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Hydrogen Production from Methanol or Methane by the Use of Thermally Generated Holes in TiO_2

Keiji MATSUMOTO, Yoshiyuki SATO, Toru EBARA, and Jin MIZUGUCHI

E-mail: mizu-j@ynu.ac.jp

Department of Applied Physics, Graduate School of Engineering, Yokohama National University

79-5 Tokiwadai, Hodogaya-ku, Yokohama, 240-8501 Japan

Previously involved in complete decomposition (H_2O + CO_2) of organic wastes (mainly thermoplastic and thermosetting polymers), as well as exhaust of diesel engines by the use of thermally generated holes in TiO_2 at about 350–500°C under sufficient O_2. Then, we struck on an idea that H_2 can be produced in place of H_2O under O_2–deficient conditions. Because of this, an attempt has been made in the present investigation to produce hydrogen from methanol or methane. Hydrogen is found to be successfully produced from methanol at 350–400°C under 5–20% O_2, or from methane at 450–500°C under 50% O_2. The conversion efficiency amounts to about 70–85% for methanol while about 40% for methane.

Keywords: Titanium Dioxide, Hydrogen Production, Methanol, Methane, Partial Decomposition

Introduction

Titanium dioxide was once extensively investigated as a photoconductor for the electrophotographic photoreceptor early on (Ishibai, 1992). Nowadays, it has attracted attention as a material for photocatalyzers (Wang *et al*., 1997) and solar cells (Nazeeruddin *et al*., 2005; Miyasaka *et al*., 2007). We report here a new application of titanium dioxide for hydrogen production by the use of thermally excited holes at high temperatures.

Hydrogen has attracted much attention as a clean energy source for the future, especially for fuel cells. Therefore, hydrogen production with low cost is one of the most important issues at the moment. We have previously reported that complete decomposition of organic wastes (mainly thermoplastic and thermosetting polymers) as well as the exhaust of diesel engines is achieved by a great number of holes produced at about 350–500ºC in TiO_2 (Mizuguchi, 2001; Mizuguchi and Shinbara., 2004; Shinbara *et al.*, 2005; Makino *et al*, 2007; Matsumoto *et al*., 2007). Our system is characterized by the use of thermally excited holes at high temperatures (*e.g.*, about 350ºC) in combination with a molten state of thermoplastics, for example, polycarbonate (PC) as shown in **Figure 1**. A great deal of charge carriers are available in TiO_2 at high temperature as shown by the product of the Fermi–Dirac distribution function and the density of states (Kittel, 1986). The number of carriers at room temperature (RT) and 350ºC ($n_{RT} = n_0\exp[-E_g/2kT_{RT}]$ and $n_{623K} = n_0\exp[-E_g/2kT_{623K}]$, respectively] gives a ratio of $n_{623K}/n_{RT} \approx 8.8\times10^{13}$, where $E_g = 3.2$ eV.

The initial process of the PC decomposition is the capture of bonded electrons to form radicals by thermally generated holes, followed by their propagation throughout the substance to break up PC into fragments, ending up with their complete decomposition into H_2O and CO_2 under oxygen-sufficient conditions (Shinbara *et al.*, 2005). Then, we arrived at the idea that H_2 can be produced in place of H_2O under oxygen-deficient conditions. As a result, the present investigation attempts to produce hydrogen from methanol or methane by the use of thermally generated holes in TiO_2 at high temperatures. The former is inexpensive and seems to be easily decomposed into H_2; whereas the latter is the major component of the city gas, offering an opportunity to locally produce hydrogen.

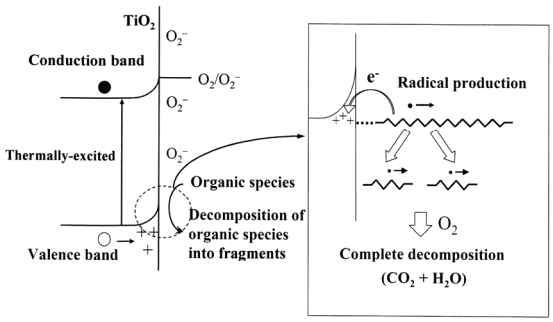

Fig. 1 Decomposition process of PC by means of thermally generated holes

1. Experimental

1.1 Material

TiO_2 powders (ST-01) were obtained from Ishihara Sangyo Kaisha Ltd. (ISK). The powder was calcinated in air at 500ºC for 1 h before use, unless otherwise stated. Calcination brought about a stabilization of ST-01, leading to reproducible results. Methanol was purchased from Junsei Chemical Co., Ltd. Methane of the G2 grade was purchased from Taiyo Nippon Sanso Co., Ltd.

