PHOTOCATALYTIC ACTIVITY OF ARTIFICIAL TITANIUM(IV) OXIDE-TIO$_2$(B)-AND TITANATES SUSPENDED IN AQUEOUS SOLUTION OF ALIPHATIC ALCOHOLS

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Abstract — Powders of artificial crystallites of titanium(IV) oxide, TiO$_2$(B), were synthesized by the calcination of tetratitanic acid (hydrate, H$_2$Ti$_4$O$_9$H$_2$O; TTA). The relating titanates, potassium octatitanate (K$_2$Ti$_8$O$_{17}$) and octatitanic acid(H$_2$Ti$_8$O$_{17}$), were also prepared. These powders, loaded with small amount of Pt, were suspended in an aqueous solution of 2-propanol and irradiated under argon atmosphere at 298 K $\pm$ 0.5 deg. All the photocatalysts tested in this study produced almost equimolar amount of acetone and molecular hydrogen (H$_2$). Among them TiO$_2$(B) and TTA showed the higher photocatalytic activity but rather lower than commercial titanium(IV) oxide (TiO$_2$) powders. The photocatalytic activity of TiO$_2$(B) for 2-propanol dehydrogenation in deaerated aqueous suspension increased with the elevating calcination temperature. Comparison of rate of H$_2$ formation from methanol and 2-propanol solutions by the TiO$_2$(B) photocatalyst suggested a possibility of selection of substrate with its molecular size by TiO$_2$(B)

INTRODUCTION

TiO$_2$ has been found naturally in three crystal forms; anatase, rutile, and brookite,[1,2] the first two forms of which belong to tetragonal and the third to orthorhombic crystal system. All of them, as well as amorphous form, can be also synthesized in industrial and/or laboratory processes in the form of powder or film, and have shown photocatalytic activity when suspended or immersed, respectively, in aqueous and/or organic media.[3-7] By using the TiO$_2$ photocatalyst, we have shown that several organic syntheses can be accomplished under mild conditions.[8-15] Further development of photocatalytic selective organic syntheses might be achieved by the use of photocatalyst with its reaction sites recognizing shape and/or size of reactant molecules. The TiO$_2$'s obtained so far, however, have no micro porous or layered crystal structures and, thereby, no selective photocatalytic reaction due to the size or shape of reactants can be counted on.

Marchand and coworkers have reported the synthesis of artificial (naturally unobserved form of) TiO$_2$, TiO$_2$(B), in monoclinic crystal structure.[16] Being

different from the naturally-occurring TiO$_2$ crystals, TiO$_2$(B) has tunnels parallel to b-axis in its crystal structure. Although unique function is expected from the characteristic structure, a few articles have been published on the utilization of TiO$_2$(B) for catalyst or electrode material.[17-19] Only a unique report has been published concerning the photocatalytic activity of TiO$_2$(B) for decomposition of water.[20] Herein, the authors show the preparation and the results of photoinduced reaction by aqueous suspension of TiO$_2$(B) and some relating titanates.

MATERIALS AND METHODS

Materials. All chemicals were of the best available grade and used without further purification. TiO$_2$(B) was prepared according to the literature.[16] A 1:3.5 molar ratio mixture of potassium carbonate (Wako Pure Chemicals) and anatase TiO$_2$ (Merck) was thoroughly brayed in a porcelain mortar and calcined at 1023 K for 20 h in an alumina crucible. The resulting white powder (20 g), showing an X-ray diffraction (XRD) pattern identical to K$_2$Ti$_4$O$_9$,[21] was suspended and stirred in an aqueous solution of nitric or hydrochloric acid (1mol/L, *ca* 1.3 L) at room temperature for 48 h. The white powder was filtered, washed thoroughly with ion-exchanged water, and dried overnight at 383 K. The thus obtained tetratitanic acid, hydrate (H$_2$Ti$_4$O$_9$H$_2$O, TTA) was heat-treated at various temperatures (T$_c$) to obtain octatitanic acid

