

Generation of Basic Sites on TiO₂ by Reduction with H₂

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The generation of basic sites on a TiO₂ surface by reduction is discussed on the basis of the results of catalytic reactions, temperature-programmed desorption of adsorbed CO₂, and measurements of the numbers of surface hydrogen acceptors and donors (DPPH₂ and DPPH methods). The results of catalytic reactions show that both acidic and basic active sites are present on TiO₂ surfaces and reduction of TiO₂ increases its basic character. The TPD profile of adsorbed CO₂ suggests that basic sites increase following the reduction of TiO₂ but their strengths are not high. Reduction of TiO₂ not only suppresses the surface acidity but also increases the number of surface proton acceptors. This is also supported by DPPH–DPPH₂ experiments. These results lead to the conclusion that basic sites generated by the reduction of TiO₂ are surface oxygen species which can abstract protons from adsorbed species. © 1991 Academic Press, Inc.

INTRODUCTION

Titanium dioxide is an important component of various catalysts and is widely used not only as a catalyst support, but also as a catalyst itself. In connection with photocatalysis, recently, the nature of titanium dioxide has been extensively investigated in terms of its semiconductivity (1). However, there have been relatively few studies (2–8) focusing on its acid–base properties although these relate closely to a lot of chemical applications.

Surface acid sites of anatase have been characterized by infrared spectroscopy using pyridine probe molecules (3–5). It has been found that both Lewis and Brønsted acid sites exist on the surface evacuated at low temperatures (<673 K) (3). With in-

creasing evacuation temperature, Brønsted acid sites vanish first and Lewis acid sites gradually decrease (3). On the other hand, there are some reports (4, 5) that the samples free from sulfur do not possess Brønsted acid sites.

In any case, evacuation of the sample at high temperature suppresses the acidity because acidic OH groups are removed. Partial reduction of TiO₂ also occurs on evacuation, resulting in an increase in electron density on a surface titanium cation which has been a Lewis acid site. In previous work (6, 7), the variation of acidic properties with evacuation temperature was confirmed by measurements of the catalytic activity for isomerization of 1-butene. Furthermore it was found that titania can function as a solid base when it is reduced. From the results of combined use of ESR and tracer techniques, it was deduced that Ti³⁺ generated by evacuation provides an electron-donating site where the π -allyl anion is stabilized in the case of isomerization of 1-butene. However, in the paper dealing with ESR spectroscopy by Che *et al.* (8) it was proposed that electron-donating sites of TiO₂ are OH⁻ ions on

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the surface of TiO_2 evacuated at low temperatures (<573 K) and weakly coordinated O^{2-} ions on the surface evacuated at higher temperatures (>573 K). Neither group states explicitly that the electron-donating site is a basic site. However, specification of such a site is different from each group. The inconsistency of the active species generated by reduction of TiO_2 and the relation between the electron-donating site and the basic site have not been clarified yet.

In the present paper, to elucidate the nature of the active sites generated by partial reduction of TiO_2 , we have carried out the characterization of TiO_2 by temperature-programmed desorption (TPD) technique and chemical reactions taking place individually on basic sites or on acid sites. In addition, we have used a DPPH (2,2-diphenyl-1-picrylhydrazyl)-DPPH₂ (1,1-diphenyl-2-picrylhydrazine) technique to examine the presence of basic sites.

EXPERIMENTAL

Catalyst preparation. TiO_2 was prepared by calcination of $\text{Ti}(\text{OH})_4$ at 873 K for 3 h in air. $\text{Ti}(\text{OH})_4$ was obtained by hydrolysis of commercially supplied $\text{Ti}(\text{SO}_4)_2$ at 363 K, followed by washing precipitates by filtration until no sulfate ions were detected with BaCl_2 solution, and finally drying at 383 K for 20 h. Reduction of catalysts was carried out under a stream of atmospheric hydrogen at 773 K for 1 h (9). Catalysts were evacuated at 773 K for 1 h before use.

Catalytic reactions. The amination of methanol was carried out in the conventional glass circulating system. The reactant gas consisting of equimolar CH_3OH and NH_3 was circulated through a catalyst bed in a quartz reactor maintained at several different temperatures. A small portion of reaction gases were sampled for analysis by gas chromatography. 1-Butene isomerization was performed as described elsewhere (6). The isomerization of β -pinene was carried out in a continuous flow reactor using cyclohexane as a diluent for β -pinene under a He stream.

