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Photocatalytic Dehydrogenation of 2-Propanol over TiO_2 and Metal/TiO_2 Powders

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A series of TiO_2 catalysts loaded with transition metals were prepared by photodeposition. The activity order for these catalysts in the title reaction was as follows: Pt/TiO_2>Rh/TiO_2>Pd/TiO_2>Ru/TiO_2>Ir/TiO_2>TiO_2. Upon heat treatment the activities of all the metal/TiO_2 catalysts were enhanced, but the above sequence was unaltered.

The recent and on-going concern with photocatalytic production of hydrogen from water or organic materials is related to solar energy conversion and storage. Among the catalysts used in this type of reactions are metal-loaded oxides[1,2] such as Pt/TiO_2 and Rh/$SrTiO_3$ as well as binary oxides[3,4] such as NiO–$SrTiO_3$ and RuO_2–TiO_2. In our laboratory we prepared a series of polycrystalline metal/TiO_2 powders (metal=Ru, Rh, Pd, Ir, Pt), and compared their photocatalytic activities, relative to TiO_2, for dehydrogenation of 2-propanol. A few related experiments were also made to gain a better understanding of this reaction. This paper reports the results of these experiments.

Experimental

Materials. Anatase was purchased from Kanto Chemical Co., Inc.: the absence of rutile was confirmed by X-ray powder diffraction, and the BET surface area was determined to be 11.5 m^2/g. Metal salts (H_2PtCl_6, $RhCl_3$, $IrCl_4$, $PdCl_2$, $RuCl_3$) used for catalyst preparation were also commercially obtained. 2-Propanol (Wako Pure Chemical Ind., Guaranteed grade) was used without further purification. All aqueous solutions or suspensions of these chemicals were prepared using distilled water.

Apparatus. Figure 1 illustrates the photochemical reaction vessel used for both catalyst preparation and kinetic studies. The reaction vessel consists of two parts separable at joint J. There are two interchangeable inner parts of an identical shape and size, one made of pyrex glass and the other of quartz. Unless otherwise stated, the experiments in this report were conducted using the quartz unit. An irradiation lamp can be placed inside the innermost wall A. Water from a thermostatically controlled bath can flow through the thin space between A and B, cutting off the thermall energy from the irradiation lamp. The outer part is a three side-necked flask, one sideneck connected to a cooler, a second used for sampling, and the other (not indicated in the figure) for bubbling of N_2 or Ar to purge air before reaction. During reaction the third sideneck was sealed with a pinchcock. The outermost space D between walls B and C is the reaction region. The whole reaction vessel is immersed in a thermostatted water bath. The reaction temperatures recorded are those of this bath.

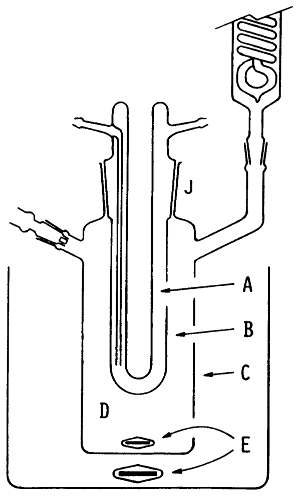

Fig. 1. Reaction vessel.
A—D: See text, E: Teflon-coated magnetic bars.

Catalyst Preparation. Three metal/TiO_2 catalysts (metal=Ru, Pd, Pt) were prepared by photodeposition of the metal on TiO_2 according to a method similar to that of Kraeutler and Bard.[5] As a typical example, anatase powders (3 g) were homogenized in water (50 ml) for 1 h in a Mitamura Riken ultrasonic cleaner (70 W). To the resulting slurry was added an aqueous solution of an appropriate concentration of H_2PtCl_6, a CH_3COOH–CH_3COONa buffer (pH=4, *ca.* 10 ml), and water to adjust the whole volume to *ca.* 250 ml. The whole mixture was transferred to space D of the reaction vessel, and N_2 was bubbled for 20 min to eliminate dissolved air. To commence the photocatalytic deposition of the metal, a 30-W low-pressure Hg lamp was switched on, and irradiation was carried out at 40 or 55 °C under continued stirring and N_2 bubbling until metal deposition was complete (1 h for Pd; 2.5 h for Ru and Pt). After irradiation, the mixture was filtered off through a Gelman Membrane Filter DM-450 (pore size 0.45 μm), washed with water until the washings were neutral. The precipitate collected was dried first at 45 °C overnight between filter papers in an electric oven and then under reduced pressure for several days at room temperature, and finally stored in a vial under a nitrogen atmosphere.