1.2 Equipment

An autoclave equipped with a quadrupole mass spectrometer (model: RG-102 from ULVAC Inc.; abbreviated to Q-Mass) was used to produce hydrogen from methanol or methane. Details of the equipment have been described in our previous report (Makino *et al*., 2007). The volume of the reaction vessel was 300 mL, in which 40 g of TiO_2 powder was charged. Gases were introduced from the bottom of the autoclave into the reaction vessel while the stirrer was rotated at 150 rpm. The temperature range was variable between room temperature and 500ºC.

1.3 Experimental conditions

Methanol-saturated vapors were prepared at room temperature by bubbling air, O_2/Ar, or O_2/N_2 into methanol. The methanol content of the total gas was 4.88 mol% with a flow rate of 50 mL/min. The gas emerged from the autoclave was sampled and analyzed by Q-Mass. On the other hand, methane was directly introduced into the autoclave together with O_2 at room temperature.

In the present study, gas concentration is expressed in mol%.

2. Results and Discussion

2.1 Hydrogen formation from methanol under O_2-deficient conditions

As a step to find the conditions for hydrogen production, we began with the study of the complete decomposition process of methanol in air as a function of temperature. Then, we attempted to optimize the conditions for hydrogen production

as a function of both temperature and oxygen concentration.

Figure 2 shows the decomposition process of methanol in air (i.e., under O_2-sufficient conditions) as a function of temperature at a flow rate of 50 mL/min. Methanol is found to start decomposing at about 250ºC, and be nearly completed at about 400ºC, accompanied by the decrease in oxygen and the increase in H_2O and CO_2. The ratio of CO_2 to H_2O is nearly 1 to 2 in the temperature range between 400 and 500ºC (i.e., molar ratio of C/H = 1/4). This ratio is consistent with that in methanol (CH_3OH) in the initial state. As seen from Figure 2, incomplete decomposition is assumed to occur in the temperature range between 250 and 400ºC, where methanol is under decomposition and the ratio of CO_2/H_2O is not yet 1/2.

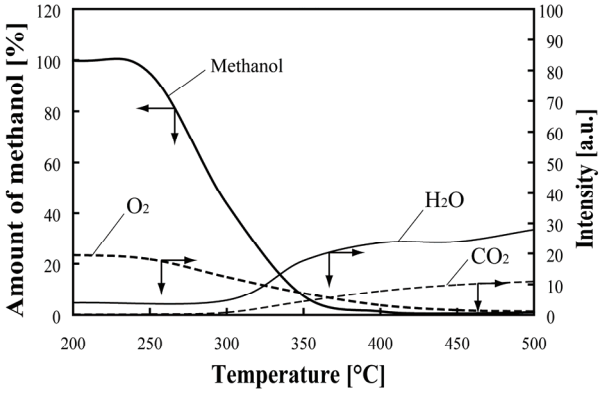

Fig. 2 Complete decomposition of methanol in air

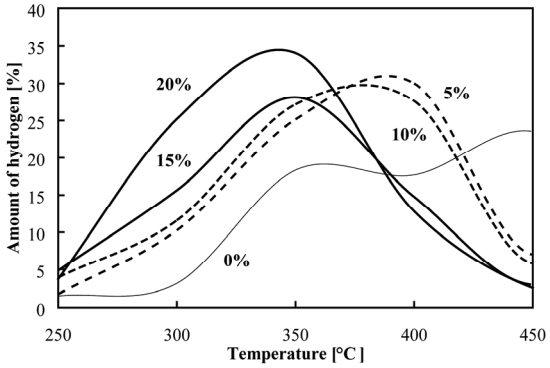

Fig. 3 Temperature dependence of hydrogen formation as a function of O_2 concentration