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($H_2Ti_8O_{17}$) or $TiO_2(B)$. Potassium octatitanate ($K_2Ti_8O_{17}$) was obtained by partial extraction of potassium cation from $K_2Ti_4O_9$ by refluxing water. Structure of $TiO_2(B)$ and the intermediates were confirmed by their XRD (a Rigaku Geigerflex 2013 diffractometer, Cu-K$_\alpha$) patterns (in the original report,[16] XRD data for $K_2Ti_8O_{17}$ and $TiO_2(B)$ might be interchanged as pointed out previously[17]). For the further confirmation of composition of $TiO_2(B)$, colorimetric and atomic absorption analyses, respectively, for titanium and potassium in the sample dissolved in a hot concentrated sulfuric acid with ammonium sulfate[22] were performed to obtain almost satisfactory results (60.2% Ti; theoretical value for $TiO_2(B)$, 59.9%, and negligible K (< 0.1%). Raman spectra of the powders were recorded on a Jobin Yvon T-64000 spectrometer equipped with an argon-ion laser (NEC GLG3260; 514.5 nm, 50 mW) and a charge coupled device (CCD) detector (1 inch) in a backscattering geometry. Two different types of commercial TiO_2 powders (Degussa P-25 and Merck anatase) were used for comparison. Platinum (Pt) loading on these photocatalysts was mainly achieved by impregnation from aqueous chloroplatinic acid (H_2PtCl_6) solution followed by hydrogen (H_2) reduction at 473 K.[13]

Photoirradiation and product analyses. A suspension of catalyst (50 mg) in an aqueous alcoholic solution (5.0 mL) of 2-propanol or methanol (500 μmol) was placed in test tube (18 mm × 180 mm, transparent for the light of wavelenght > 300 nm) and was purged by argon (Ar). The tube was sealed with a rubber septum and irradiated with a 400 W mercury arc (Eiko-sha) at 298 K($\pm$0.5 deg) under magnetic stirring (1000 rpm). After the irradiation, products in the gas phase and liquid phase were analyzed by gas chromatography (GC). The detailed conditions for the GC analyses were reported elsewhere.[12,13]

RESULTS AND DISCUSSION

Photocatalysts, titanium(IV) oxides and titanates, are listed in Table 1 as a function of T_c. At the low T_c(<673 K), $H_2Ti_8O_{17}$ was obtained from TTA while treatment at higher T_c led to the $TiO_2(B)$ formation. Further higher T_c(>923 K) produced a mixture of $TiO_2(B)$ and anatase, and then anatase and rutile (1173 K). These results are consistent with the previous report.[16] Table 1 also shows the results of photocatalytic reaction by the powders loaded with 2 wt% of Pt. Photoirradiation onto aqueous 2-propanol suspensions under Ar induced the formation of acetone and H_2. The molar ratio of these products was approximately unity, suggesting the stoichiometry of

$$(CH_3)_2CHOH = (CH_3)_2CO + H_2$$
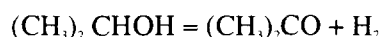
In the absence of loaded Pt, negligible production of H_2 and acetone was observed. This is consistent with the previous report of anatase and rutile TiO_2

Table 1. Rate of photocatalytic H_2 evolution by titanates and titanium(IV) oxides (50 mg) suspended in aqueous 2-propanol solution (500 μmol, 5.0 mL) at 298 K ($\pm$ 0.5 deg) under an Ar atmosphere.

catalyst[a]	T_c[b]/K	R_0[c]/μmolh^{-1}	acetone/H_2[d]
$K_2Ti_4O_9$	—	0.75	0.99
$K_2Ti_8O_{17}$	—	3.6	0.83
$H_2Ti_4O_9 \cdot H_2O$	383	6.0	0.91
$H_2Ti_8O_{17}$	523	1.8	1.2
$TiO_2(B)$	673	3.6	0.92
$TiO_2(B)$	773	5.2	0.95
$TiO_2(B)$	823	6.8	0.89
$TiO_2(B)$	873	6.1	0.91
anatase+$TiO_2(B)$	923	27	—[e]
rutile+anatase	1173	1.1	—[e]
Merck	—	24	0.84
Aerosil P-25	—	86	0.73

[a]Loaded with 2 wt% of Pt by impregnation from H_2PtCl_6 followed by H_2 reduction. [b]Temperature of calcination of TTA. [c]Inital rate of H_2 production. [d]Molar ratio of acetone and H_2 obtained by 24h irradiation. [e]Not determined.

powders.[4,23] The loaded Pt may enhance the evolution of H_2 on its surface by decreasing the activation energy which is much larger for the bare TiO_2 surface.[24]

The initial rate of H_2 formation (R_0) by $TiO_2(B)$ was increased with T_c up to 923 K; the mixture of $TiO_2(B)$ and anatase showed photocatalytic activity comparable to a commercial TiO_2 (Merck), but a mixture of anatase and rutile obtained at higher T_c (1173 K) was less active. Among the parent and relating titanates, TTA showed relatively higher activity for the photocatalytic dehydrogenation of 2-propanol, and detailed investigation on the activity of this layered-structured titanate will be reported elsewhere.

