CHEMISTRY LETTERS, pp. 779-782, 1987.

The Mechanism of the Photocatalytic Dehydrogenation of Methanol

Masayuki OHNO, Hisaji UZAWA, Teruhisa MIYAZAKI, and Kimio TARAMA
Kansai Technical Engineering Co., LTD, 3-1 Fukuzaki, Minato-ku, Osaka 552

We have studied on the mechanism of the photocatalytic dehydrogenation of methanol over Pt/TiO_2. D_2 was only evolved from CH_3OD, and D_2, HD, and H_2 were detected in the evolved gas in the case of the mixed sample of CH_3OD and CH_3OH. These results show that the evolved hydrogen came from hydroxyl hydrogen atom of methanol. And the rate determining step was discussed in connection with comparison among the evolution rates of H_2, HD, and D_2, respectively.

There are many reports concerned with the photocatalytic dehydrogenation of alcohol over Pt/TiO_2 catalysts.$^{1-4)}$ However, the correlations between the catalytic activities and the properties of photocatalyst Pt/TiO_2 were mainly reported, and the mechanism of this photocatalytic reaction was not so much investigated.
So, in this report, the mechanism and the rate determining step of this reaction were investigated by use of deuterated methanol.

The reaction was carried out in a Pyrex glass vessel (200 ml). The reactants were CH_3OH, CH_3OD (Merck D 99%), and mixture of them (20 ml). Pt/TiO_2 catalyst (0.1 g) was dispersed in the reactant and stirred magnetically, and irradiated with a 400W high pressure mercury lamp. Pt(0.1wt%)/TiO_2 was prepared in accordance with the modified Courbon procedure.$^{5)}$ The impregnation of H_2PtCl_6 solution over the TiO_2 powder which was prepared by calcination of $Ti(OH)_4$, was followed by drying at 373 K, oxidation at 773 K in air, and reduction with H_2 at 773 K. H_2, HD, and D_2 were analyzed by a gas chromatograph.$^{6)}$

The results of the measurment are summarized in Table 1. In the case of CH_3OD was used alone for reactant (Run 1), D_2 was only evolved, and H_2 and HD were not detected. This shows that the evolved hydrogen was formed with the hydrogen atoms came from hydroxyl groups of two methanol molecules, and the hydrogen atom of methyl groups are not concerned in the hydrogen gas formation. And it supported the above scheme that HD was evolved from the mixture of CH_3OH and CH_3OD (Runs 2-5).

Table 1. Production rates of H_2, HD, and D_2 from the mixture of CH_3OH and CH_3OD

Run	CH_3OD (ml)	CH_3OH (ml)	a) $r(H_2)$ ml/h^{-1}	b) $r(HD)$ ml/h^{-1}	c) $r(D_2)$ ml/h^{-1}	d) R ml/h^{-1}
1	20	0	-	-	2.4	2.4
2	19	1	-	0.7	1.4	2.1
3	17	3	0.6	1.1	0.8	2.5
4	15	5	0.7	0.9	0.6	2.2
5	10	10	1.4	0.7	-	2.1
6	0	20	2.3	-	-	2.3

a), b), c) $r(H_2)$, $r(HD)$, $r(D_2)$ are the production rates of H_2, HD, and D_2, respectively.

d) $R = r(H_2) + r(HD) + r(D_2)$.

It has been reported that methanol is oxidized to HCHO on a single-crystal TiO_2[7]) or ZnO[8]) photoanode by a current doubling process, and $\cdot CH_2OH$ radical has been proposed as intermidiate in a photocatalytic reaction of methanol.

Thus, the scheme of the D_2 formation from deuterated methanol can be represented as follows.

$$TiO_2 + h\nu \longrightarrow e^- + h^+\text{(hole)} \qquad (1)$$

electron transfer from TiO_2 to Pt (on TiO_2) (2)

$$CH_3OD + h^+ \longrightarrow CH_3O\cdot + D^+ \qquad \text{(on } TiO_2\text{)} \quad (3)$$

D^+ transfer to Pt (on TiO_2) (4)

$$D^+ + e^- \longrightarrow D\cdot \qquad \text{(on Pt)} \quad (5)$$

$$D\cdot + D\cdot \longrightarrow D_2 \qquad \text{(on Pt)} \quad (6)$$

$$CH_3O\cdot + CH_3OD \longrightarrow CH_3OH + \cdot CH_2OD \qquad \text{(on } TiO_2\text{)} \quad (7)$$