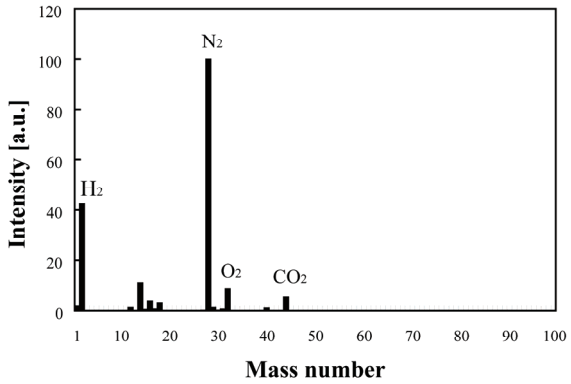

Fig. 4 Gas analysis in air at 350°C

Then, the formation of H_2 was studied as a function of both temperature and O_2 concentration as shown in **Figure 3**. One can see clearly the formation of H_2, peaking at about 350ºC for 15–20% O_2, and around 400ºC for 5–10% O_2. This indicates that the peak of the hydrogen production is displaced toward higher temperatures as the concentration of oxygen decreases. This tendency is also recognized under 0% O_2, although another peak also appears at approximately 350°C.

Figure 4 shows typical mass spectra measured under 20% O_2 at 350°C, where the formation of H_2 is clearly observed. The peaks are assigned as follows: CO_2 (m = 44), CH_4 (m = 15, 16), N_2 (m = 28, 14), O_2 (m = 32, 16), CH_3OH (m = 31, 29), and H_2 (m = 2).

2.2 Reaction path from methanol to hydrogen

Figures 5(a), (b), and (c) show the mass spectra for the hydrogen formation from methanol at 350°C as a function of oxygen concentration: 0, 5, and 10%. The formation of H_2 is clearly observed in mass spectra together with other species: CO_2 (m = 44), CH_4 (m = 15, 16), CH_3OCH_3 (m = 45, 46), N_2 (m = 28, 14), O_2 (m = 32, 16), CH_3OH (m = 31, 29), and H_2 (m = 2).

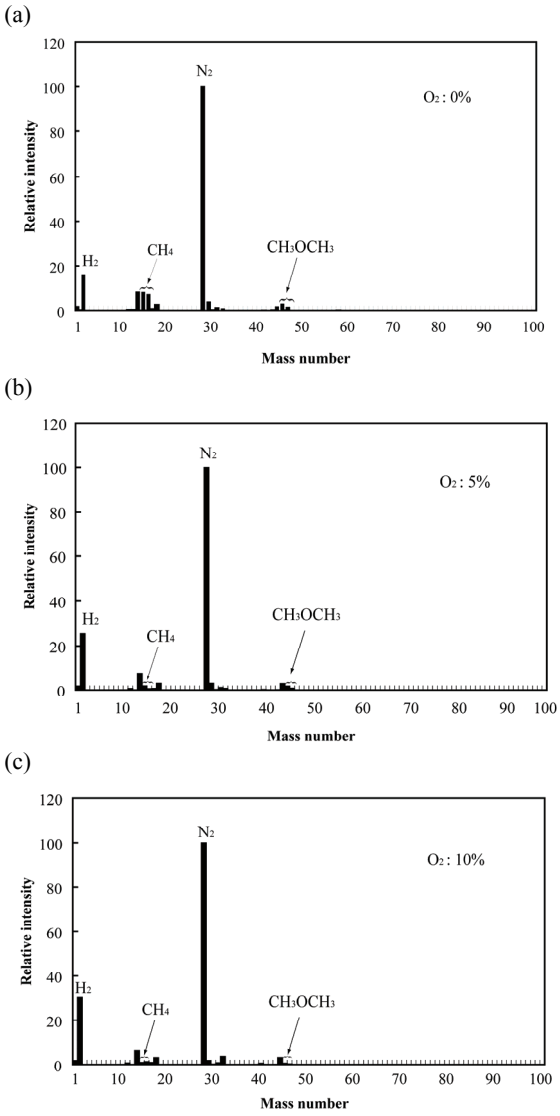

Fig. 5 Gas analysis for the decomposition of methanol at 350°C under O_2 concentration: (a) 0%, (b) 5%, and (c) 10%

It is remarkable to note that methane and dimethylether (CH_3OCH_3) are formed as intermediates under 0% O_2 and that these species disappear to increase the fraction of hydrogen as the oxygen concentration is increased. This tendency is further intensified under 10% O_2. These results clearly suggest that the increase of O_2 provides a preferential reaction path for the formation of H_2.