Figure 1 shows an XRD pattern of the $TiO_2(B)$ powder calcined at 873 K. All the peaks appeared here could be assigned to the $TiO_2(B)$ crystallites; the powder seemed to be in single crystal phase. Since the most intense peak of anatase crystallites appears at 25.4 deg, being almost identical to that of $TiO_2(B)$, it was undetectable even if small quantity of anatase crystallites was contaminated. Therefore, we could not exclude a possibility that coexisting hidden anatase crystallites, but not $TiO_2(B)$, account for the photocatalytic activity. Figure 2 shows Raman spectra of $TiO_2(B)$ powders. Being consistent with the above-mentioned XRD results, these spectra closely resembles that reported previously.[17] In the literature, assignment of a small peat at 143.5 cm^{-1} has been
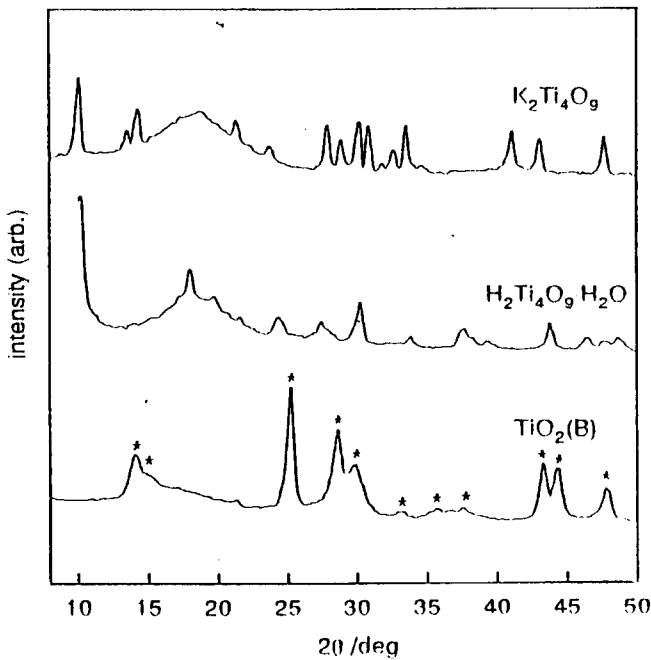
Figure 1. Parts of XRD (CuK$_\alpha$) patterns of K$_2$Ti$_4$O$_9$ (upper), H$_2$Ti$_4$O$_9$H$_2$O (middle), and TiO$_2$(B) (T$_c$=873 K; lower). All of these patterns closely resemble those reported. Asterisks in the lower pattern show the peak position in the literature.
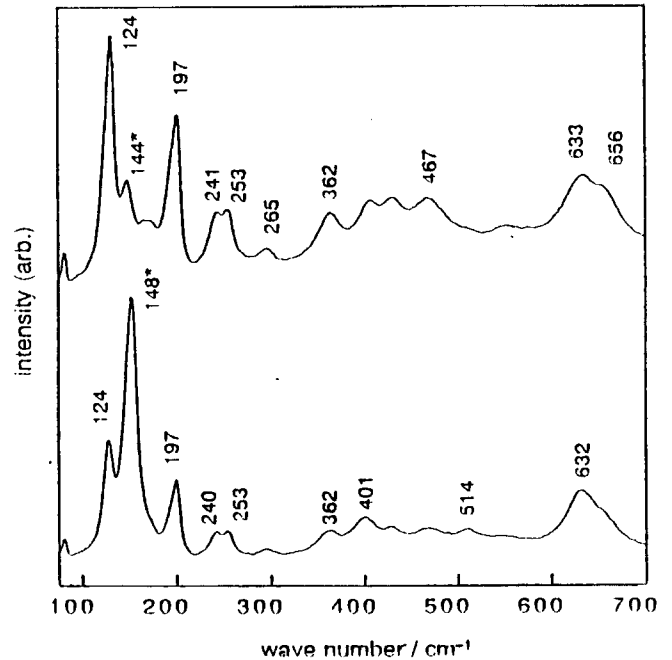

Figure 2. Parts of Raman spectra of TiO$_2$(B) (T$_c$=873 K; upper) and anatase-TiO$_2$(B) mixture (T$_c$=923 K; lower). Numbers denote wave numbers and asterisk shows peak assigned to anatase crystallites.

