Ultra-highly Active Titanium(IV) Oxide Photocatalyst Prepared by Hydrothermal Crystallization from Titanium(IV) Alkoxide in Organic Solvents

Hiroshi Kominami,* Takeshi Matsuura, Kunihiro Iwai,† Bunsho Ohtani,† Sei-ichi Nishimoto,† and Yoshiya Kera
Department of Applied Chemistry, Faculty of Science and Engineering, Kinki University, Kowakae 3-4-1, Higashiosaka 577
†Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Yoshida, Kyoto 606-01

(Received May 1, 1995)

Microcrystalline titanium(IV) oxide (TiO_2) powders having high surface area and high crystallinity were synthesized by high-temperature hydrolysis of titanium(IV) alkoxide in organic media. They were platinized and then used for photocatalytic dehydrogenation of 2-propanol in aqueous solution. The TiO_2 catalysts exhibited much higher production rates of hydrogen and acetone than representative active TiO_2 catalysts (P-25).

Titanium(IV) oxide (TiO_2) powders have been known to exhibit photocatalytic activities for many kinds of reactions.[1] The TiO_2 powders have been usually prepared from titanium(IV) salts or alkoxides by precipitation (or hydrolysis) method.[2] This method produces amorphous hydrated TiO_2; therefore, thermal treatment at higher temperature (>ca. 673 K) is necessary to obtain anatase crystallites, which generally show higher photocatalytic activity than amorphous or rutile phase. However, the crystallization of the anatase phase caused the drastic decrease in surface area.[2]

A part of the authors has shown that the rate of photocatalytic reaction induced by TiO_2 is expressed as a function of rates of recombination and capture of photoexcited electron and positive hole by surface-adsorbed substrates.[3] This finding suggests significant information on the requisites for active TiO_2 photocatalyst; 1) high surface area to adsorb large amount of substrates, 2) high crystallinity, i.e., less defects, to prevent the recombination of electrons and positive holes. However, it seems difficult to prepare such TiO_2 photocatalyst which satisfies both properties by the conventional methods such as precipitation and subsequent calcination process as mentioned above. As reported recently, we could synthesize microcrystalline TiO_2 (anatase form) with both high surface area and sufficient crystallinity by high-temperature hydrolysis of titanium alkoxide with a limited amount of water dissolved in organic solvents.[4] Here we show the remarkably higher photocatalytic activities of this TiO_2.

The microcrystalline TiO_2 samples were synthesized by high-temperature hydrolysis of titanium(IV) tetrabutoxide (TNB) in organic media under the autogenous pressure (1 - 3 MPa).[4] The method will be called as HyCOM (Hydrothermal Crystallization in Organic Media) in this article. TNB in an organic solvent was heated at temperatures up to 573 K for 2 h in an autoclave in the presence of water (15 cm^3) which was not in contact with the organic solvent. During the thermal treatment, water dissolved in the organic solvent from gas phase hydrolyzed the alkoxide, fulfilling hydrothermal conditions under which crystallization of TiO_2 took place. Limited solubility of TiO_2 in organic solvents with a small portion of water inhibited excess growth of TiO_2 crystals, resulting in the formation of microcrystalline TiO_2. The TiO_2 samples obtained were washed repeatedly with acetone, dried (yield >98%), and further annealed in air at calcination temperatures up to 1123 K. Platinization was performed by incipient wetness method from an aqueous solution of chloroplatinic acid ($H_2PtCl_6 \cdot 6H_2O$; Kanto Chemical) followed by hydrogen (H_2) reduction at 773 K. The platinized TiO_2 catalyst (50 mg) was suspended in an aqueous solution (5.0 cm^3) of 2-propanol (500 µmol) and photoirradiated at wavelength > 300 nm under argon for 1 h at 298 K with vigorous magnetic stirring (1000 rpm). The details of

Table 1. Physical properties of TiO_2 samples prepared under various conditions and their photocatalytic activities for dehydrogenation of 2-propanol in aqueous solutions