TPD. After probe molecules were ad-

sorbed at room temperature, the catalyst bed was heated up at a rate of 10 K min^{-1} and desorbed molecules were monitored by a quadrupole-type mass spectrometer.

Measurements of the number of sites of hydrogen radical donor and acceptor. The number of hydrogen radical donor sites on the surface was determined by measuring the number of DPPH₂ (1,1-diphenyl-2-picrylhydrazine) formed by the reaction between a DPPH (2,2-diphenyl-2-picrylhydrazyl) molecule and a surface hydrogen donor in dry benzene by UV/VIS spectroscopy (9, 10). When the surface exhibit is nonbasic, the DPPH₂ molecule is not trapped on the surface to be extracted into the benzene solution. The number of hydrogen radical acceptor sites on the surface was determined from the intensity of ESR signal of DPPH formed by the reaction of DPPH₂ with the surface acceptor site (10).

RESULTS

Amination of methanol with ammonia. If a metal oxide is used as a catalyst for the reaction, the reaction takes place only over a solid acid, and a solid base like magnesium oxide cannot catalyze the reaction at all. Therefore we can use this reaction to confirm acidity on the catalyst (11). Figure 1 shows the time course of aminations of methanol with ammonia over both unreduced and reduced TiO_2 . The main products were monomethylamine (MMA) and trimethylamine (TMA). Dimethyl ether (DME) was also formed as a by-product. Over the unreduced catalyst, the reaction proceeds immediately, while over the reduced one, an induction period to start the reaction was observed. As shown in Fig. 1b, the reaction started and about 1 h after reactant gas mixture was introduced in the circulating system. During the induction period, the color of the sample changed from gray to faintly yellow. This means that the sample was oxidized in the induction period. Acidity was greatly suppressed initially for the reduced catalyst and was recovered by oxidation in the induction period.

1-Butene isomerization. Results of 1-bu-

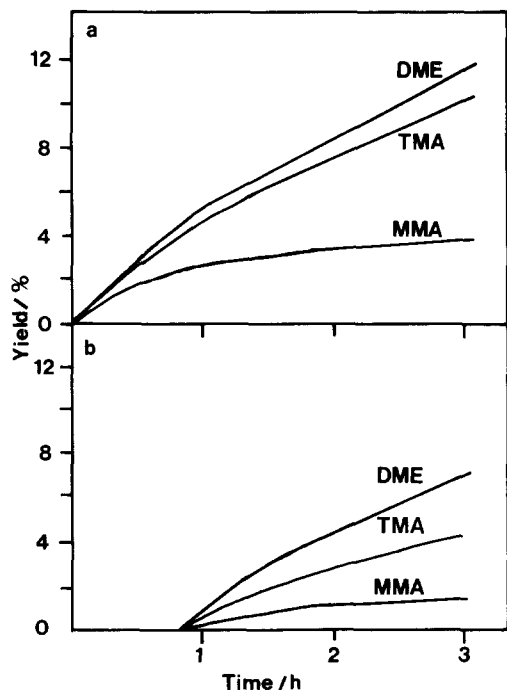


FIG. 1. Time evolution of product yields in amination of methanol over (a) oxidized TiO₂ and (b) reduced TiO₂. For discussions of MMA, TMA, DME, see text.

TABLE 1

Isomerization of 1-Butene over Titanium Oxides^a

Catalyst	Conversion (%)	<i>cis/trans</i>
Oxidized TiO ₂	72.3	0.17
Reduced TiO ₂	34.0	13.9
Reduced TiO ₂ poisoned with CO ₂ ^b	18.4	7.6

^a Reaction temperature, 423 K; reaction time, 200 min; catalyst amount, 100 mg; initial pressure of 1-butene, 85.0 Torr; dead volume of the system, 390.0 cm³.