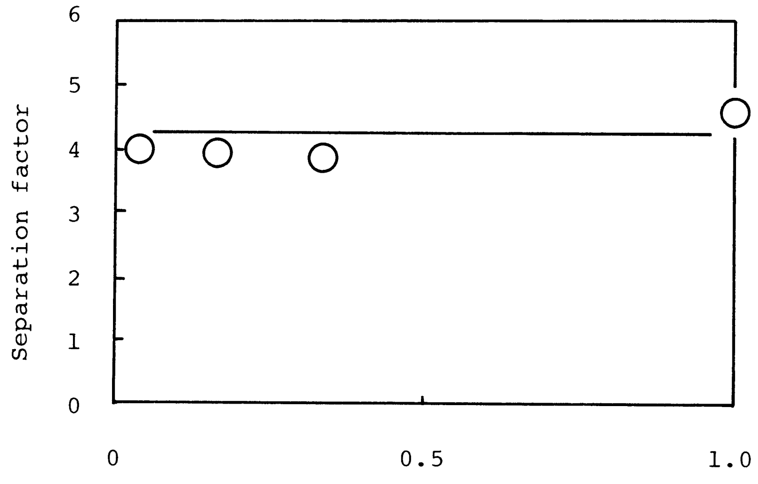
$$\cdot CH_2OD \longrightarrow HCHO + D^+ + e^- \qquad \text{(on } TiO_2\text{)} \quad (8)$$

The re-formed methanol has a light hydrogen atom in the hydroxyl group (Eq. 7), and it will appear in the gas phase as H_2 or HD. However, since the concentration of the re-formed methanol was at most 0.2% in the liquid phase after 10 hours from start of irradiation, the amounts of H_2 and HD were very small and not be detected.

Figure 1 shows the dependence of the separation factors (SF) on mixing ratio of CH_3OH to CH_3OD. The separation factor (SF) is described as

$$SF = \frac{N(H)_{gas}/\ N(D)_{gas}}{(CH_3OH)/(CH_3OD)}$$

where $N(H)_{gas}$ and $N(D)_{gas}$ are the amount of the hydrogen and the deuterium atoms in the gas phase, respectively.



Mixing ratio of CH_3OH to CH_3OD

Fig. 1. Dependence of the separation factors on mixing ratio of CH_3OH to CH_3OD.

$N(H)_{gas}/\ N(D)_{gas}$ were about 4 times as large as $(CH_3OH)/(CH_3OD)$ in the mixed systems of CH_3OH and CH_3OD (Runs 2-5). These isotope effects are observed at the hydrogen electrode reaction (HER) in the electric decomposition of H_2O and D_2O mixture, and the separation factor is 3 to 4 at the Pt electrode.[9)] Since this value is comparable to the value in this reaction, the mechanism of the photocatalytic hydrogen formation seems to be similar them of HER.[10,11)] However, in the individual systems of CH_3OH and CH_3OD, the rates of hydrogen evolution, $r(H_2)$ and $r(D_2)$ are not so different (Run 1,6). And there are little differences among the total gas evolution rates (R) in the mixed systems (Runs 2-5).

Thus, it is supposed that the hydrogen atoms and/or the hydrogen ions are not concerned in the rate determining step in this reaction because the isotope effect does not appear in the hydrogen evolution rates, and that the rate determining step is the electron transfer process from TiO_2 to Pt on TiO_2, reaction process (2).

References

1) I. Ait-Ichou, M. Formenti, B. Pommier, and S. J. Teichner, J. Catal., 91, 293 (1985).
2) H. Nakamatsu, T. Kawai, A. Koreeda, and S. Kawai, J. Chem. Soc., Faraday Trans. 1, 82, 527 (1985).
3) S. Teratani, J. Nakamichi, K. Taya, and K. Tanaka, Bull. Chem. Soc. Jpn., 55, 1688 (1982).
4) T. Kawai and T. Sakata, J. Chem. Soc., Chem. Commun., 1980, 694.
5) H. Courbon, J. M. Merrman, and P. Pichat, J. Catal., 72, 129 (1981).
6) I. Yasumori and S. Ohno, Bull. Chem. Soc. Jpn., 39, 1302 (1966).
7) M. Miyake, H. Yoneyama, and H. Tamura, Chem. Lett., 1976, 635.
8) Ju-seong Lee, T. Kato, A. Fujishima, and K. Honda, Bull. Chem. Soc. Jpn., 57, 1179 (1984).
9) M. Hammerli, J. P. Mislan, and W. J. Olmstead, J. Electrochem. Soc., 116, 779 (1961); 117, 751 (1970).
10) R. Baba, S. Nakabayashi, and A. Fujisima, J. Phys. Chem., 89, 1902 (1985).
11) K. Watanabe, K. Ichimura, N. Inoue, and I. Matsuura, J. Phys. Chem., 90, 866 (1986).

(Received January 21, 1987)