Partial decomposition of methanol by means of thermally-generated holes in TiO_2 for the production of hydrogen

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Abstract

Titanium dioxide was once extensively investigated as a photoconductor for the electrophotographic photoreceptor at its incunabula. Nowadays, it has attracted attention as a material for photocatalyzers, solar cells as well as their related areas. We report here another application of titanium dioxide. Hydrogen has attracted attention as a clean energy source for the future. We have been involved in complete decomposition of organic wastes (mainly thermoplastic and thermosetting polymers) as well as exhaust of diesel engines (benzene, toluene and particulate matter) in excess of oxygen by means of thermally-generated holes in TiO_2 *at about 350-500 ºC. In the present investigation, an attempt has been made to prepare hydrogen by means of thermally-excited holes under oxygen-deficient conditions. Hydrogen is found to be successfully produced from methanol via methane and dimethylether at 400 ºC under 5-10 % oxygen together with carbon monoxide and carbon dioxide.*

1. Introduction

Hydrogen has attracted attention as a clean energy source for the future, especially for fuel cells. Therefore, the hydrogen production with low cost is one of the critical issues that we must address.

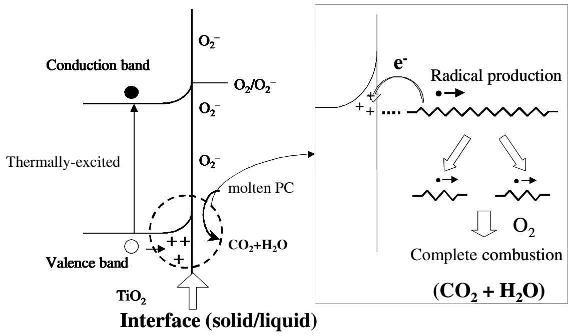

Figure 1. *Decomposition process of PC by means of thermally-generated holes.*

We have previously reported that complete decomposition of organic wastes (mainly thermoplastic and thermosetting polymers) is achieved by means of a great number of holes produced at about 350-500 ºC in TiO_2 [1-3]. The appealing point of the system is the utilization of thermally-excited holes at high temperatures (say, about 350 ºC) in combination with a molten state of thermoplastics, for example, polycarbonate (PC) as shown in Fig. 1. A great deal of charge carriers is available in TiO_2 at high temperature as shown by the product of the Fermi-Dirac distribution function and the density of state [4]. The number of carriers at room temperature (RT) and 350 ºC [$n_{RT}=n_{00}\exp[-E_g/2k_BT_{RT}]$ and $n_{623K}=n_0\exp[-E_g/2k_BT_{623K}]$, respectively] gives a ratio of $n_{623K}/n_{RT}\approx 8.8\times10^{13}$ where E_g=3.2 eV. The key factor for the complete decomposition is the initial formation of radicals in organic materials due to thermally-generated holes and their propagation throughout the substance to give fragments [3]. Then, the fragments burn perfectly to give H_2O and CO_2 under oxygen-sufficient conditions

In the present investigation, we changed drastically our way of thinking not to completely decompose organic wastes under oxygen-sufficient conditions but to partially decompose them under oxygen-deficient conditions in order to form hydrogen. As organic species, we focused on methanol or methane, the former is inexpensive and seems to be easy to partially decompose into H_2; whereas the latter is the major component of the city gas, offering an opportunity to locally produce hydrogen.

2. Experiment

2.1 Material

TiO_2 powders (ST-01) were obtained from Ishihara Sangyo Kaisha (ISK). α-Al_2O_3 and methanol were purchased from Junsei Chemical Corporation, Ltd. All powdered samples were calcinated in air at 500 ºC for 1 h before use, unless otherwise stated. Methane of the G2 grade was obtained from Taiyo Nippon Sanso Corporation, Ltd.

2.2 Equipment

A quadropole mass spectrometer (model: RG-102 from ULVAC; abbreviated to Q-Mass) was used for the gas analysis. An autoclave equipped with a Q-Mass was designed for the present experiment. The temperature range was between room temperature and 500 ºC. The volume of the reaction vessel is 300 ml, in which 40 g of TiO_2 powders were charged. The stirrer rotates at 150 rpm. Gases to be decomposed were introduces from the bottom of the autoclave into the reaction vessel while the stirrer being rotated.

2.3 Experimental conditions

Methanol-saturated vapors were prepared by bubbling air, or O_2/Ar, or O_2/N_2 in methanol, at room temperature. The flow rate of the bubbling gas was 50 or 200 ml/min and the methanol content was controllable between 0 % and 100 %. The methanol content of the total gas used in experiments was 4.88 % (flow rate:

50 ml/min). The gas exhausted 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.