Then, we focused on the amount of methane or dimethylether formation as a function of both oxygen concentration and temperature. **Figure 6** shows the result for methane. The formation of methane is completely suppressed above 325ºC under 5–20% O_2. On the other hand, methane remains in the whole temperature range under 0% O_2, peaking at about 400ºC. **Figure 7** shows the decomposition of dimethylether under the same conditions. Decomposition occurs in the presence of 5–20% O_2, the same way as that of methane, although the suppression degree is not complete; whereas dimethylether decomposes completely above 350ºC under 0% O_2.

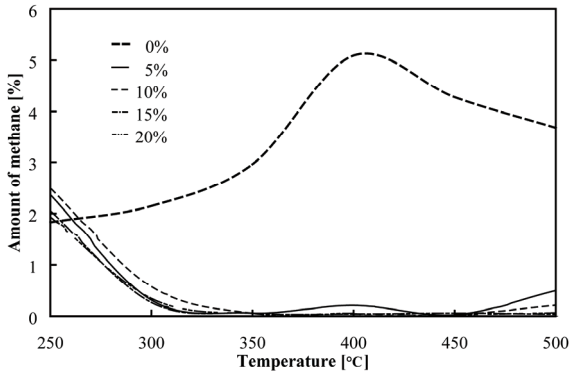

Fig. 6 Temperature dependence of methane decomposition as a function of O_2 concentration

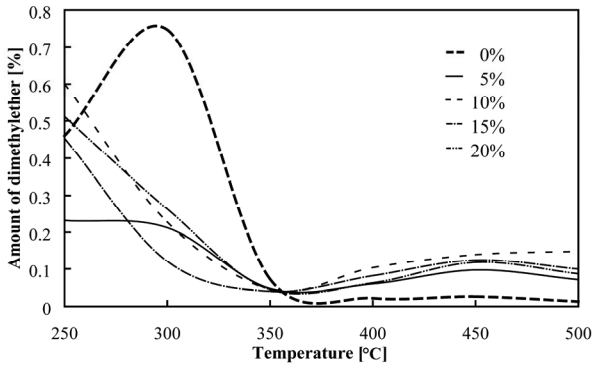

Fig. 7 Temperature dependence of dimethylether decomposition as a function of O_2 concentration

2.3 Hydrogen formation directly from methane

As shown in the previous sections, decomposition of methane leads to the formation of H_2 by way of methane and dimethylether. Now, we study the hydrogen formation directly from methane by thermally generated holes, using methane together with oxygen.

We started again with complete decomposition of methane in order to find conditions for hydrogen formation. **Figure 8** shows the decomposition process of methane under 90% O_2 (i.e., molar ratio of CH_4/O_2 = 1/9) at a flow rate of 100 mL/min in an attempt to achieve complete decomposition (H_2O + CO_2). Methane is found to start decomposing at about 400ºC and decrease to about 5% of the initial amount at 550ºC; whereas the amount of CO_2 and H_2O increases with the formation of methane. As judged from Figure 8, incomplete decomposition (i.e., formation of H_2) is expected to occur at temperaturesabove 400ºC to give H_2.

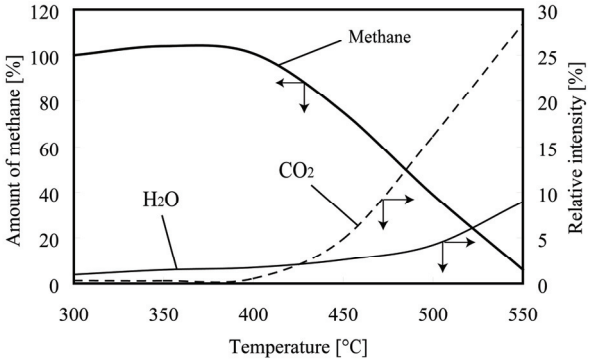

Fig. 8 Decomposition process of methane under 90% O_2 as a function of temperature