^b CO₂ pressure, 20.0 Torr.

tene isomerization are summarized in Table 1. As reported before (9), the reduction of TiO₂ results in the decrease of the isomerization activity while the ratio of *cis*- to *trans*-2-butene (*cis/trans* ratio) becomes dramatically higher. It is well known that the *cis/trans* ratio is a good index to determine whether the catalyst is acidic or basic. In the former case, the ratio is usually less than 2 and in the latter case, the ratio is much higher than 2 because of the difference between the stable intermediates (12). The activity exhibited by a CO₂-poisoned catalyst, which had been reduced with H₂, decreased by half without changing the *cis/trans* ratio greatly. These results suggest that the reduction of TiO₂ suppresses its acidity in addition to generating basic sites.

Isomerization of β-pinene. Isomerization of β-pinene yields a variety of products depending on the acid–base properties of the catalyst. In the presence of acid sites, rearrangement of the position of a tertiarily

carbon adjacent to a double bond occurs to form camphene or limonene as the first step (13), and limonene is converted to terpinolene, *p*-mentadienes, and *p*-cymene (14), while in the presence of basic sites, only double bond migration takes place to form α-pinene selectively (15). Table 2 shows the results of isomerization of β-pinene over pretreated TiO₂ catalysts together with the results over MgO and Nb₂O₅ · *n*H₂O. Over unreduced TiO₂, the catalytic activity is very high and the main product is camphene. This is the typical result for an acid-catalyzed reaction, as observed for Nb₂O₅ · *n*H₂O. On the other hand, over reduced TiO₂, the catalytic activity became lower and α-pinene was selectively formed accompanied by the formation of camphene as a minor product. In the case of MgO, a typical solid base catalyst, the selectivity to α-pinene is found to be high, also. With the results for MgO taken into account, the results obtained for TiO₂ suggest that both acid and base sites are present on the surface and acid- and base-catalyzed reactions proceed competitively on the catalyst. Reduction of TiO₂ makes its basic character stronger.

Temperature-programmed desorption. Figure 2 shows the TPD profile of carbon dioxide adsorbed on oxidized and reduced TiO₂ catalysts. TiO₂ has sites adsorbing carbon dioxide even in the oxidized state. In the case of reduced TiO₂, the desorption temperature shifted to a higher value. How-

TABLE 2
Isomerization of β -Pinene over Various Catalysts

Catalyst	Conv. (%)	Selectivity (%)		
		α -Pinene	Camphene	Others ^d
Oxidized TiO ₂ ^a	86.7	14.0	51.3	34.7
Reduced TiO ₂ ^a	17.1	60.9	19.8	22.9
MgO ^b	12.6	59.4	12.0	28.5
Nb ₂ O ₅ · nH ₂ O ^c	13.2	17.7	50.0	32.1

^a Reaction temperature, 400 K; catalyst amount, 200 mg.

^b Reaction temperature, 373 K; catalyst amount, 200 mg; pre-treatment condition, 873 K in He stream for 2 h.

^c Reaction temperature, 373 K; catalyst amount, 100 mg; pre-treatment condition, 523 K in He stream for 2 h.

^d Containing limonene, α -terpinene, γ -terpinene, terpinolene, and *p*-cymene. These products originate from limonene (14).

ever, the desorption temperature is lower than that for MgO, a representative solid base. This shows that the basic sites generated by the reduction of TiO₂ are rather weak.

The measurements of the numbers of HRD and HRA sites. The numbers of HRD and HRA sites of a metal oxide determined by the DPPH method may be interpreted as the numbers of nonbasic OH groups and the number of basic sites, respectively. In the ordinary case, the HRA sites are thought to be surface O²⁻ and/or basic OH⁻ which can abstract a hydrogen atom as a proton from

a hydrogen-donor. Therefore, the numbers of HRD and HRA sites shown in Table 3 can be regarded as the population of Brønsted acidic sites and basic sites on TiO₂ surfaces, respectively (9, 10). H₂ treatment of TiO₂ not only suppresses the acidity but also increases the number of basic sites. This is consistent with the results of the TPD experiments, if the adsorption sites for carbon dioxide molecules are representative of basic sites.

DISCUSSION

The results mentioned above are summarized as follows:

(1) TiO₂ can promote both acid-catalyzed and base-catalyzed reactions. However, acid-type reactions are favored on TiO₂ in the oxidized state. In the case of reduced TiO₂, the basic character of TiO₂ is enhanced.

(2) Following reduction of TiO₂, the number of adsorption sites of carbon dioxide increases accompanied by an increase in the strength of the adsorption.