ambiguous. The previous report by Feist and coworkers showed the Raman spectra of their TiO$_2$(B) samples, but did not mention the small peak at ca 140 cm⁻¹.[25] Bamberger and coworkers described that the peak was attributed to the most intense anatase peak since they detected anatase crystallites in the XRD pattern of their sample.[17] Surprisingly, they referred the previous report[25] as an authentic pure sample of TiO$_2$(B). Any way, we regard the 143.5 cm⁻¹ peak as the contaminated anatase crystallites, because its intensity relative to the other peaks changed drastically with the preparation conditions; intensities of the other peaks fluctuated in parallel (see Figure 2). As was pointed out in the above-mentioned literature,[17] the Raman peak at ca 143 cm⁻¹ by anatase crystallites is much intense and, thereby, the Raman spectroscopy might be more sensitive to anatase than TiO$_2$(B). Furthermore we could see negligible anatase peaks at 394, 514 and 637 cm⁻¹. These facts strongly suggest the low concentration of contaminated anatase crystallites in our TiO$_2$(B) sample. This indicates that TiO$_2$(B) itself but not contaminated anatase exhibits the photocatalytic activity shown in Table 1. Although it is very interesting to know that mixture of TiO$_2$(B) and anatase (923 K) exhibited the highest activity and investigation on this mixture is now in progress, we focused in this paper the photocatalytic activity of

almost pure TiO$_2$(B).

Recently, Inoue and coworkers reported the photocatalytic decomposition of water into molecular hydrogen and oxygen by several titanates and TiO$_2$(B), which have tunnel structure. It has been shown that TiO$_2$(B) can not produce hydrogen and oxygen molecules photocatalytically; only small amount of hydrogen evolved. Therefore, to the best of our knowledge, the present article is the first report of photocatalytic activity of TiO$_2$(B).

Table 2 shows the rates of photocatalytic H$_2$ production from aqueous solutions of methanol and 2-propanol. In these series of experiments, influence of the source and condition for Pt loading on the photocatalytic activities was examined. In the case of P-25 TiO$_2$, the rates were almost constant regardless of the source and time of impregnation; the ratio of methanol and 2-propanol systems seems independent of the time for impregnation duration in each souce (though at present we have no interpretation of different ratios caused by these sources). On the contrary, the ratios increased for TiO$_2$(B). Moreover, they were affected by the impregnation conditions; the highest ratio was obtained by the Pt loading from Pt(NH$_3$)$_4$Cl$_2$ with prolonged impregnation durations. As clearly seen, the use of Pt(NH$_3$)$_4$Cl$_2$ and extension of impregnation duration reduced the rate of H$_2$ formation from both alcohols, but 2-propanol system

was more sensitive toward this retardation, resulting in the larger ratio.

Since the suspension of $TiO_2(B)$ was dried up after impregnation, total amount of Pt loaded on TiO_2 was constant (2 wt%). Transmission electron microscopic study showed no significant difference of Pt deposits depending on these conditions. Therefore, the difference in size and morphology of loaded Pt may not account for such dependence of the photocatalytic activity. A plausible mechanism based on the characteristic tunnel-structured $TiO_2(B)$ and non-porous anatase and rutile can interpret the results. Both $Pt(NH_3)_4^{2+}$ and $PtCl_6^{2-}$ may not go into the tunnels of $TiO_2(B)$ (presumably 0.4-0.7 nm in diameter), but the cationic precursor could interact with the entrance of tunnels to narrow it after the prolonged impregnation duration. Assuming that the alcohols are oxidized both on the surface and in the tunnels, the above narrowing effect may reduce the rate of reaction of 2-propanol, of larger molecular size, more significantly as observed in Table 2. Further investigation to clarify the mechanism inducing the selectivity for alcohols are in progress.

Table 2. Rate of photocatalytic H_2 evolution by TiO_2-Pt (2 wt%) powders suspended in an aqueous methanol or 2-propanol solution.

catalyst	Pt impregnation		rate[a]/μmol h^{-1}		methanol/
	source	time/h	methanol	2-propanol	2-propanol[b]
$TiO_2(B)^c$	Pt(NH$_3$)$_4$Cl$_2$	168	13.3	10.3	1.29
$TiO_2(B)^c$	Pt(NH$_3$)$_4$Cl$_2$	24	15.1	12.6	1.20
$TiO_2(B)^c$	H$_2$PtCl$_6$	168	17.1	14.4	1.19
$TiO_2(B)^c$	H$_2$PtCl$_6$	24	16.6	14.4	1.15
P-25	Pt(NH$_3$)$_4$Cl$_2$	168	111	120	0.92
P-25	Pt(NH$_3$)$_4$Cl$_2$	24	108	114	0.94
P-25	H$_2$PtCl$_6$	168	125	114	1.09
P-25	H$_2$PtCl$_6$	24	128	119	1.08
P-25	H$_2$PtCl$_6$	2	104	97.9	1.06

[a]Average of three experiments. [b]Ratio of rate for methanol to that for 2-propanol. [c]Calcined at 773 K.

CONCLUSION

In conclusion, the photocatalytic activity of artificial TiO_2, $TiO_2(B)$, has been confirmed for the 2-propanol dehydrogenation under deaerated conditions, and the possibility of selection of alcohols due to its characteristic tunnel structure was suggested.

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