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Reduction of CO_2 with H_2O on $TiO_2(100)$ and $TiO_2(110)$ Single Crystals under UV-irradiation

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The reduction of CO_2 with H_2O was investigated on the single crystals of $TiO_2(100)$ and $TiO_2(110)$; the former $TiO_2(100)$ exhibiting a higher efficiency in the formation of CH_4 and CH_3OH than $TiO_2(110)$. Measurements of the intermediate species formed on the $TiO_2(100)$ single crystal were carried out using a high resolution electron energy loss spectroscopy (HREELS).

In the field of heterogeneous photocatalysis the photosynthetic reduction of CO_2 with H_2O on semiconducting materials is of special interest. Somorjai et al.,1) Fujishima et al.,2) and Halmann et al.3) have found that the reduction of CO_2 with H_2O proceeds on various types of semiconductors involving TiO_2. Furthermore, Anpo et al.4,5) have found that UV-irradiation of highly dispersed titanium oxide anchored onto transparent Vycol glass or extremely small TiO_2 particles in the presence of CO_2 and H_2O leads to the formation of CO, CH_4, and CH_3OH. Although these studies suggest that the efficiencies and selectivities in the photocatalytic reduction of CO_2 strongly depend on the physical and chemical properties of the catalysts, details of the reaction have not yet been clarified. With a well-defined catalyst surface such as a single crystal, detailed information on the reaction mechanism can be obtained on a molecular scale.6) In the present study, the photocatalytic reduction of CO_2 with H_2O on $TiO_2(100)$ and $TiO_2(110)$ surfaces and the detection of the reaction intermediates formed on the surfaces were investigated using high resolution electron energy loss spectroscopy (HREELS) because of its high sensitivity.

The wafers (10x10x1 mm) of the rutile TiO_2 single crystals with (100) and (110) surfaces were used. Photocatalytic reactions were carried out with a wafer (430 mg) in a quartz cell with a flat bottom (60 ml) connected to a conventional vacuum system (10^{-6} Torr range).4,5) The single crystal catalysts were degassed at 725 K for 4 h and heated in O_2 at 725 K for 5 h. Prior to the photoreaction and HREELS measurements, the catalysts were degassed at 725 K for 4 h until 10^{-6} Torr and 10^{-10} Torr in vacuum, respectively, while CO_2 and gaseous H_2O were then introduced at 295 K. UV irradiation of the catalysts in the presence of CO_2 and gaseous H_2O was carried out using a 75-W high-pressure Hg lamp ($\lambda > 290$ nm) at 275 K. Products were analyzed by gas chromatography. HREELS measurements were conducted in a stainless ultrahigh vacuum apparatus (UHV: 10^{-10} Torr range) equipped with an analyzer for Auger electron spectroscopy

(AES).7) Cleaning of the $TiO_2(100)$ surface was performed by repeating the Ar^+ bombardment several times at room temperature, annealing and oxidation in O_2 at 800 K.

UV-irradiation of the $TiO_2(100)$ surface in the presence of a mixture of CO_2 and H_2O led to the evolution of CH_4 and CH_3OH in the gas phase at 275 K, whereas only CH_3OH was detected with the $TiO_2(110)$ single crystal catalyst. As shown in Fig. 1, the yields of these photo-formed CH_4 and CH_3OH increased linearly with the UV-irradiation time, at least for several hours. Reaction products could not be detected in the dark for both $TiO_2(100)$ and $TiO_2(110)$ catalysts. These results suggest that the photoinduced reduction of CO_2 in the presence of H_2O to produce CH_4 and CH_3OH takes place photocatalytically on the surfaces of TiO_2 single crystals.

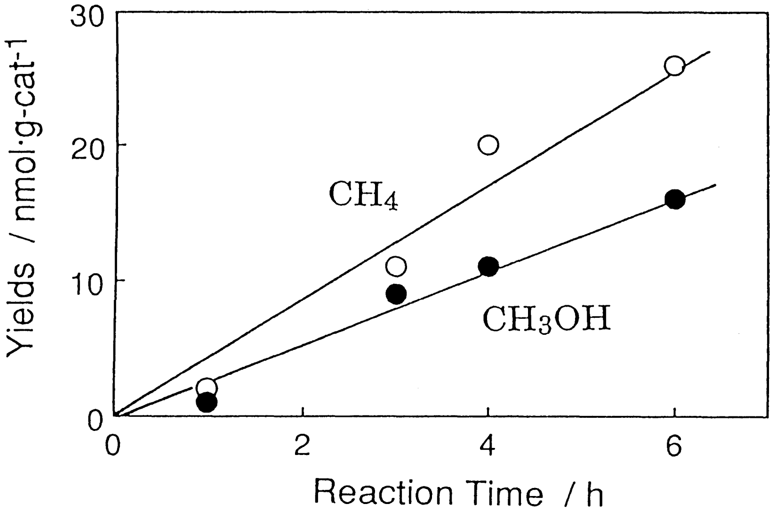

Fig. 1. Time profile of the photocatalytic reduction of CO_2 (124 μmol·g^{-1}) with H_2O (868 μmol·g^{-1}) to produce CH_4 and CH_3OH on $TiO_2(100)$ at 275 K.

