

Photoreduction of carbon dioxide with hydrogen over ZrO_2

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Among many transition-metal oxides, zirconium oxide is found to be active for photocatalytic reduction of carbon dioxide to carbon monoxide with hydrogen in the gas phase.

From the viewpoint of environmental problems, catalytic reduction of carbon dioxide to more valuable compounds has been investigated extensively.^{1–3} However, this reaction often requires severe conditions of high pressure and/or high temperature. In contrast, by photoirradiation, photocatalytic reduction of carbon dioxide with hydrogen may occur even under mild conditions.

As a photocatalyst for such types of reactions, noble metal/titanium oxide systems are the most well known and have been extensively investigated so far.^{4–6} Zirconium oxide has rarely been reported to be active; however, Sayama *et al.* recently reported that zirconium oxide showed excellent photocatalytic activity for the decomposition of liquid water and photoreduction of aqueous carbonate.^{7,8} They also reported that metal loading inactivated zirconium oxide, in contrast to the case of titanium oxide. In the present study, we report that zirconium oxide without metal loading is active for photocatalytic reduction of gaseous carbon dioxide with hydrogen under mild conditions of low pressure and room temperature. The wide band-gap of ZrO_2 (5.0 eV) permits the photoreduction of carbon dioxide with hydrogen.

Zirconium oxide used in this study was prepared from an aqueous solution of zirconium oxychloride by precipitation with 25 mass% $\text{NH}_3(\text{aq})$. The precipitate obtained was washed with distilled water followed by filtration until the filtrate was negative towards AgNO_3 . The sample was 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 zirconium oxide in a mixture of monoclinic and tetragonal phases. Other metal oxides were commercially available ones and they were calcined at 773 K for 5 h prior to use. Before reactions, the oxides were heated at 673 K for 30 min in the air and evacuated for 30 min at the same temperature, followed by treatment with 8 kPa O_2 for 75 min and evacuation for 30 min at 673 K.

The photocatalytic reaction 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 the light source. A metal oxide sample (0.3 g) was spread on the flat bottom of a quartz reactor and subjected to illumination from the bottom. A mixture of CO_2 (150 μmol) and H_2 (50 μmol) was admitted to the reactor, and the total pressure in the reactor was *ca.* 25 kPa. After the irradiation, the gases were analysed by an on-line TCD gas chromatograph (Shimadzu GC-8A) using argon as a carrier gas, which can detect H_2 , CH_4 and CO . Temperature programmed desorption (TPD) experiments were carried out for zirconium oxide, and the desorbed gases were detected by a quadrupole-type mass spectrometer (ULVAC Massmate-100). To avoid the interference of nitrogen at the signal $m/z = 28$, ^{13}C labelled CO or CO_2 was used.

Activity for photoreduction of CO_2 was investigated using TiO_2 , ZrO_2 , V_2O_5 , Nb_2O_5 , Ta_2O_5 , WO_3 and ZnO . Among these, only ZrO_2 was found to be active, and other metal oxides showed no activity for this reaction at all. With ZrO_2 , 1.0 μmol

of CO was detected after 6 h photoirradiation, and no other reduced product was detected by an FID gas chromatograph (which can detect gaseous hydrocarbons and oxygenates) and a mass spectrometer, as well as the on-line TCD gas chromatograph. ZrO_2 is stable under photoirradiation and no appreciable difference was found in Zr L_{III} edge XANES spectra of ZrO_2 before and after photoreaction. When the reaction was carried out in the dark, no CO was detected, although CO_2 is known to be adsorbed on the surface of ZrO_2 . This indicates that photoirradiation is essential for this reaction. When the short wavelength region of the irradiated light was cut off by a series of filters which permits light with wavelength $\lambda > 370$, 330, 310 and 290 nm, the amount of evolved CO after 6 h photoirradiation changed from 1.0 μmol to 0, 0, 0.1 and 0.4 μmol , respectively. From these results, it can be concluded that the light with wavelength < 300 nm was required to enable this reaction to proceed.