3. Results and Discussion

3.1 Hydrogen formation by means of partial decomposition of methanol

As a step toward understanding of the partial decomposition conditions of methanol, we started by studying the process of complete decomposition of methanol in air as a function of temperature. Then, we optimized the condition for the production of hydrogen as a function of temperature and oxygen concentration.

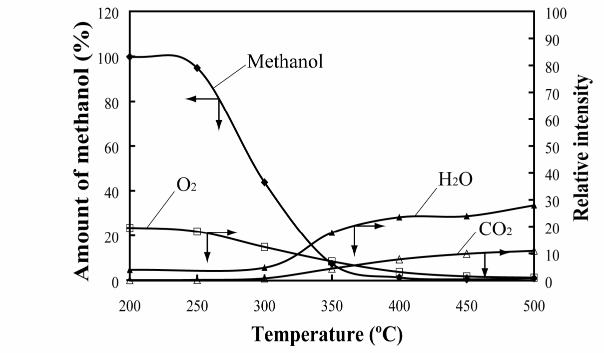

Figure 2. *Complete decomposition of methanol in air.*

Fig. 2 shows the decomposition process of methanol in air as a function of temperature at a flow rate of 50 ml/min. Methanol is found to start decomposing at about 250 °C and nearly completed at about 400 °C, 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 500 °C (*i.e.* ratio of C/H = 1/4). This ratio is consistent with that in methanol (CH_3OH) in the initial state. Fig. 2 suggests that incomplete decomposition occurs in the temperature range between 250 and 400 °C (*i.e.* the region where methanol starts decomposing and the ratio of CO_2/H_2O is not yet 1/2).

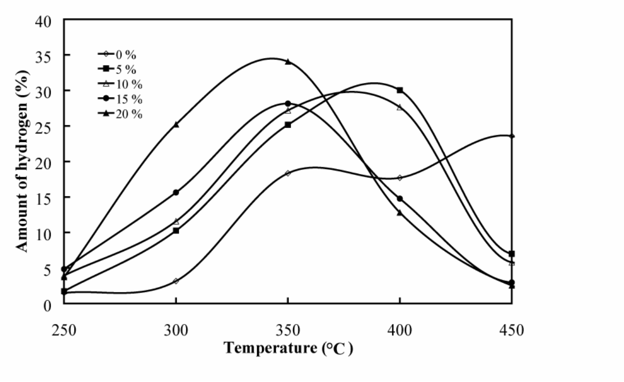

Figure 3. *Temperature dependence of hydrogen formation as a function of oxygen concentration.*

Then, the formation of H_2 was studied as a function of temperature and O_2 concentration (Fig. 3). One can see clearly the formation of H_2, peaking at 350 °C for 15-20 % O_2. Another peak is also observed around 400 °C for 5-10 % O_2. This indicates that the peak is displaced toward higher temperatures as the concentration of oxygen decreases.

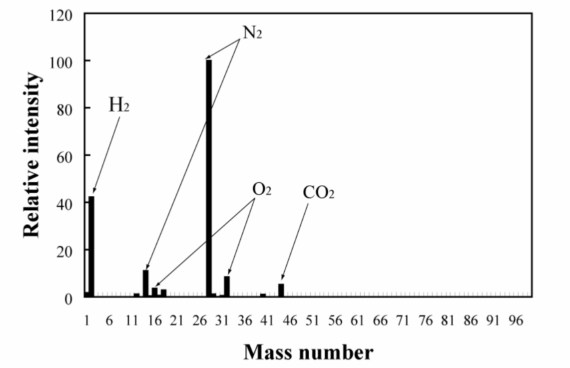

Figure 4. *Gas analysis in air at 350 °C.*

The formation of H_2 is clearly observed in mass spectra as shown in Fig. 4 where the analysis was made in air at 350 ºC. 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 ($m= 2$).

3.2 Reaction path from methanol to hydrogen

The decomposition fragments were then studied as a function of oxygen concentration while the temperature was fixed at 350 ºC (Fig. 5). Under 0 % O_2, CH_4 (methane; $m = 15, 14$) and CH_3OCH_3 (dimethylether; $m = 46, 45$) are clearly observed. However, these species are significantly suppressed under 5 % O_2, contributing to the formation of H_2. This tendency is further intensified under 10 % O_2. These results clearly indicate that the increase of O_2 provides a preferential reaction path for the formation of H_2.

Fig. 6 shows the amount of methane *vs* temperature as a function of oxygen concentration. Under 0 % O_2, methane remains undecomposed, quite independent of the temperature. On the contrary, in the presence of oxygen (5-20 %), methane disappears almost entirely above 300 ºC.

Fig. 7 shows the decomposition of dimethylether under the same conditions. Decomposition occurs in the presence of 5-20 % O_2, exactly in the same way as that of methane. However, dimethylether decomposes completely above 350 ºC even in complete absence of oxygen.