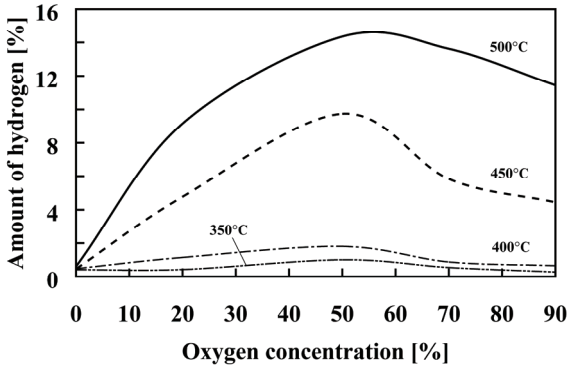

Fig. 9 Temperature dependence of H_2 formation arising from methane as a function of oxygen concentration

Based upon the above preliminary experiment, the formation of H_2 was studied as a function of both temperature and oxygen concentration (**Figure 9**). One can see clearly the formation of H_2 with increasing temperature, peaking at the oxygen concentration of 50%, almost irrespective of the temperature. Especially, the formation of H_2 is significant at temperatures of 450 and 500ºC.

Figure 10 shows the gas analysis under 50% O_2 at 500ºC. The peaks are assigned as follows: CO_2 (m = 44), CO (m = 28), O_2 (m = 32, 16), CH_4 (m = 15, 16), and H_2 (m = 2).

In addition, we tried to minimize the formation of CO. **Figure 11** shows the formation of CO as a function of temperature and oxygen concentration. The CO amount increases almost linearly at 500ºC as the oxygen concentration increases. On the other hand, at 450ºC, the CO formation increases exponentially above 70% O_2.

To summarize the results, the conditions for the maximum H_2 formation with minimum CO are: 50% O_2 at 450ºC.

2.4 The efficiency of hydrogen production from methanol or methane

When methanol or methane is partially decomposed in the

presence of oxygen, the H-containing species in the final product are only H_2O or H_2. The ratio of $H_2/(H_2 + H_2O)$ determines the conversion efficiency of H_2 formation. In the case of methanol, the efficiency amounts to about 70–85% under 15–20% O_2 at 350–400ºC. On the other hand, in methane, the efficiency is about 40% under 50% O_2 at 450-500ºC.

The efficiency of hydrogen production from methane is, for the time being, much lower than that from methanol. This is mostly attributed to the larger quantity of methane (50%) relative to the carrier gas as compared with that of methanol (4.88%). A remarkable improvement can be expected by passing a mixture of methane and oxygen through TiO_2 powders for a long distance.

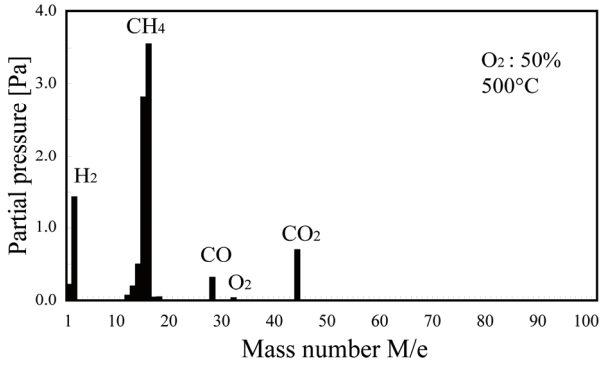

Fig. 10 Mass spectra of the emerging gas at 500°C under 50% O_2

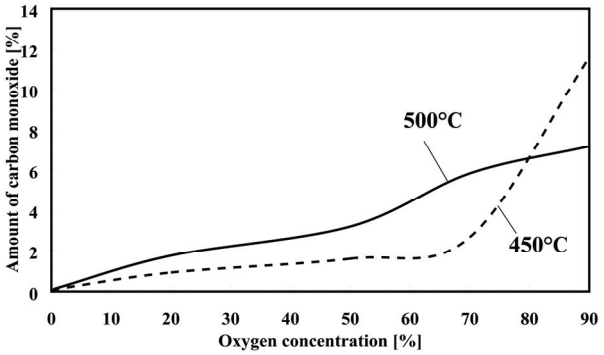

Fig. 11 Temperature dependence of carbon monoxide formation starting from methane

Conclusions

An attempt has been made to form hydrogen by the use of thermally generated holes in TiO_2 at high temperatures. Hydrogen is found to be produced from methanol under 10–15% O_2 in the temperature range between 350 and 400ºC, or from methane under 50% O_2 above 450ºC. The conversion efficiency is about 70–85% for methanol and about 40% for methane.

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