Formation of Methanol by Microwave-Plasma Reduction of CO_2 with H_2O

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(Received June 14, 1995)

Reduction of CO_2 with H_2O was carried out by microwave plasma for the formation of methanol. The results of steam chromatography and mass spectrometry showed that the plasma products contained methanol. The methanol formation was also found in H_2O-plasma-cleaning process, in which materials which had been deposited in the reaction between CO_2 and H_2O were removed. The most adequate plasma energy density for the formation of methanol was found to be 0.26 $\mathrm{GJ\,kg^{-1}}$ of *W*/*FM*. The methanol yield at the system pressure of 400 Pa was 3.5 times higher than at 240 Pa for both the CO_2–H_2O synthetic process and the H_2O-cleaning process.

As a utilization of low-temperature microwave plasma, we tried to reduce CO_2 with H_2O, which is the reversed reaction of "combustion", in order to create a new and possibly beneficial reaction. The concept to promote this unusual reaction stems from the viewpoints of global environmental problem and energy deficiency we have been facing: CO_2 should be reduced and needs to be utilized an energy resource. There are some other efficient methods to reduce CO_2 and create organic compounds;[1—4] but in our system, aided by plasma energy, we used H_2O, which is the most ubiquitous and cheap hydrogen source, instead of H_2 or CH_4.

In our previous work[5] on the plasma reduction of CO_2 with H_2O, we found some organic compounds as products, such as oxalic acid and formaldehyde as well as hydrogen peroxide; these were separated and identified by liquid chromatography. In this study, steam chromatography and gas chromatography-mass spectrometry (GC-MS) were used for the separation and identification of the plasma products. The organic compound we focused on this time was methanol. In the steam chromatography, we used a flame ionization detector. It is very sensitive to detect methanol[6] and many kinds of water-soluble and water-insoluble organic compounds[7] from a very dilute aqueous solution.

Experimental

The plasma reduction of CO_2 with H_2O was carried out by a tubular-type quartz reactor, basically the same as the one used in our previous report,[5] and was carried out as described here. Deionized and degassed H_2O and CO_2 (99.9% purity) were used as starting materials. During the plasma reaction, the flow rate of CO_2 was controlled by a mass flow controller in the range of 10 to 40 $\mathrm{cm^3(STP)\,min^{-1}}$, while that of H_2O was fixed at 40 $\mathrm{cm^3(STP)\,min^{-1}}$ by a metering valve. For the prevention of the condensation of water, the stainless tubing between the water container and the reactor was heated to about 40 °C. The system pressure was controlled and maintained during the reaction at either 240 or 400 Pa by adjusting the main valve between the cold trap and vacuum pump. The input power of microwave plasma was varied from 300 to 680 W. Each experimental run of the plasma reaction was done for 60 min. The plasma products were collected in a dry ice–methanol cold trap as an aqueous solution, which was then subjected to the analyses by steam chromatography and GC-MS for the separation and identification of methanol and possible organic compounds formed in the plasma reaction.

For steam chromatography, an Ohkura Riken SSC-1 with a Porapak® R column (3 m) was used, while a Shimadzu QP-2000 with a Poraplot® Q wide-bore capillary column (25 m) was used for GC-MS.

Results and Discussion

Identification and Confirmation of the Formation of Methanol. Figure 1 shows steam chromatograms of methanol (0.01% aq) and plasma products. There is a sharp peak at the retention time of 5.2 min for methanol. For plasma products, a small but clear peak was found at the same retention time as for methanol. From these chromatograms, plasma products are assumed to contain methanol. Some other simple water-soluble organic compounds such as formaldehyde and acetic acid, which could be detected by the steam chromatography, were not found in plasma products.

In order to confirm the presence of methanol in the plasma products, we used GC-MS and compared the spectra of plasma products and methanol. Figure 2 is a mass spectrum and fragmentation pattern of methanol. However, since the concentration of the intended compound in the plasma product was very low, a clear mass spectrum was not obtained. Therefore, we enlarged some peaks of the mass spectrum at characteristic mass numbers for methanol. We chose the mass numbers of 32, 31, 29, and 15; their intensity ratio in the spectrum of methanol was approximately 3/4 : 1 : 2/3 : 1/4. Figure 3 shows those four peaks of the plasma products in GC-MS spectrum enlarged with the mag-