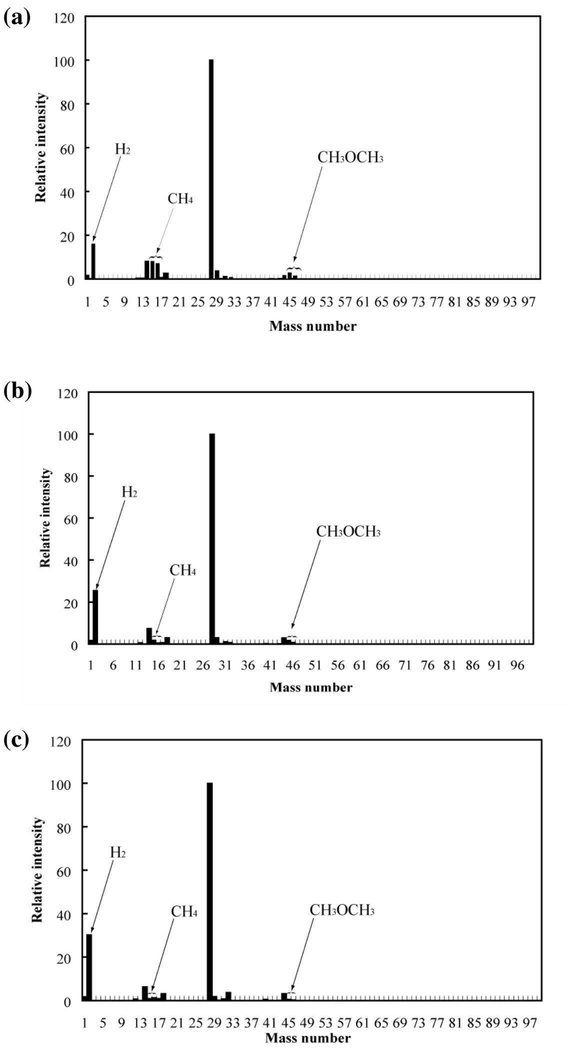

Figure 5. Gas analysis for the decomposition of methanol at 350 °C under O_2 *concentration: (a) 0 %, (b) 5 %, (c) 10 %.*

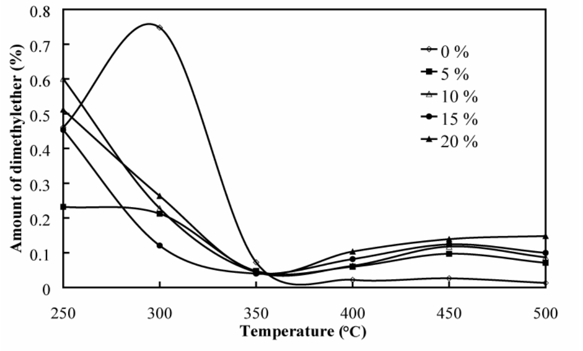

Figure 6. Temperature dependence of methane decomposition as a function of O_2 *concentration.*

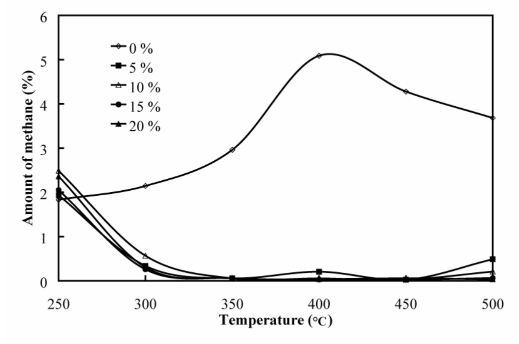

Figure 7. Temperature dependence of dimethylether decomposition as a function of O_2 *concentration.*

3.3 Hydrogen formation by means of partial decomposition of methane

As discussed in the previous sections, decomposition of methane leads to the formation of H_2. Here, we study the hydrogen formation directly from methane by means of partial decomposition, using methane gas together with oxygen (not air).

At first, we began again with complete decomposition. Fig. 8 shows the decomposition process of methane under 90 % O_2 (*i.e.* ratio of $CH_4/O_2 = 1/9$) at a flow rate of 100 ml/min in an attempt to achieve complete decomposition. Methane is found to start decomposing at about 400 ºC and decrease to about 5 % of initial amount at 550 ºC. As judged from Fig. 8, incomplete decomposition is assumed to occur in the temperature above 400 ºC that can lead to the formation of H_2.