Cat.	Organic solvent[a]	TNB[b] charged /g	Synthesis temp./ K	Calcination temp./ K	Phase[c]	d_{101}[d] / nm	S_{BET}[e] / m^2g^{-1}	Pt loading / wt%	H_2 / µmol	Acetone / µmol	H_2 / acetone
A	T	6	573	823	A	14	111	0	3	4	0.8
B	T	6	573	823	A	14	111(106)	0.05	194	195	0.99
C	T	6	573	823	A	14	111(66)	0.5	317	318	1.00
D	T	6	573	823	A	14	111	2	174	170	1.02
E	H	6	573	823	A	15	95	0.5	315	291	1.08
F	H	6	423	823	A	19	78	0.5	123	120	1.03
G	T	12	573	773	A	14	86(77)	0.5	173	189	0.92
H	T	12	573	823	A	15	67(53)	0.5	261	274	0.95
I	T	12	573	973	A	20	37(27)	0.5	214	208	1.03
J	T	12	573	973	A	20	37	0.2	302	273	1.10
K	T	12	573	1123	R, (A)	33 (R)	12(11)	0.5	8	7	1.1
UV[f]					A	-	>250[g]	0.5	195	183	1.07
P-25[f]					A, R	24 (A)	50[g]	0.5	125	111	1.13

[a]Used as a medium for TiO_2 synthesis (70 cm^3). H; hexanol, T; toluene. [b]Titanium tetrabutoxide. [c]A; anatase, R; rutile. [d]Crystallite size calculated from the 101 and 110 diffraction peaks of the anatase and rutile phases, respectively. [e]BET surface area. Surface area after platinization is shown in the parenthesis. [f]UV; Sachtleben Hombikat UV-100, P-25; Degussa P-25. [g]Data reported by the suppliers.

photoirradiation and product analyses were reported elsewhere.[5]

Physical properties and photocatalytic activities of the HyCOM TiO_2 catalysts are summarized in Table 1. It has been reported that photocatalytic reaction of 2-propanol under deaerated conditions gives predominantly H_2 and acetone, and the rate is markedly accelerated by Pt loading.[6] All the HyCOM TiO_2 catalysts produced almost equimolar H_2 and acetone, along with negligible formation of CO_2. A bare HyCOM TiO_2 (Cat. A) showed the negligible activity. The activity was remarkably enhanced by only a small amount of Pt loading (0.05 wt%, Cat. B) and was increased with increasing Pt content (Cat. C), while further loading decreased the activity (Cat. D). Such negative effect of excess Pt has been also observed in the case of Degussa P-25.[7]

It is well known that P-25 shows high photocatalytic activities for various reactions and, therefore, it has been widely used for photocatalytic reactions as a reference catalyst. In the present study, activities of several kinds of commercial TiO_2 powders were also examined under the same reaction conditions and Hombikat UV-100 (Sachtleben) and P-25 showed higher activities (Table 1). However, the HyCOM TiO_2, e.g., Cat. C, exhibited much higher production rates than these two commercial TiO_2 powders. These results clearly indicate the extraordinarily high activity of the HyCOM TiO_2 catalysts.[8]

The effect of preparation conditions on the activity of the HyCOM TiO_2 was also shown in Table 1. Use of hexanol instead of toluene as the organic solvent gave negligible influence on the activity (Cat. E). HyCOM TiO_2 synthesized at low temperature showed low activity (Cat. F). Increase in the amount of TNB charged resulted in slight decrease in the activity (Cat. H). The latter two preparation parameters might control the crystallinity of the HyCOM TiO_2.[4] Therefore, high crystallinity of TiO_2 before annealing seems to be essential for highly active TiO_2 catalyst.

With elevating calcination temperature, surface area gradually decreased as commonly seen for conventionally prepared TiO_2 samples. However, it should be noted that, even after calcination at 973 K, the HyCOM TiO_2 still possesses relatively high surface area of 37 m^2g^{-1} and remains in the anatase form. The photocatalytic activity increased with elevating calcination temperature up to 823 K (Cat. G and H), but decreased at >973 K (Cat. I). However, the fact that the activity was recovered by decreasing the Pt content to 0.2 wt% (Cat. J) shows the essentially higher photocatalytic activity of TiO_2 calcined at 973 K. The catalyst which almost consisted of the rutile phase (Cat. K) showed negligible activity.