The yields of the formation of CH_4 and CH_3OH on the two types of TiO_2 single crystals are shown in Table 1. Of special interest is the comparison of the photocatalytic reactivities of these single crystals with that of the widely used TiO_2 powders. In comparisons with previous results obtained on extremely small TiO_2 particles,5) the photocatalytic activity of the $TiO_2(100)$ single crystal (12 μmol·h^{-1}m^{-2}) which was normalized by a unit surface area was much higher than that of small TiO_2 particles (3.5 nmol·h^{-1}m^{-2}). The high efficiency of the single crystal wafer as a photocatalyst may be attributed to the high efficiency of UV-absorption.

From the results in Table 1, it is clear that the photocatalytic activity and selectivity were found to strongly depend on the type of TiO_2 single crystal surface. The yield of CH_3OH formation was much higher on $TiO_2(100)$ than on $TiO_2(110)$, while the formation of CH_4 was only observed on $TiO_2(100)$ and not on $TiO_2(110)$. It is likely that the photo-formed electrons localized on the surface sites of the excited TiO_2 play a significant role in the photoreduction of CO_2 molecules into intermediate carbon species on the TiO_2 surfaces.4) The surface Ti atoms may act as an electron moiety on the surfaces, i. e., a reductive site. According to the surface geometric models for $TiO_2(100)$ and $TiO_2(110)$, the atomic ratio (Ti/O) of top-surface Ti and O atoms which have geometric spaces large enough to have direct contact with CO_2 and H_2O molecules is higher on $TiO_2(100)$ than $TiO_2(110)$. In the excited state, the surface with a higher Ti/O surface ratio, i. e.

TiO_2(100), exhibits a more reductive property than TiO_2(110). Such a reductive surface allows a more facile reduction of CO_2 molecules especially for the formation of CH_4 which was found to be a vital step in the photoreduction of CO_2 with H_2O on the TiO_2 catalyst.

Table 1. Yields of the Formation of CH_4 and CH_3OH in the Photocatalytic Reduction of CO_2 (124 $\mu mol \cdot g^{-1}$) with H_2O (372 $\mu mol \cdot g^{-1}$) at 275 K

Single Crystal	Yields ($nmol \cdot h^{-1} g\text{-}cat^{-1}$)	
	CH_4	CH_3OH
TiO_2 (100)	3.5	2.4
TiO_2 (110)	0	0.8

Furthermore, the photocatalytic activities of TiO_2(100) and TiO_2(110) single crystal surfaces for the isomerization of cis-2-butene were also investigated and in these reactions only trans-2-butene was produced on both single crystals while the photocatalytic activity of TiO_2(110) was higher than that of TiO_2(100). This is in contrast to the above results showing that TiO_2(100) exhibited higher photocatalytic activity for the reduction of CO_2 than TiO_2(110). Previous results indicating that butene was adsorbed and activated on the lattice oxygen sites, which act as hole centers trapping a photo-formed hole under UV-irradiation of TiO_2,8) as well as the higher photocatalytic activity of TiO_2(110) for the isomerization of butene suggest that TiO_2(110) is more suitable for the formation of oxidative surface sites under UV-irradiation than TiO_2(100). These results suggest that under UV-irradiation the surface of TiO_2(100) may form many reductive sites which act as the active sites for the reduction of CO_2 while the surface of TiO_2(110) exhibits oxidative properties which are related to the activation of butene.

