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THE MECHANISM OF PHOTOCATALYTIC HYDROGEN PRODUCTION FROM GASEOUS METHANOL AND WATER: IR SPECTROSCOPIC APPROACH

Maki KAWAI, Shuichi NAITO, Kenzi TAMARU
Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-Ku, Tokyo 113, Japan

and

Tomoji KAWAI *
Institute for Molecular Science, Myodaiji, Okazaki 444, Japan

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IR spectroscopic and volumetric study under reaction conditions of the mechanism of photocatalytic hydrogen production from gaseous methanol and water revealed that CO_2 and H_2 were produced by reaction between adsorbed $CH_3O(ad)$ and H_2O. Another reaction path for H_2 production, $CH_3OH(ad) \rightarrow H_2 + HCHO$, was suggested which is dominant in the absence of water.

Numerous studies have been carried out on reactions over powdered photocatalysts from the viewpoint of solar energy conversion [1]. Especially, the reactions connected with hydrogen evolution are regarded as very important, because of future applications in the hydrogen energy system. Hydrogen production from methanol and water over Pt/TiO_2 is an interesting process, since the quantum yields at 380 nm exceeds 40% in liquid-phase experiments [2,3]. In spite of the importance of the reaction, little is known of the mechanism of these photocatalytic reactions, especially on the state of absorbed species over the catalyst during the reaction. In this paper, we report on the reaction of gaseous methanol in the absence and presence of water under irradiation, in connection with the successful measurement of the adsorbed species during these photocatalytic reactions taking advantage of an IR technique and a volumetric method.

TiO_2 loaded with 2 wt% Pt (Pt/TiO_2) was used as a photocatalyst. Pt was deposited on an ultrafine powder of TiO_2 (Aerosil Co., average diameter 300 Å) by the photodecomposition of K_2PtCl_6. The catalyst thus prepared was pretreated with 100 Torr of oxygen at 400°C for 20 h followed by evacuation at 500°C for 1 h before use, in order to remove contaminations on the surface. The catalyst (0.67 g) for the volumetric measurement was placed at the bottom of a glass reaction cell, connected to a glass closed-circulation system whose total volume was 326 ml. The IR cell was constructed in order to take IR spectra of the adsorbed species during the irradiation of the Pt/TiO_2 disk (50 mg). A 500 W Xe lamp (Ushio Co.) was used as light source, and the light of wavelength between 350 and 400 nm was selected for the irradiation by means of a colored glass filter. FT IR (Jeol JIR10) and gas chromatography were used for the determination of surface species and the gas-phase analysis, respectively. All of the photocatalytic reactions dealt with in this paper were carried out at room temperature (25°C). The quantum yield was measured as described previously [3].

When gaseous methanol (6.0 Torr) alone was introduced over Pt/TiO_2 under irradiation, hydrogen was produced, while only a very small amount of CO_2 was detected in the gas phase (less than 1% of H_2)

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* Present address: Institute of Scientific and Industrial Research, Osaka University, Ibaraki, Osaka 567, Japan.

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Table 1
The amount of H_2 and CO_2 produced after 20 h of reaction under irradiation

	ml *STP*	
	H_2	CO_2
CH_3OH (6.0 Torr)	1.70	0.01
CH_3OH (8 0 Torr) + H_2O (11.9 Torr)	7.25	1.25
CH_3O(ad) + H_2O (12.0 Torr)	3.53	1.30
H_2O (9.0 Torr) 0.13	0.13	0.05

(table 1, fig. 1). Formaldehyde was simultaneously detected in the gas phase by IR spectroscopy and gas chromatography, although its amount could not be determined quantitatively, because of its polymerization in the reactor. The surface-adsorbed species under these conditions were mainly physisorbed methanol CH_3OH(ad) and the surface methoxy group CH_3O(ad). When the gaseous methanol was removed by a liquid-nitrogen trap, the production of H_2 stopped and the physisorbed CH_3OH(ad) immediately disappeared from the surface while the CH_3O(ad) species remained unchanged.

When a mixture of H_2O and CH_3OH was introduced, the H_2 production in 20 h increased by 4.5 times and CO_2 began to be evolved (table 1, fig. 1). The quantum yield under these conditions corresponded to 10%. In order to elucidate the reaction mechanism and the role of H_2O for this drastic enhancement of the reactivity in this system, the following experiments were carried out. First, methanol and water vapor were introduced over the catalyst under irradiation. This leads to the production of H_2 and CO_2 (fig. 1). Then the gas phase was switched to H_2O vapor alone. As shown in fig. 1 and table 1 the rate of CO_2 production was identical before and after the change in the gas phase. This means that the CO_2 and part of the H_2 were produced by reaction between the H_2O vapor and the adsorbed species.