Without introduction of CO_2 no trace of CO was detected after UV irradiation. When $^{13}\text{CO}_2$ was used instead of $^{12}\text{CO}_2$, only ^{13}CO was detected. These results show that CO was produced from the CO_2 admitted to the system.

Fig. 1 shows the time dependence of the amount of CO formed and H_2 consumed. The rate of CO formation mildly decreased from 8 to *ca.* 40 h irradiation. On the other hand, the consumption rate of H_2 was very fast at the beginning, and then slowed. The amount of consumed H_2 was larger than the amount of evolved CO at all times. This suggests that H_2 may be adsorbed onto the catalyst surface in a dissociated form⁹ or incorporated into other compounds containing carbon atom(s). We then tried to decompose any adsorbed species by heating the catalyst sample after photoirradiation. More CO evolution was observed, while the amount of desorbed H_2 was small. After 6 h of photoirradiation, 1.0 μmol of CO was detected (as mentioned above), and when the catalyst sample was heated at 673 K for 20 min after 2 min evacuation, 3.3 μmol of CO was evolved. When the photoirradiation time was extended to 40.5 h, 3.2 μmol of CO was formed, and by heating the catalyst, 5.8 μmol of CO was evolved. This observation shows that

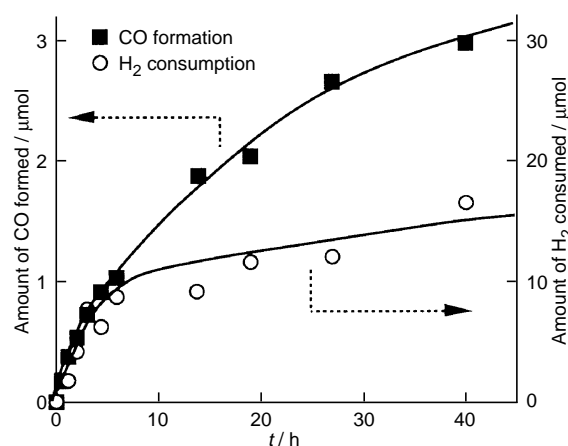


Fig. 1 Time dependence of CO formation and H_2 consumption over ZrO_2 under irradiation; initial amounts of CO_2 and H_2 were 150 μmol and 50 μmol , respectively

photoirradiation of the catalyst surface produces some material decomposed into CO by heat. The most intriguing question at this stage is whether this CO source is photoadsorbed CO or arising from surface intermediates.

To elucidate this, TPD experiments were carried out. Samples of CO adsorbed ZrO_2 under photoirradiation and ZrO_2 used as the photocatalyst for CO_2 reduction were investigated. The CO TPD profiles are shown in Fig. 2. A single peak was observed for both samples in the range from 500–700 K, but the

temperatures of the maxima are different. Photoadsorbed CO was desorbed at *ca.* 630 K, while the CO desorption maximum from the surface of the catalyst after photoreaction was observed at *ca.* 610 K. This result firmly suggests that the surface species differ for the two samples. In other words, surface intermediates may exist on the catalyst surface under irradiation, and the reaction is expected to proceed *via* intermediates to yield CO. Future studies will clarify the reaction mechanism through detection and identification of these intermediates.

Footnote

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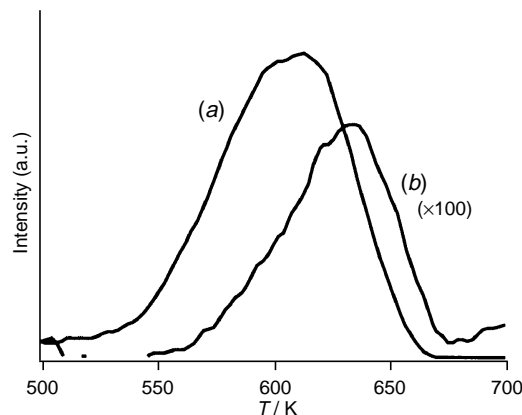


Fig. 2 TPD profiles for (a) CO desorbed from the catalyst surface after photoreaction and (b) CO simply photoadsorbed on ZrO_2 ; the intensity of profile (b) is multiplied by 100