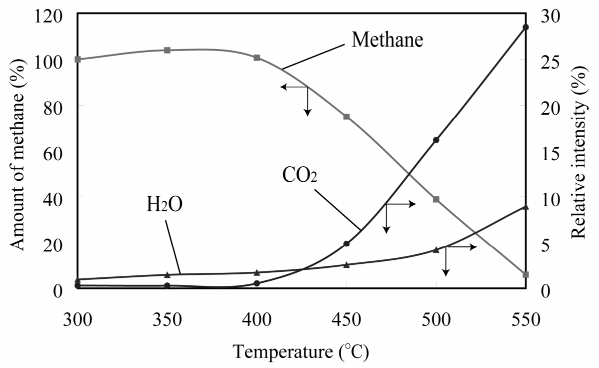

Figure 8. Decomposition process of methane with 90 % O_2 *as a function of temperature.*

On the basis of the above preliminary experiment for complete decomposition, the formation of H_2 was studied as a function of temperature and oxygen concentration (Fig. 9). One can see clearly the formation of H_2 with increasing temperature, peaking at the concentration of 50 % O_2, quite independent of the temperature. Especially, the formation of H_2 is significant above 350 ºC. Fig. 10 shows the gas analysis under 50 % O_2 at 500 ºC.

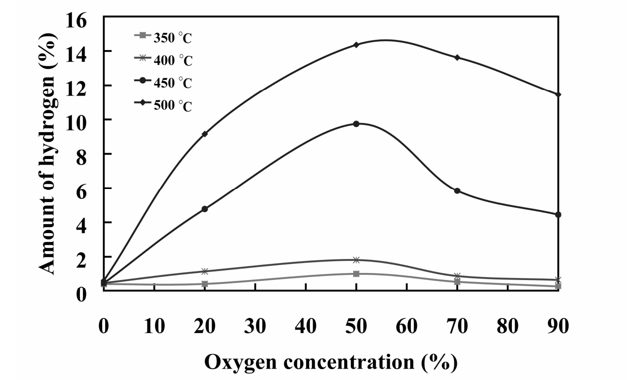

Figure 9. *Temperature dependence of H_2 formation arising from methane as a function of oxygen concentration.*

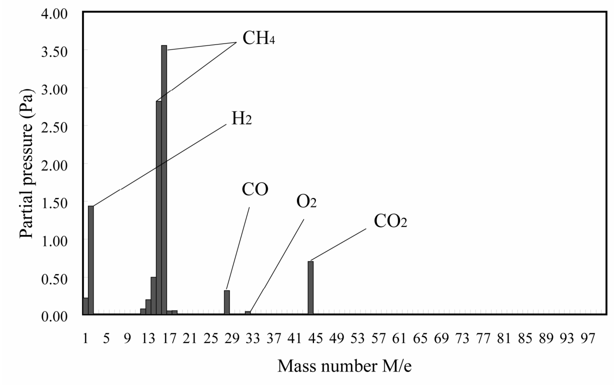

Figure 10. *Mass spectra of the emerging gas at 500 °C under 50 % O_2.*

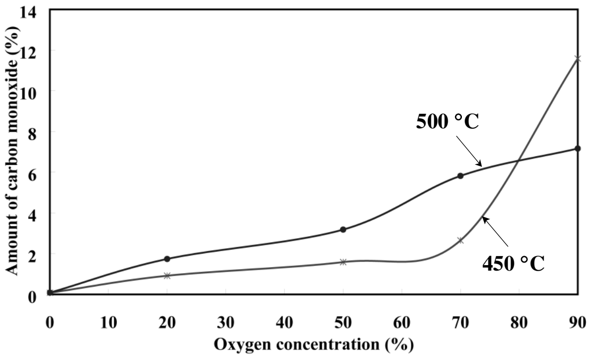

Figure 11. *Temperature dependence of carbon monoxide formation starting from methane.*

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. Fig. 11 shows the formation of CO as a function of temperature and oxygen concentration. The CO amount increases almost linearly at 500 °C as the oxygen concentration is increased. On the other hand, at 450 °C, the CO formation increases abruptly above 70 % O_2. To summarize the result, the conditions for the maximum H_2 formation with minimum CO are: 50 % O_2 at 450 °C.

3.4 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 stage are only H_2O or H_2. The ratio of $H_2/(H_2 + H_2O)$ determines the conversion efficiency of the H_2 formation. In the case of methanol, the efficiency amounts to about 70-85 % under 15-20 % O_2 at 350-400 °C. On the other hand, in methane, the efficiency is about 40 % under 50 % O_2 at 450-500 °C.

4. Conclusions

An attempt has been made to form hydrogen by means of partial decomposition of methanol or methane utilizing thermally-generated holes in TiO_2. Hydrogen is found to be produced from methanol under 10-15 % O_2 in the temperature range between 350 and 400 °C, and from methane under 50 % O_2, independent of the temperature.

References

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Author Biography

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