(3) Nonbasic OH groups which supply hydrogen atoms to DPPH molecules greatly decrease in number for reduced TiO₂ in comparison with oxidized TiO₂. In contrast, basic sites which abstract protons from

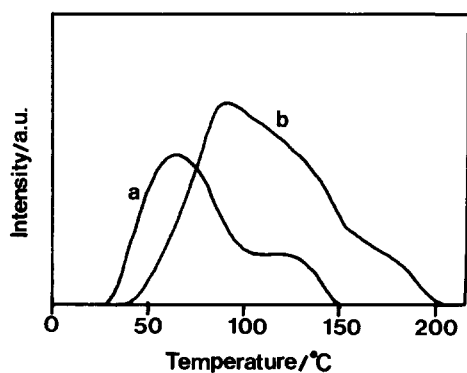


FIG. 2. TPD profiles of carbon dioxide having been adsorbed on (a) oxidized TiO₂ and (b) reduced TiO₂.

TABLE 3

Concentration of Hydrogen Radical Donor (HRD) and Hydrogen Radical Acceptor (HRA) on Oxidized and Reduced TiO₂

Catalyst	HRD ^a ($\times 10^{-18}$ sites \cdot m ⁻²)	HRA ^b ($\times 10^{-16}$ sites \cdot m ⁻²)
Oxidized TiO ₂	5.9	0.6
Reduced TiO ₂	0.8	1.6

^a Concentration of formed DPPH₂ by the reaction of DPPH with the surface.^b Concentration of DPPH by the reaction of DPPH₂ with the surface.

DPPH₂ molecules become greater in number when TiO₂ is reduced.

These results strongly suggest the presence of basic sites on the reduced TiO₂ surface as active sites. In the case of 1-butene isomerization, the 1-methyl- π -allyl anion might be stabilized on Ti³⁺. Taking into account that the initiation of the reaction is an abstraction of a proton from 1-butene, it is implausible that a Ti³⁺ site functions as a basic site abstracting a proton. If a proton were abstracted by Ti³⁺ ions, the proton would have interacted with a Ti³⁺ cation. However, the electron on Ti³⁺ to be donated is thought to occupy an orbital mainly consisting of a Ti 3d atomic orbital which is hardly supposed to interact with an H⁺ 1s empty orbital due to mismatch of symmetry. Therefore, a site other than Ti³⁺ should be considered as an active site functioning as a basic site although Ti³⁺ may be admitted to be a kind of electron-donating site.

In the case of niobium oxide, Morikawa *et al.* (16) have found that H₂ reduction of niobium oxide remarkably enhanced the activity of niobium oxide for butenes isomerization in the absence of gaseous hydrogen. Although they have not argued whether the mechanism of isomerization is an acid-type or a basic-type, they have postulated that Nb⁴⁺ is an active site from the result of the combined use of ESR. It is very likely that a surface reduced cation becomes an active species for butene isomerization, by the analogy as found by Kodama *et al.* (17). In

this case, the isomerization mechanism is rather close to the one containing radical intermediate species.

If the same phenomena occurred in the present case, reduction of TiO₂ should enhance the isomerization activity as well as keep the *cis/trans* ratio relatively low. The present results shown in Table 1 indicate that the butene isomerization takes place on TiO₂ via a different mechanism from that on niobium oxide mentioned above.

From this discussion, we can propose that the butene isomerizations over oxidized TiO₂ and reduced TiO₂ take place via acid-catalyzed and base-catalyzed mechanisms, respectively, and the active site of reduced TiO₂ is not the Ti³⁺ but another basic site. The presence of basic sites on a reduced TiO₂ surface is indicated by the results of isomerization of β -pinene, amination of methanol, and TPD of adsorbed carbon dioxide. The DPPH₂ technique showed that proton acceptors such as surface O²⁻ species and basic OH⁻ groups increased by the reduction of TiO₂. The following evacuation must bring about the dehydroxylation of the surface promoting the formation of O²⁻ (18). Therefore, we conclude that generated basic sites on a reduced TiO₂ surface are surface coordinatively unsaturated oxygen species and/or basic OH⁻ species, as proposed by Che *et al.* (8). Accumulation of electron(s) on the surface Ti cation site resulting from the reduction of TiO₂ may coincide with an increase in electron density on

surface oxygen species adjacent to the Ti cation.

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