In fig. 2 are shown the IR spectra during the

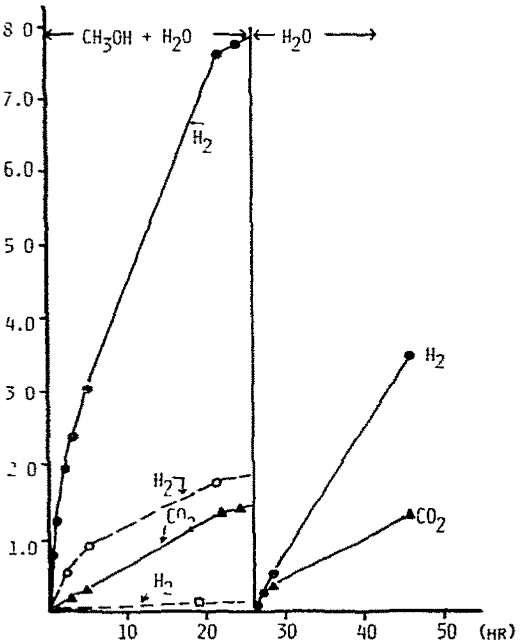

Fig 1 Photocatalytic H_2 production from CH_3OH and H_2O on 2 wt% Pt/TiO_2 (solid line). CH_3OH(g) = 8.0 Torr, H_2O(g) = 11.9 Torr. After 27 h, gas phase was switched to H_2O vapor alone. H_2O(g) = 12.0 Torr. ●; H_2, ▲; CO_2. The broken line with open circle (o) shows the H_2 production from CH_3OH (6.0 Torr) alone. The broken line with open square (□) shows the H_2 production from H_2O vapor alone.

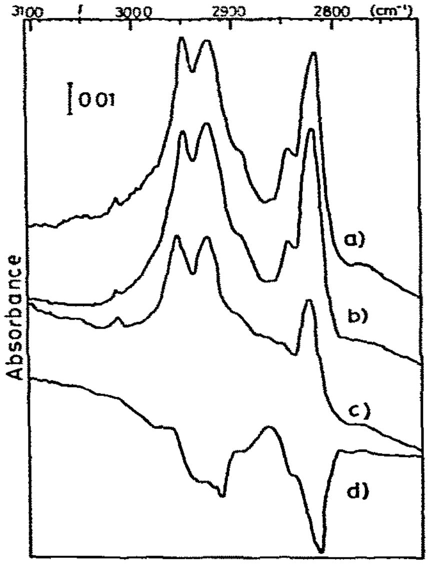

Fig. 2. IR spectra during the course of the reaction. (a) The surface species just after the reaction of methanol and water under irradiation followed by the evacuation of the gas phase. (b) The system was evacuated for 1.5 h under irradiation after (a). (c) H_2O vapor was introduced over (b) for 1.0 h under irradiation. (d) Difference spectrum of (b) and (c).

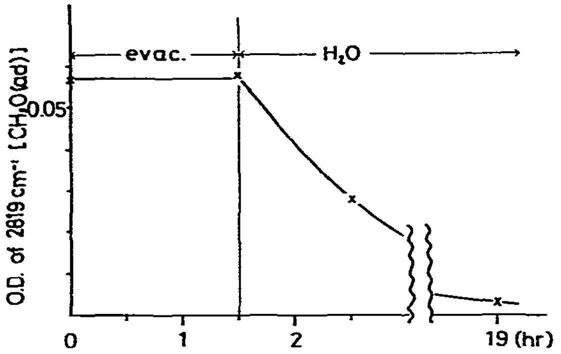

Fig. 3. Changes in the amount of surface $CH_3O(ad)$ under irradiation estimated by IR spectroscopy.