The above procedure was not applicable to the preparation of Rh/TiO_2 and Ir/TiO_2 because of the difficulty to achieve complete reduction of $RhCl_3$ and $IrCl_4$ to the metallic state. The following modifications were thus made: methanol was used instead of the CH_3COOH–CH_3COONa buffer, and the irradiation source was replaced by a more intense 100-W high-pressure Hg lamp.

Air treatment of the metal/TiO_2 catalysts was conducted by heating for 2 h at 380 °C under a stream of air in an electric furnace. Before heat treatment, all the metal/TiO_2 catalysts were off-white. Upon heat treatment, Ru/TiO_2 acquired a slightly blueish tint, while there was no significant variation in appearance for the other metal/TiO_2 catalysts.

Kinetic Procedure. The photocatalytic dehydrogenation of 2-propanol was conducted as follows. To space D of the reaction vessel were introduced a metal/TiO_2 catalyst (0.1 g) and a water–2-propanol mixture (1 : 1 by vol., 200 ml). Argon was bubbled through the suspension for 30 min, then the photocatalyzed dehydrogenation was started by irradiating at 40 °C with the 100-W high-pressure Hg lamp. Small portions of the reaction solution were withdrawn at intervals and analyzed for product acetone by a gas chromatograph using a 2 m×3 mm i.d. column of 30% PEG 20 M on 30—60 mesh chromosorb WAW at 60 °C. The gas evolved was led through the cooler-attached sideneck into water or aqueous $Ba(OH)_2$ solution, and collected in a gas burette.

Results and Discussion

Stoichiometry and Reaction Profile. The gas evolved under irradiation in the presence of metal/TiO_2 catalysts did not make the aqueous $Ba(OH)_2$ solution turbid, and consisted almost exclusively of hydrogen, judged from mass spectral data. It has been confirmed with Pt/TiO_2 that acetone and H_2 are produced in nearly equal amounts by photocatalytic dehydrogenation of 2-propanol (Inset a, Fig. 2). A small amount of 2,3-dimethyl-2,3-butanediol (pinacol) was detected as the only by-product (Inset b). Pinacol formation was completely suppressed upon replacing the quartz inner part of the reaction vessel by the pyrex glass one. Thus it is very likely that pinacol is produced by the reaction of 2-propanol with ultraviolet-excited acetone. No reaction occurred at all with the mercury lamp switched off. The rates of acetone formation in duplicate experiments conducted under identical conditions were reproducible within 5%.

At the beginning of the reaction, as seen from Fig. 2, the amount of acetone produced increased almost linearly with time, and then gradually leveled off. With the metal/TiO_2 catalysts containing 1 wt% metal, the extent of the initial linear region ranged from *ca.* 1 h (Pd, 0.05% conversion) to 2.5 h (Pt, 1.2% conversion). The photocatalytic dehydrogenation rates of a series of Pt/TiO_2 catalysts were estimated from the initial slope, and are plotted in Fig. 3 (curve A) as a function of Pt content. It is seen that as the Pt loading increases, the rate increases almost linearly and then approaches a constant value. The rate per mg Pt (curve B) remains almost constant in the low Pt loading region, and then decreases with increasing Pt loading.

