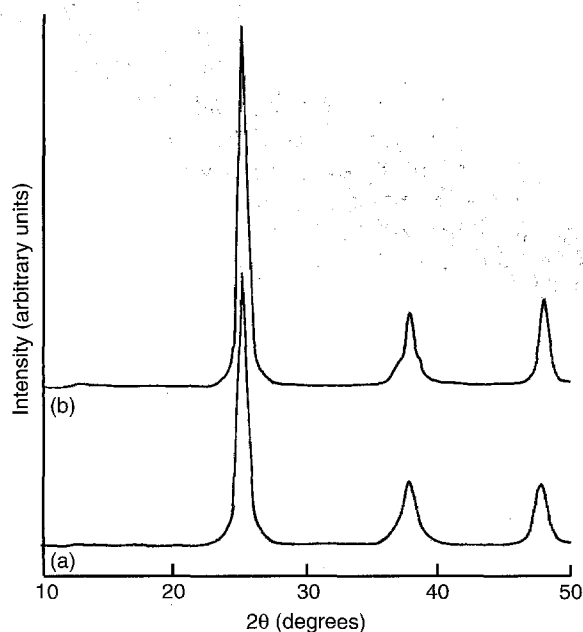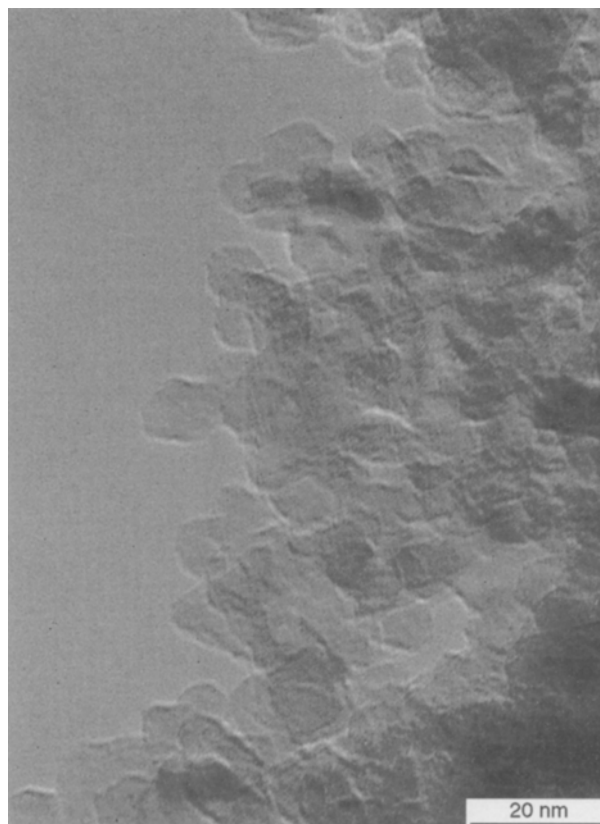

Figure 1 XRD patterns of (a) the product obtained by the hydrolysis of titanium n-propoxide in hexanol at 300 °C and (b) the sample after calcination of the product at 550 °C.

TABLE I Typical properties of nanocrystalline titania samples obtained under various reaction conditions and of the calcined samples

Ti alkoxide	Organic solvent	Water (mol)	Reaction temperature (°C)	Reaction time (h)	Product		After calcination at 550 °C for 1 h			
					Crystallite size[a] (nm)	Surface area $(m^2 g^{-1})$	Crystallite size[a] (nm)	Surface area $(m^2 g^{-1})$	Pore volume[b] $(cm^3 g^{-1})$	Mode pore diameter (nm)
TNB[c]	Hexanol	0.8	125	2	No reaction					
TNB	Hexanol	0.8	150	2	6.3	224	19	78	0.16	6.5
TNB	Hexanol	0.8	200	2	6.6	204	15	87	0.22	7.4
TNB	Hexanol	0.8	270	2	7.8	158	14	95 (32)[d]	–	–
TNB	Hexanol	0.8	300	2	9.0	117	15	95	0.31	10
TNB	Hexanol	0.8	200	8	7.1	192	11	107	0.29	7.5
TNB	Hexanol	0.8	200	32	8.5	137	12	112	0.33	9.8
TNB	Hexanol	0	300	2	No reaction					
TNB	Propanol	0.8	300	2	16	94	17	83	0.35	15
TNB	Octanol	0.8	300	2	10	134	13	112	0.42	13
TNB	Decanol	0.8	300	2	11	122	13	119	0.51	18
TIP[e]	Hexanol	0.8	300	2	8.7	119	12	100	–	–
TIP	Toluene	0.8	300	2	11	125	13	99	–	–
TIP	Xylene	0.8	300	2	10	131	12	109	–	–
Amorphous titania A[f]					–	452	18	29	–	–
Amorphous titania B[g]					–	74	42	6	–	–
Commercial titania[h]					–	–	24	40	0.07	–

[a]Calculated from the 101 diffraction peak of anatase by the Scherrer equation.
[b]<30 nm.
[c]Titanium n-butoxide.
[d]After calcination at 700 °C for 1 h.
[e]Titanium isopropoxide.
[f]Prepared by the ordinary hydrolysis method: water was added to the alcoholic solution of TIP.
[g]Prepared by hydrolysis of TIP with water vapour under atmospheric pressure for two months (humidity 85%).
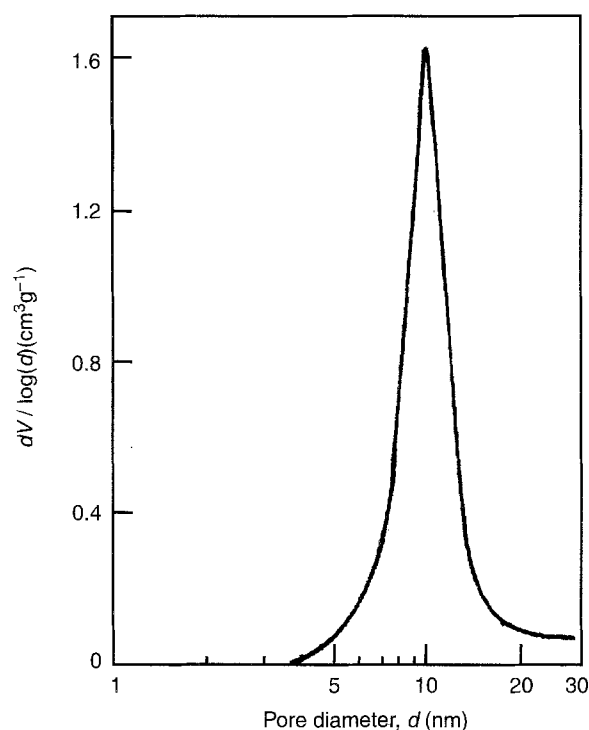[h]JRC-TIO-4, provided by the Catalysis Society of Japan.

Figure 3 Pore size distribution curve of the calcined sample. The calcination conditions are described in Fig. 1.

elevating reaction temperature and prolonged reaction time. Because the nitrogen adsorption–desorption isotherm of the sample showed the E-type hysterisis classified by De Boer [13], the pores were explained by voids between the nanosized crystals of anatase.

In conclusion, hydrolysis of titanium alkoxide at high temperatures with water dissolved in organic solvent from gas phase yielded nanocrystalline anatase which showed high thermal stability. The physical properties, such as crystallite size, pore size and pore volume, can be controlled by reaction conditions and the choice of organic solvents.

Acknowledgements

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