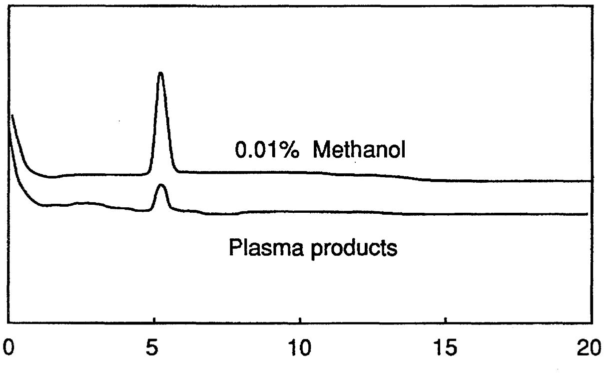

Fig. 1. Steam chromatograms of 0.01% methanol and plasma products (0.26 GJ kg^{-1}, 240 Pa).

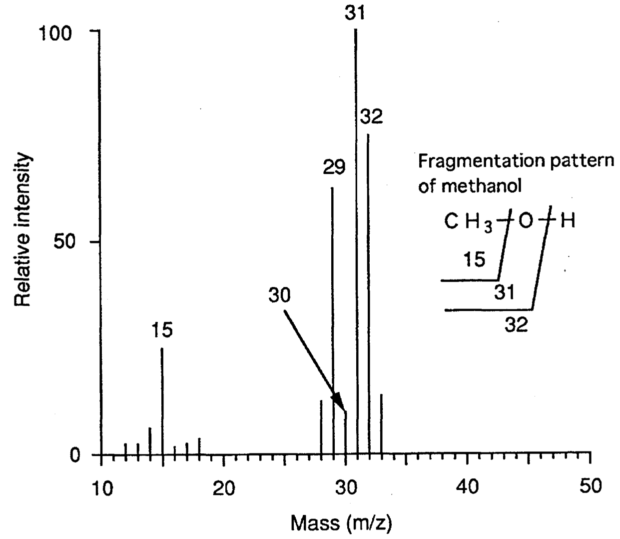

Fig. 2. Mass spectrum and fragmentation pattern of methanol.

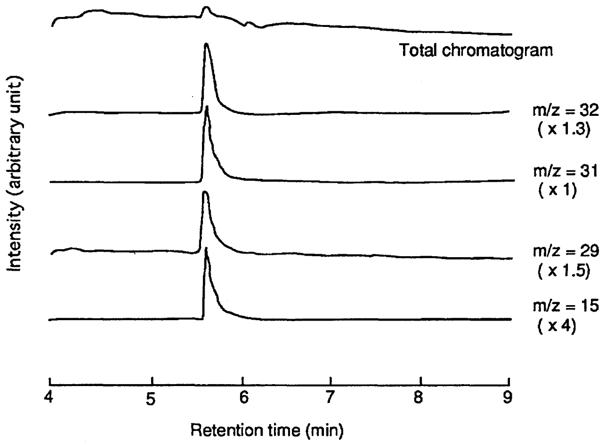

Fig. 3. Total and enlarged mass chromatograms of some characteristic fragment peaks of the plasma product eluted at 5.2 min in steam chromatography. The numbers in parenthesis indicate enlargement scale for respective mass peak.

nification of 4/3 : 1 : 3/2 : 4. The peak heights are almost identical; therefore, the mass-spectral pattern of the plasma products corresponded to that of methanol, and the compound eluted at the retention time of 5.2 min in the steam chromatography can be confirmed to be methanol.

Deposition of Solid Material and Its Effect on the Methanol Formation. In the early stage of this study on the plasma reduction of CO_2 with H_2O, we could not find the reproducibility in methanol yield or dependence of plasma energy density on methanol yield. During the reaction, however, we have realized that a transparent solid film had formed on the inside of the quartz reactor at the downstream and the outside of the plasma zone. And naturally, the deposited film became thicker by continued experiments without cleaning of the reactor. We concluded that the failure to obtain the reproducibility or the plasma-energy dependence was the result of the difference in reactor cleanness, which had often been pointed out by many researchers.[8] Therefore, we used H_2O plasma after each run to clean the reactor. The H_2O-plasma cleaning was done as the same manner as the ordinary experimental run. The reactor became clean enough after 30-min duration of H_2O plasma.

The most striking phenomenon we found in this H_2O-plasma cleaning was that methanol was obtained in the cold trap after the cleaning. This result means that this process can be a main pathway to produce methanol which may be formed through the reaction of H_2O-plasma and the deposited film. The deposited material should be a kind of organic plasma polymer.