Table 2 shows photocatalytic activity of bare HyCOM TiO_2 catalysts suspended in an aqueous silver sulfate solution (Ag_2SO_4, 0.025 mol dm^{-3}).[5] In this case, silver metal deposits on the TiO_2 surface and oxygen evolves with the molar ratio of 4:1 without the aid of loaded Pt.[5] The photocatalytic activity of HyCOM TiO_2 increased with elevating calcination temperature and the highest activity was obtained when calcined at 973 K. The catalyst which predominantly consisted of rutile (1123 K) also exhibited a fairly high activity. As clearly seen, the higher activity of the HyCOM TiO_2 in comparison with P-25 was also confirmed for this photocatalytic reaction.

Table 2. Photocatalytic activities of TiO_2 samples for Ag deposition and O_2 evolution from Ag_2SO_4 solutions[a]

Calcination temp./ K	Ag / µmol	O_2 / µmol	Ag / 4 $\times O_2$
823	12.1	2.6	1.2
923	34.6	8.9	0.97
973	101.7	24.4	1.04
1123	86.6	20.5	1.06
(P-25)	54.6	13.3	1.03

[a] TiO_2 was synthesized at 573 K in toluene and calcined in air.

The HyCOM TiO_2 powders maintained relatively high surface area after annealing compared with amorphous TiO_2 powders obtained by the conventional hydrolysis or precipitation methods. Therefore, relatively large amount of substrates could be adsorbed on the surface, which increased the rate of capture of electron and positive hole by substrates. Crystallinity of the HyCOM TiO_2 might be further improved by the annealing at higher temperatures, which presumably produced the surface with lesser defects, without marked decrease in surface area. Therefore, the recombination of electrons and positive holes might be suppressed, resulting in enhancement of the photocatalytic activity. Similar annealing effect was also observed for amorphous-derived TiO_2 sample. However, the activity abruptly decreased on calcination at about 873 K due to transformation into rutile and drastic decrease in the surface area.[5] The difference in the physical and photocatalytic properties between these two types of TiO_2 powders would be attributed to whether, before annealing, TiO_2 powders were crystalline or not.

We thank Professor Takeo Shimidzu (Kyoto University) for his permission to use an atomic absorption spectrometer.

References and Notes

1 for a review, see M. A. Fox and M. T. Dulay, *Chem. Rev.*, **93**, 341 (1993).

2 for example, I. A. Montoya, T. Viveros, J. M. Dominguez, L. A. Canales, and I. Schifter, *Catal. Lett.*, **15**, 207 (1992).

3 B. Ohtani and S.-i. Nishimoto, *J. Phys. Chem.*, **97**, 920 (1993) and references therein.

4 H. Kominami, Y. Takada, H. Yamagiwa, Y. Kera, M. Inoue, and T. Inui, *J. Mater. Sci. Lett.*, accepted for publication.

5 S.-i. Nishimoto, B. Ohtani, and T. Kagiya, *J. Chem. Soc., Fraday Trans. 1*, **81**, 61 (1985).

6 a) S.-i. Nishimoto, B. Ohtani, and T. Kagiya, *J. Chem. Soc., Fraday Trans. 1*, **81**, 2467 (1985); b) K. Domen, S. Naito, T. Onishi, and K. Tamaru, *Chem. Lett.*, **1982**, 555; c) S. Teranishi, J. Nakamichi, K. Taya, and K. Tanaka, *Bull. Chem. Soc. Jpn.*, **55**, 1688 (1982).

7 for example, P. Pichat, M.-N. Mozzanega, J. Diadier, J.-M. Herrmann, *Nouv. J. Chim.*, **6**, 559 (1982).

8 Preliminary experiments showed the quantum efficiency of the HyCOM TiO_2 (Cat. J) to be at least 30% for the photocatalytic dehydrogenation of 2-propanol by monochromatic irradiation (365 nm, 3.66×10^{-9} einstein sec^{-1}). A prolonged experiment (9 h) for the catalyst under the condition same as in Table 1 gave the turnover frequency of >5 per titanium atom without lose of the activity.