Photoreduction of Carbon Dioxide with Methane over ZrO_2

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Over zirconium oxide, carbon dioxide is reduced to carbon monoxide selectively by methane at room temperature under photoirradiation. From temperature programmed desorption experiments, this reaction is expected to proceed *via* stable surface intermediates. The carbon atom of evolved CO derives from carbon dioxide only.

Carbon dioxide and methane are both known to cause harmful greenhouse effect, and what is worse, they are fairly inert. So the way to convert them into more reactive compounds is requested. From this point of view, the catalytic reforming of CO_2 and CH_4 to produce CO and H_2 (CO_2 reforming of methane) is a desirable reaction and has been investigated so far.[1-4] However, this thermal reaction is not essentially an ideal reaction because it is an endothermic reaction and requires a great amount of heat supply.

In this paper, we report the photoreduction of carbon dioxide by methane over zirconium oxide without heat supply. Zirconium oxide has been reported to be effective as a catalyst support for CO_2 reforming of methane; however, the zirconia support itself was reported to have no catalytic activity for this reaction.[5] On the other hand, zirconium oxide absorbs lights with the wavelength shorter than 250 nm, and has been reported to have excellent catalytic activity for photodecomposition of water and photoreduction of aqueous carbonate.[6,7] We also found that zirconium oxide without metal loading catalyzes reduction of gaseous carbon dioxide with hydrogen under photoirradiation.[8] It can be rephrased that zirconium oxide itself has an ability to activate carbon dioxide by photoirradiation. Besides, the energy of illuminated light permits reaction in the absence of additional heating and pressuring, which is a superior point to be emphasized in photoreactions. Therefore, zirconium oxide is expected to enhance the reduction of CO_2 with methane under photoirradiation without heat input.

Zirconium oxide used in this study was prepared by precipitation using zirconium oxychloride as a precursor. To be hydrolyzed to zirconium hydroxide, an aqueous solution of zirconium oxychloride was slowly mixed with 25 wt% NH_3 (aq) at room temperature. The precipitate obtained was washed with distilled water repeatedly until the filtrate was negative towards $AgNO_3$, dried at 373 K overnight, grounded to powder, and calcined at 773 K for 5 h in a dry air stream. The XRD pattern indicated that the resulting powder was a mixture of zirconium oxide in monoclinic and tetragonal phases.

The photoreaction was carried out in a closed static system connected to a vacuum line. A 500 W ultrahigh-pressure mercury lamp (Ushio Denki USH-500) was used as a UV light source. Zirconium oxide weighed 0.3 g was placed on the flat bottom of a reactor made of quartz. Prior to the photoreaction, zirconium oxide was heated for 30 min in the air and evacuated for 30 min at 673 K, followed by treatment with 8 kPa oxygen for 75 min and evacuation for 30 min at the same temperature. A mixture of CO_2 (150 μmol) and CH_4 (50 μmol) was introduced to the reactor, which made the total pressure in the reactor *ca.* 25 kPa. The UV light was illuminated from the bottom of the reactor. After a given time of photoreaction, the gaseous products were analyzed, and after 2 min evacuation at room temperature, the sample was heated at 673 K for 20 min and the desorbed gases were also analyzed. The zirconium oxide was pretreated again in the manner described above and the next run was carried out. The analysis of products was accomplished with an on-line TCD gas chromatograph (Shimadzu GC-8A) using argon as a carrier gas, which could detect H_2, CH_4, and CO. In temperature programmed desorption (TPD) experiments, 0.1 g of zirconium oxide was used and the desorbed gases were detected by a quadrupole-type mass spectrometer (ULVAC Massmate-100).

Firstly, we examined the reactivity of zirconium oxide for the reaction of CO_2 reduction with methane. After 5 h of photoirradiation, 0.7 μmol of CO and very small amount (0.03 μmol) of H_2 were detected in the gas phase. Any other products were not detected by an FID gas chromatograph which could detect gaseous hydrocarbons and oxygenates, as well as by the on-line TCD gas chromatograph. Figure 1 shows the time dependence of CO formation under photoirradiation (thick line in Figure 1). The amount of CO formation increases with the irradiation time, although the rate of CO formation is slightly slowed down. Without photoirradiation, even trace of CO was not detected, although CO_2 adsorption on zirconium oxide does not need photo-excitation. When the short wavelength region ($\lambda < 290$ nm) of irradiated light was cut off by a glass filter, merely small amount of CO evolution (0.1 μmol) was observed. In case that either of CO_2 or CH_4 was admitted to the reactor and the other was not, no CO was detected even after UV irradiation.