Plasma-Energy Dependence on Methanol Yield. In order to reveal the most adequate plasma condition for the methanol formation, we investigated the relation between methanol yield and plasma energy density at two different system pressures. Figure 4 shows the relation between the methanol yield, Y_s, calculated from steam chromatogram and plasma energy density (W/FM) in the reaction between CO_2 and H_2O at the system pressure of 240 and 400 Pa. W/FM is a composite parameter which indicates energy input against a unit mass of a gas introduced to the system, where W and FM represent the discharge power and mass flow (F, volume flow rate; M, molecular weight of a gas), respectively. In this figure, maxima can be seen at the W/FM of about 0.26 GJ kg^{-1} for each system pressure and the W/FM region in which methanol can be obtained is relatively narrow. However, the methanol yield at 400 Pa is obviously higher than that at 240 Pa. A higher system pressure at the same flow rate means longer residence time for each molecule and higher molecule density, which can increase the collision frequency between activated species formed in the plasma. In this system for the methanol formation, pressure at 400 Pa was found to be preferable compared to 240 Pa. The reason for the existence of the optimum energy density for the formation of methanol is that at a low energy density, the plasma energy was not high enough to form methanol, while at a high energy density, decomposition of methanol might occur.

The results in Fig. 4 were obtained from the ordinary synthetic reaction between CO_2 and H_2O. As we stated earlier, methanol can be produced in H_2O-plasma-cleaning process. Figure 5 is similar to Fig. 4 but shows the methanol

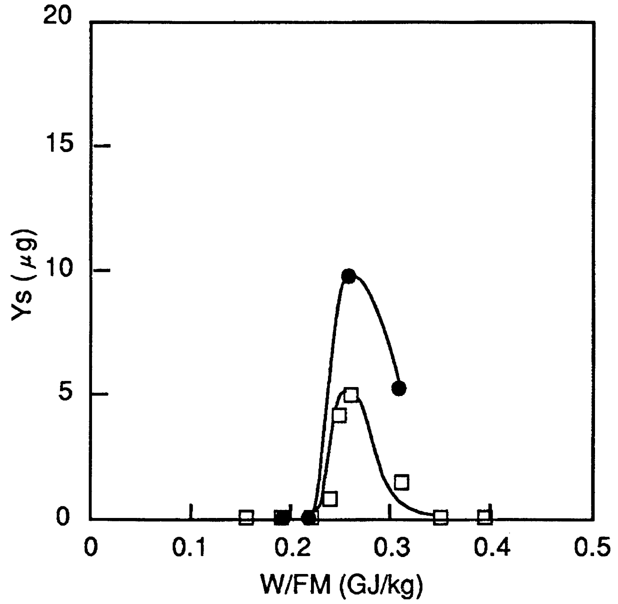

Fig. 4. Relationship between methanol yield in the ordinary plasma synthetic reaction, Y_S, and plasma energy density. □, 240 Pa; ●, 400 Pa.

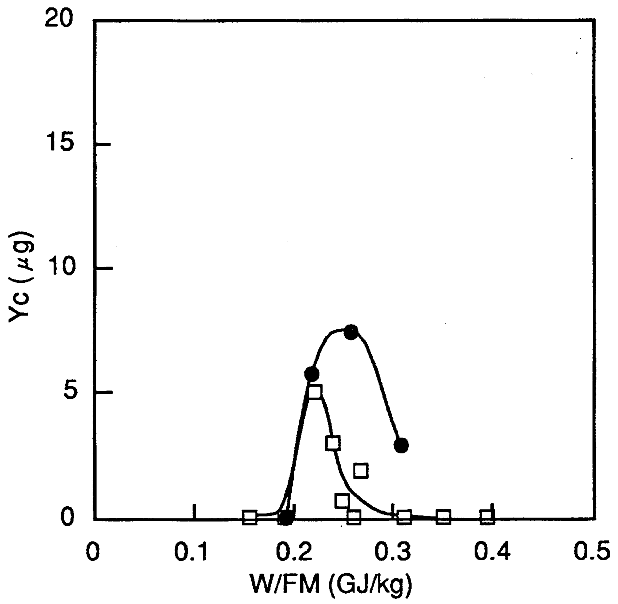

Fig. 5. Relationship between methanol yield in the H_2O-plasma-cleaning process, Y_C, and plasma energy density. □, 240 Pa; ●, 400 Pa.