course of the reaction. Gaseous methanol and water were evacuated after $CH_3O(ad)$ was accumulated on the surface of the catalyst by the reaction under irradiation. The absorption bands at 2920 and 2820 cm^{-1} are due to the asymmetric and symmetric CH vibration modes of $CH_3O(ad)$, respectively, and 2950 cm^{-1} to the HCOO(ad) species (fig. 2a) [4]. The IR cell was then irradiated in vacuo for 1.5 h, during which the amount of surface $CH_3O(ad)$ remained unchanged (figs. 2b and 3). But when H_2O vapor was introduced to this system, $CH_3O(ad)$ immediately began to decrease (figs. 2c and 3). The difference spectrum of figs. 2b and 2c is shown in fig. 2d. The absorption band at 1140 cm^{-1} due to the C–O stretching mode of surface $CH_3O(ad)$ also decreased by the reaction with H_2O. It is clear from the above observations that $CH_3O(ad)$ reacted with H_2O under irradiation, producing H_2 and CO_2 in the gas phase. Absorption bands at 1600 and 1374 cm^{-1} due to surface CO_2 or CO_3 species [4] increased in intensity. The ratio of H_2 to CO_2 by the volumetric experiment was 2.7, which was close to the stoichiometric ratio considered from the reaction between $CH_3O(ad)$ and H_2O (see eq. (2) below). These facts indicated that the H_2 and CO_2 were produced via the following reaction mechanism over Pt/TiO_2 under irradiation:

$$CH_3OH(g) \rightarrow CH_3O(ad) + H(ad)\,, \tag{1}$$

$$CH_3O(ad) + H_2O \rightarrow CO_2(g) + \tfrac{5}{2}H_2(g)\,. \tag{2}$$

In table 1 are summarized the amounts of H_2 and CO_2 produced after 20 h under irradiation in the presence of methanol, water–methanol, surface $CH_3O(ad)$–water vapor, and water vapor alone. It should be noted that no other gases such as CO or CH_4 were observed in this particular photocatalytic reaction, while these gases were produced as main products when the reaction was carried out at 150°C without irradiation.

The catalytic production of CO_2 in these systems can only be explained by the participation of H_2O in the reaction, as shown in eq. (2). Although H_2 production from H_2O alone was very slow (see table 1), H_2O plays an important role in the H_2O–methanol system. When H_2O was introduced to Pt/TiO2 under irradiation, ·OH is produced by a hole in the valence band of TiO_2 [5]. This ·OH can easily be reduced by the electron at the conduction band to form H_2O again in the absence of methanol, so that the electron cannot be used for efficient H_2 production. However, in the presence of methanol or the methoxy group, ·OH would work as an oxidizing agent to the methoxy species by the following mechanism, subtreating –H from C–H to form CO_2 and H_2O:

$$H_2O + p \rightarrow \cdot OH + H^+\,, \tag{3}$$

$$5\,\cdot OH + CH_3O(ad) \rightarrow CO_2 + 4H_2O\,. \tag{4}$$

An electron at the conduction band is simultaneously used for H_2 production through the Pt catalyst:

$$e + H^+ \rightarrow \tfrac{1}{2}H_2\,. \tag{5}$$

Combination of (3), (4) and (5) leads to eq. (2).

Even in the absence of water vapor, methanol decomposes under irradiation, producing H_2 and HCHO without CO_2 evolution in the gas phase. Since H_2 production stopped when the physisorbed methanol was removed from the surface, the following mechanism is suggested for one of the routes of the decomposition of methanol under irradiation:

$$CH_3OH(g) \rightarrow CH_3OH(ad)\,, \tag{6}$$

$$CH_3OH(ad) + 2p \rightarrow HCHO(g) + 2H^+\,, \tag{7}$$

$$2H^+ + 2e \rightarrow H_2(g)\,. \tag{8}$$

The total photocatalytic H_2 production (7.25 ml *STP*/20 h) for the water–methanol mixture exceeds the simple addition of eq. (2) and (8) (3.53 + 1.70 = 5.25 ml *STP*), in spite of the good accord of CO_2 production. This phenomenon may be explained as follows: The ·OH could attack not only the $CH_3O(ad)$ species but also CH_3OH directly in the presence of physisorbed methanol to form HCHO,

$$CH_3OH + 2\cdot OH \rightarrow HCHO + 2H_2O\,, \qquad (9)$$

and H_2 [eq. (5)] without producing CO_2. Thus the amount of H_2 produced for methanol and water can exceed the simple addition of eq. (2) and (8). The total H_2 and CO_2 production is the combination of the mechanisms (2), (8) and (9).

Finally, we would like to emphasize that the IR technique is a very powerful method to determine the surface species and to pursue its reactivity during the course of the photocatalytic reaction, because of the applicability of this technique to the determination of molecular structure.

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