To clarify the intermediate species formed in the photocatalytic reduction of CO_2 with H_2O, the surface species on TiO_2(100) which exhibits a high efficiency in the photoreduction of CO_2 with H_2O have been investigated using HREELS because of its extremely high sensitivity. The clean TiO_2(100) surface prepared in UHV exhibited an AES peak ratio of O(KLL)/Ti(LMM) as 1.5~2.0 which was the same as the value observed previously with clean TiO_2(100).6) Figure 2 shows the typical HREELS spectra of a clean TiO_2(100) single crystal before (a) and after UV-irradiation for 5 min in the presence of CO_2 (1 Torr) and gaseous H_2O (3 Torr) (b), respectively. The large peak centered at 680 cm^{-1} is due to excitation of the surface optical phonon of the TiO_2 lattice. With the clean surface (a), no HREELS peak was observed except for peaks due to the phonon of the TiO_2 lattice and its weak harmonic oscillation. However, with the surface after UV-irradiation (b), two loss peaks at 2920 and 3630 cm^{-1} were detected in addition to the phonon peak. The peak at 2920 cm^{-1} can be assigned to the C-H stretching vibration of the CH_x species7) and the peak at 3630 cm^{-1} may correspond to the O-H stretch of surface hydroxyl groups.9) The phonon peaks become clear after the reaction as can be seen by comparing Fig. 2(b) with (a), where the ratio of O/Ti increased by the reoxidation of TiO_2(100) during the photoreaction. On the other hand, without UV-irradiation only a weak loss peak assigned to the OH stretching vibration was observed without the detection of any other peaks by the exposing reactant gasses. The formation of such surface hydroxyls can result from the slight surface defects remaining on $TiO_2(100)$ after cleaning. In fact, an intense peak for the hydroxyl species was observed when $TiO_2(100)$ bombarded with Ar^+ was exposed to H_2O. It has also been observed that the H_2O molecule is chemisorbed dissociatively to form OH on clean $TiO_2(100)$ surfaces at room temperature.10) Prior to UV-irradiation, no peaks of the CHx species were observed in the present system indicating that UV-irradiation is indispensable for the reduction of CO_2 molecules and the formation of active H and CHx species.

The present study clearly confirms that a reductive TiO_2 surface formed by UV-irradiation led to the facile reduction of CO_2 molecules which was found to be an important step in the photoinduced reduction of CO_2 with H_2O on the TiO_2 surface.

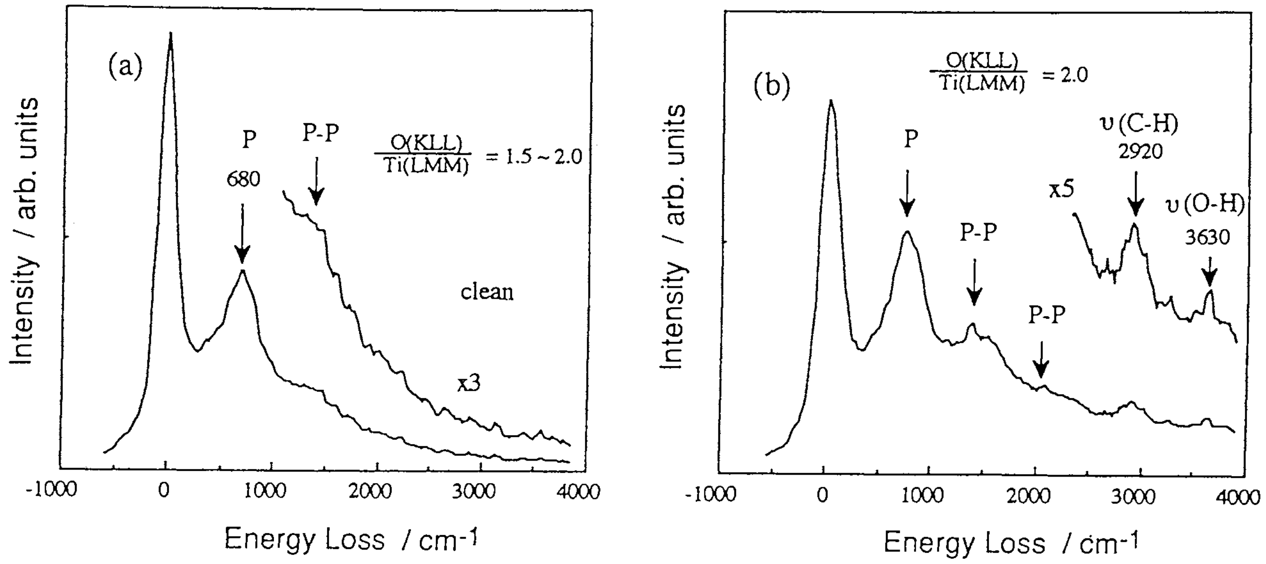

Fig. 2. HREEL spectra of $TiO_2(100)$ before and after UV irradiation. (a) clean surface, (b) after UV irradiation for 5 min in the presence of CO_2 (1 Torr) and gaseous H_2O (3 Torr).
(P; phonon peak, P-P; phonon-phonon peak.)

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