yield, Y_c, after H_2O-plasma cleaning for 1 h, which followed just after the ordinary synthetic reaction. The results were very similar to those in Fig. 4: There is a maximum at *W/FM* of about 0.26 GJ kg^{-1} and the methanol yield at 400 Pa was higher. Since H_2O does not contain a carbon source and 1-h cleaning can remove the deposited film completely, the methanol yield should be dependent on the amount of the deposited film. From the results above, it can be said that the *W/FM* of about 0.26 GJ kg^{-1} and higher pressure (400 Pa), which make the residence time longer, may be favorable for at least two of the three reactions in this successive process: formation of methanol from CO_2 and H_2O; formation of material deposited on the reactor in the reaction between CO_2 and H_2O; and formation of methanol by H_2O plasma in the presence of the deposited material.

Figure 6 shows the total yield, Y_{S+C}, and the conversion rate of methanol at the two pressure systems that combined the yields of the ordinary synthetic process and the H_2O-plasma-cleaning process. The maximum of the methanol yield (and the conversion rate) can be seen at *W/FM* of 0.26 GJ kg^{-1}, as was seen in Figs. 4 and 5, but the difference in the yield between the two systems was more pronounced.

In the previous report, oxalic acid and H_2O_2 were found in plasma products by the analysis of reversed-phase liquid chromatography using UV and conductivity detectors. In the analysis of the plasma products obtained this time by chromatography, exactly the same chromatogram pattern as the previous one was obtained. This result indicates that the methanol is formed together with oxalic acid and H_2O_2, and they are thought to be the main products in this reaction system. Among three different plasma energy densities, 0.37, 0.29, and 0.16 GJ kg^{-1} in the previous report, oxalic acid and H_2O_2 were found most at 0.29 GJ kg^{-1}; methanol was found most at 0.26 GJ kg^{-1} in this experiment.

Figure 7 shows the FT-IR spectrum of the polymer film deposited on a quartz plate. The absorption band at around 2960 cm^{-1} (C–H stretching) associated with a sharp peak at 1380 cm^{-1} (C–H bending), is thought to be assigned to methyl group bonded to carbonyl group, indicating the presence of a methyl group in the deposited polymer.

As far as the mechanism of methanol formation is concerned, there seem to be two possible pathways: One is direct formation from CO_2 and H_2O by the plasma reaction and the other is reformation from deposited polymeric material during the plasma reaction with H_2O.

Effect of Cold-Trap Temperature. The plasma reduction process was also carried out using a cold trap with

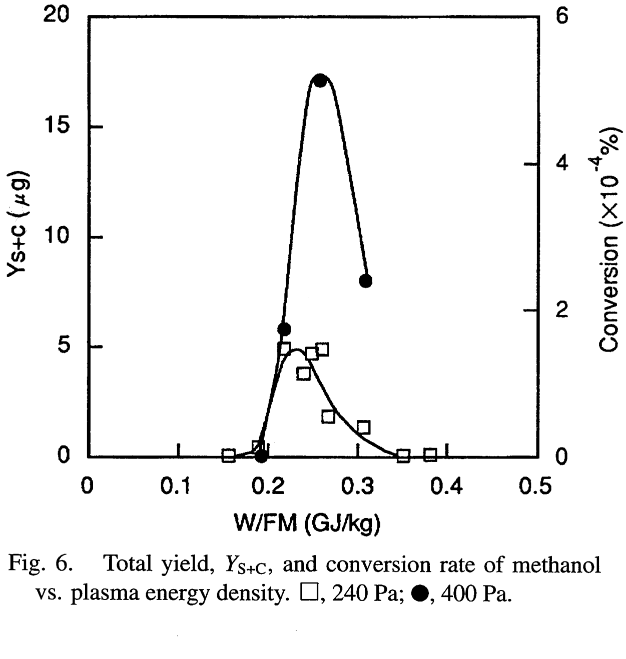

Fig. 6. Total yield, Y_{S+C}, and conversion rate of methanol vs. plasma energy density. □, 240 Pa; ●, 400 Pa.