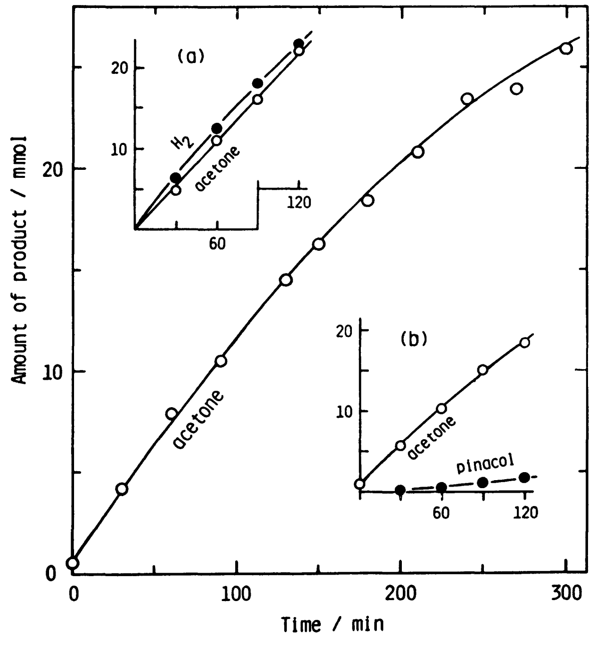

Fig. 2. A typical reaction profile for photocatalytic dehydrogenation of 2-propanol on Pt/TiO_2.
Catalyst: 1%-Pt/TiO_2 (100 mg), reactant: H_2O+2-propanol (1 : 1 by volume, 200 ml as the mixture), reaction temperature: 40 °C. Inset (a): near molar equivalence of produced H_2 and acetone. Inset (b): slight formation of pinacol as the by-product.

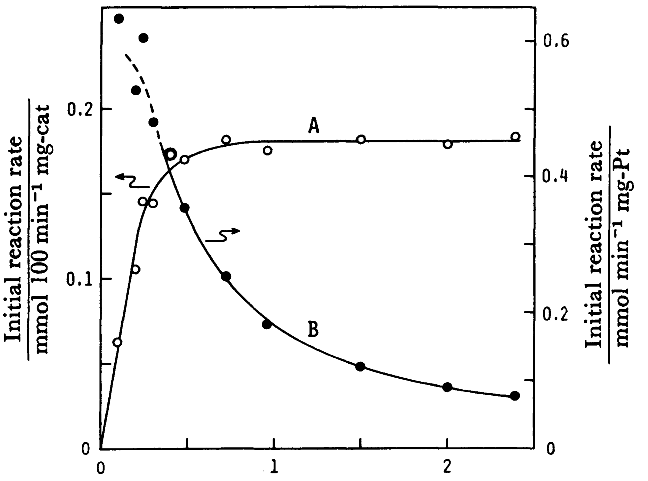

Fig. 3. The reaction rate for photocatalytic dehydrogenation per 100 mg of catalyst (Pt/TiO_2) (curve A) and that per mg of Pt (curve B).

Table 1. Activities of TiO_2 and metal/TiO_2 catalysts for photocatalytic dehydrogenation of 2-propanol to acetone

Catalyst	$V^{a)}$ / μmol min^{-1}	$R_1^{rel\ b)}$	$R_2^{rel\ c)}$
	Before heat treatment		
TiO_2	1.6(V_0)	1	—
Ru/TiO_2	7.6	4.7	0.076
Rh/TiO_2	38.4	24	0.37
Pd/TiO_2	13.1	8.2	0.12
Ir/TiO_2	4.0	2.5	0.021
Pt/TiO_2	194	121	1
	After heat treatment		
Ru/TiO_2	12.6	7.8	0.12
Rh/TiO_2	51.1	32	0.48
Pd/TiO_2	15.1	9.4	0.14
Ir/TiO_2	6.9	4.3	0.035
Pt/TiO_2	200	124	1

a) Obtained using 0.1 g of each catalyst. b) $R_1^{rel} \equiv V/V_0$, the activity relative to TiO_2. c) $R_2^{rel} \equiv \{V(\text{metal})/M(\text{metal})\}/\{V(\text{Pt})/M(\text{Pt})\}$, where M is the molecular weight. Thus, R_2^{rel} represents the activity relative to Pt/TiO_2, referred to unit molar quantity of the loaded metal.