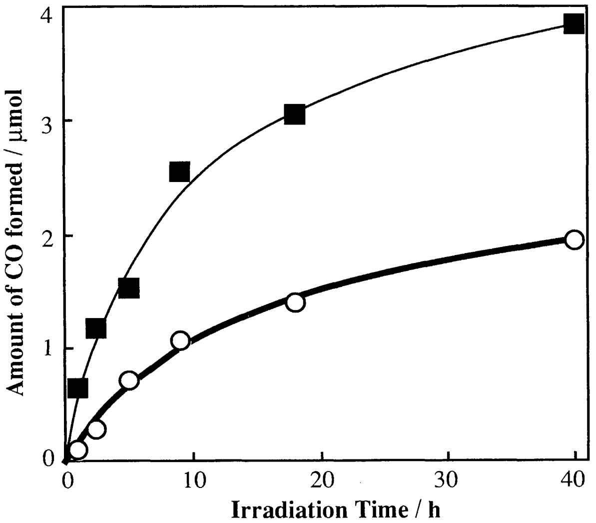

Figure 1. Time dependence of CO formation over ZrO_2 by photoirradiation (thick line) and by heat treatment after a given time of photoreaction (thin line); initial amount of CO_2 and CH_4 were 150 μmol and 50 μmol, respectively.

From these results, we concluded that this reaction was a photoreaction, not a thermal redox reaction between ZrO_2 and CO_2, or between CH_4 and ZrO_2. In other words, zirconium oxide has an ability to activate the C-H bond of methane as well as carbon dioxide under photoirradiation.

When the sample was heated in vacuo after photoreaction of a given time, the evolution of CO, H_2 and CH_4 was observed. For example, after 5 h of photoirradiation, 0.7 µmol of CO was detected (as mentioned above), and when the sample was heated at 673 K for 20 min after 2 min evacuation, 1.5 µmol of CO, 0.2 µmol of H_2 and 0.2 µmol of CH_4 were evolved. No other gases were detected also in this case. As shown in the thin line in Figure 1, the amount of CO formation by the heat treatment was also increased with the irradiation time, which indicates that some material decomposed to yield CO by heat arises on the surface of zirconium oxide by photoirradiation. To ascertain whether this CO source was photoadsorbed CO or surface intermediate, the following two TPD profiles were compared; one was the profile of ZrO_2 adsorbing CO under photoirradiation and the other was that of ZrO_2 submitted to CO_2 photoreduction with methane. To make the analysis clear, ^{13}C labelled CO or CO_2 was employed, while the carbon atom of methane was not labelled. Figure 2 shows the ^{13}CO-TPD profiles desorbed from the above-mentioned two samples. A single peak was observed for both samples in the range 500 - 700 K, but the temperatures of the maximum were different. Photoadsorbed CO was desorbed at *ca.* 630 K, while the CO desorption maximum from the surface of zirconium oxide after photoreaction was observed at *ca.* 580 K. This result indicates that the surface species differ for these two samples, and that surface intermediate exists on zirconium oxide under photoirradiation.

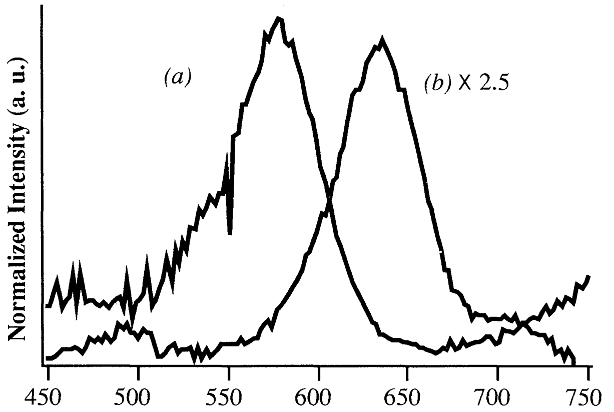

Figure 2. TPD profiles for (a) CO desorbed from the surface of ZrO_2 used for photoreaction and (b) CO simply photoadsorbed on ZrO_2; the intensity of the profile (b) is multiplied by 2.5.

Another TPD experiment, where $^{12}CO_2$ and $^{13}CH_4$ were used as substrates, was also carried out to confirm the carbon source of evolved CO. Surprisingly, no signal was observed at m/z = 29. It shows that all carbon atoms of evolved CO came from CO_2, and methane was not oxidized to CO at all. Considering this result, methane consumed to reduce CO_2 is expected to stay on the surface as carbonaceous residues, because no C_n hydrocarbons or oxygenates except for CH_4 and CO were detected in the gas phase after photoreaction, as mentioned previously.

Zirconium oxide used for photoreaction was heated at 673 K under O_2 atmosphere after evacuation at 773 K in order to oxidize any carbonaceous residues expected to exist on the surface. When this experiment was put into practice using $^{13}CO_2$ and $^{12}CH_4$ as substrates, only $^{12}CO_2$ was detected by the mass spectrometer. From this, it can be concluded that at least part of methane used for the reduction of CO_2 under illumination remains as carbonaceous residues on the surface of zirconium oxide. It is also supported by the fact that the white zirconium oxide turned brown by photoreaction, and that its color was restored to the original after this O_2 treatment.

Although carbon residues are produced during reaction, it is very interesting that CO_2 was reduced by rather inert methane without heat supply. The identification of surface intermediate and carbon residues is now under investigation, which will greatly help us to clarify the reaction mechanism.

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