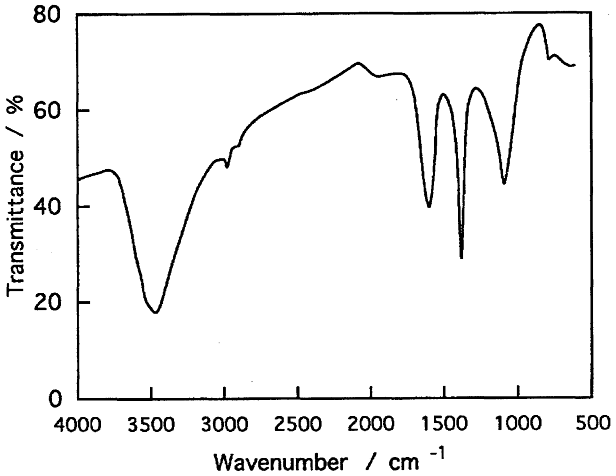

Fig. 7. FT-IR spectrum of the polymer film deposited on a quartz plate placed inside the plasma reactor during the ordinary plasma synthetic reaction.

liquid nitrogen as a refrigerant. In the reaction between CO_2 and H_2O, a solid material in blue color was found in the cold trap with liquid nitrogen, which indicated that ozone was formed during the process and was collected in the trap. In the analysis by steam chromatography, methanol was found in this product, but the peak gradually decreased with time and disappeared completely within 24 h.

In order to confirm the ozone reactivity against methanol, methanol solution was made to contact with ozone and the concentration was measured with the passage of time. The experiment was carried out using a Tesla coil as an ozone generator and the ozone containing air was bubbled into 20 mL of $1\times10^{-3}\%$ methanol solution for 10 min at 25 °C. Since the number of ozone molecules formed by Tesla coil for 10 min would be so few that fewer reactions between them might be expected compared to the microwave reactor system. The result shown in Fig. 8 indicates that the methanol is decomposed by ozone. Therefore, it can be said that the setting of the trap temperature at which ozone could not be trapped is important for the removal of ozone from this system, which may result in high recovery of methanol. Although the yield of ozone has not been measured, the formation of ozone seems to be an important factor. The formation of ozone reduces the total number of oxidizing agents (O_2, O_3) as well as the number of active oxygen (O^*), which results in the reduction of the collision frequency between the oxidizer and methanol. Therefore, if the yield of ozone is raised in the methanol-forming process and is removed from the system easily, the yield of methanol also could be raised.

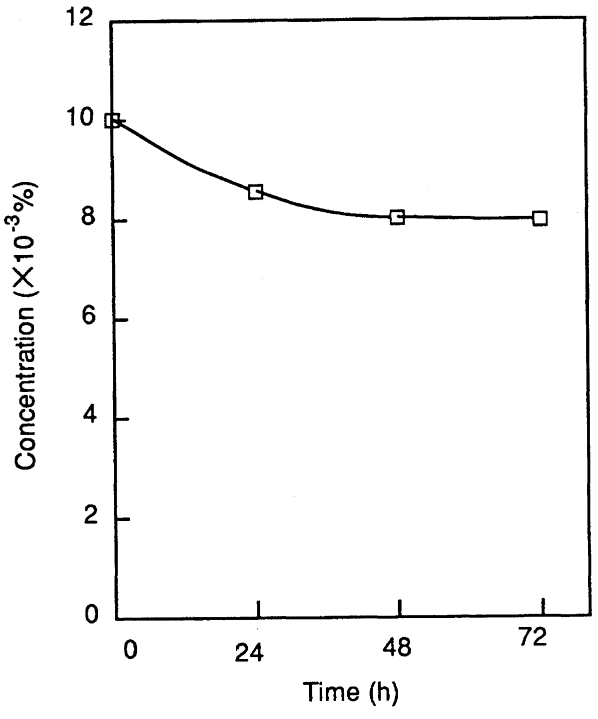

Fig. 8. Concentration change of methanol after contact with ozone for 10 min.

Conclusion. Methanol was obtained by the reaction between CO_2 and H_2O in a microwave plasma. During the process, a transparent solid film was formed on the inner wall of the quartz reactor down stream from the plasma zone. Since methanol was found when the film was exposed to the down stream of the H_2O plasma, two pathways were considered to be existed for the formation of methanol: One is direct formation from CO_2 and H_2O by the plasma reaction and the other is reformation from deposited polymeric material during the plasma reaction with H_2O. By increasing the system pressure during synthesis process from 240 to 400 Pa, the yield of methanol increased about 3.5 times in both the synthesis process and cleaning process. This revealed that the system pressure was one of the most important parameters to synthesize methanol by this method.

This work was supported by the Japan Private School Promotion Foundation and the Environmental Science Research Institute of Kinki University.

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