Catalytic Activity. The activities of these metal-loaded catalysts diminished somewhat during storage in a vial; rather rapidly in the first few days (*e.g.*, by

20—30%), and then quite slowly (*e.g.*, by a further 20—30% after storage for a few months). The activity data of Table 1 were obtained with those metal/TiO_2 catalysts that had been loaded with 1% metal and stored for about a week. The values of V for the catalyst samples before heat treatment indicate that the activities fall in the sequence

$$Pt/TiO_2 > Rh/TiO_2 > Pd/TiO_2 > Ru/TiO_2 > Ir/TiO_2 > TiO_2. \quad (1)$$

In accord with this sequence, Kawai and Sakata[1] have shown recently that Pt/TiO_2 is twice as active as Pd/TiO_2 in photocatalyzed dehydrogenation of methanol. A comparison of the V values between the heat-treated and untreated catalysts shows that the heat treatment somewhat enhanced the activity for all the metal/TiO_2 catalysts, but did not alter sequence (1). The cause of the activity enhancement due to heat treatment is not clear at present: It could be (i) the rearrangement of surface metal atoms, (ii) the burning-off of undetected surface impurities, or (iii) the partial oxidation of the loaded metal.

In connection with item (i), it is interesting to refer to Johnson and Keith's paper[6] dealing with the state of platinum in Pt/Al_2O_3 catalysts. They have found that air or O_2 treatment of the catalysts at high temperatures (427—650 °C) followed by reduction leads to a high dispersion of the platinum. In relation to item (iii), it is to be noted that the metal in metal/semiconductor catalysts acts as the pool of electrons photogenerated under irradiation. Partial oxidation of the platinum possibly increases the capacity of the pool, thereby also increases the concentration of positive holes in the TiO_2 phase.

Additional Remarks. A fundamental question about any photocatalytic phenomenon is whether it is really catalytic. To answer this question, let us estimate "the turnovers accomplished."[7] This quantity represents the total number of molecules reacted per surface site. The rough numerical calculations were made based on the acetone formation over the initial 2h-period of reaction; a surface area for TiO_2 of 11.5 m^2/g was used and a catalytic site concentration of $5 \times 10^{14}/cm^2$ was assumed. The turnovers accomplished thus estimated are listed in Table 2. The quite large values for Pt/TiO_2 and Rh/TiO_2 indicate clearly that the dehydrogenation of 2-propanol was really photocatalytic on these two catalysts. The reaction on Ru/TiO_2 and Pd/TiO_2 is also likely to be photocatalytic.

TABLE 2. THE TURNOVERS ACCOMPLISHED FOR EACH CATALYST

Catalyst	Turnovers accomplished molecules site^{-1}	
	Before heat treatment	After heat treatment
TiO_2	2	—
Ru/TiO_2	9	16
Rh/TiO_2	46	57
Pd/TiO_2	11	11
Ir/TiO_2	5	5
Pt/TiO_2	247	266

Lehn *et al.*[2] compared a variety of metal/$SrTiO_3$ catalysts for water splitting under illumination. Since these catalysts and the reaction resemble ours, it seems worthwhile to compare the activities. The activity sequence they observed was

$$Rh/SrTiO_3 > Ru/SrTiO_3 > Re/SrTiO_3 > Ir/SrTiO_3 = Pt/SrTiO_3 > Pd/SrTiO_3 > Os/SrTiO_3 > Co/SrTiO_3 > SrTiO_3. \quad (2)$$

As far as the loaded metals are concerned, sequence (1) does not conform to sequence (2). This discord might stimulate further studies in this area.

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