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Photochemistry of iron pentacarbonyl Adsorbed on titanium dioxide

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The photolysis of iron carbonyl ($Fe(CO)_5$) adsorbed on titanium dioxide (TiO_2, anatase) was studied by FT-IR spectroscopy. When adsorbed $Fe(CO)_5$ is illuminated by visible and near-UV light, the IR spectrum of its photolysis products is hardly observed, indicating that most of the $Fe(CO)_5$ is photodecomposed to iron(0) or iron oxides on TiO_2. The carbon monoxide (CO) evolution rate upon illumination depends on the wavelength of light; 433 nm light is more effective for CO evolution than 366 nm light. This result implies that the band-gap excitation of TiO_2 has little effect on the photolysis of adsorbed $Fe(CO)_5$, since the absorption edge of TiO_2 (anatase) lies at around 400 nm. The effects of substrates on the photolysis of adsorbed $Fe(CO)_5$ are discussed with reference to previous results obtained for aluminium oxide (Al_2O_3) and silicon dioxide (SiO_2), on which the photolysis leads to the formation of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$.

Keywords: Photochemistry, iron pentacarbonyl, titanium dioxide

INTRODUCTION

Surface photochemistry of organometallics and metal complexes has been investigated with the technical interest because of its application to catalysis and microelectronics. For the photochemical preparation of highly dispersed, supported, metal or metal alloy catalysts, metal carbonyls have often been used as precursors of such supported catalysts.[1] Light-induced deposition of metals from organometallic compounds has also been studied for the production of small semiconducting devices,[2] since photochemical decomposition offers effective methods for direct writing with thin films on substrates. In fact, recent progress in photodeposition techniques enables us to make a deposited metal line thinner than 1 μm. However, surface analysis techniques such as X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) have revealed that metal films made by the photodeposition of metal carbonyls contain large amounts of carbon and oxygen.[3] Therefore, a deeper understanding of the mechanism of the photodeposition is now required to improve the quality of photodeposited metal films.

A number of research papers have been published on the photochemistry of iron carbonyls at the surface of metals, semiconductors and insulators. In the photolysis of adsorbed $Fe(CO)_5$, a variety of photoproducts are found on the surface depending on acid–base conditions as well as on the electronic properties of the substrates. Whilst photo-oligomerization occurs on silica,[4–6] porous Vycor glass (PVG)[7] and alumina[8,9] giving $Fe_3(CO)_{12}$ or $Fe_2(CO)_9$ as a main product, complete photodecomposition of $Fe(CO)_5$ to iron has been reported for silicon surfaces.[10–12] We have also found that water adsorbed on Al_2O_3 gives rise to the photoformation of hydride species of iron carbonyls. It is therefore important to investigate the effects of substrate properties and pretreatments of substrates on the photolysis of adsorbed metal carbonyls. In this paper, we describe the photochemistry of $Fe(CO)_5$ adsorbed on TiO_2 (anatase), which is a semiconductor with a band-gap of 3.2 eV (~316 RJ) and exhibits weak acid properties.[13]

EXPERIMENTAL

$Fe(CO)_5$ was obtained from Aldrich, purified by vacuum distillation and stored in the dark. Titanium dioxide used in this work was Nihon Aerosil P-25 (BET surface area 50 m^2g^{-1}). Infrared spectra were obtained using a Horiba FT-300 FT-IR with a resolution of 1 cm^{-1} and were the average of 20 scans. The IR sample was prepared by pressing TiO_2 powder into a wafer of *ca* 20 mg cm^{-2}, which was outgassed at room temperature or 200 °C for 1 h before exposure to gas-phase $Fe(CO)_5$ in a Pyrex IR cell with BaF_2

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windows. The background spectrum of TiO_2 was subtracted from the total spectrum of the sample to obtain the spectrum of the adsorbed species. The light source was a 500 W high-pressure mercury lamp which was filtered through a band-pass filter. Measurements of CO evolution rates during the photolysis were carried out using a closed recirculating system (Pyrex, volume 189 cm^3) equipped with an ANELVA NAG-515B quadrupole mass spectrometer. A quartz cell with a flat bottom was used in the system. The TiO_2 sample was spread uniformly on the bottom of the cell and illuminated from the top using a mirror. The base pressure of vacuum line connecting to the IR cell and the recirculating system is less than 10^{-6} Torr.

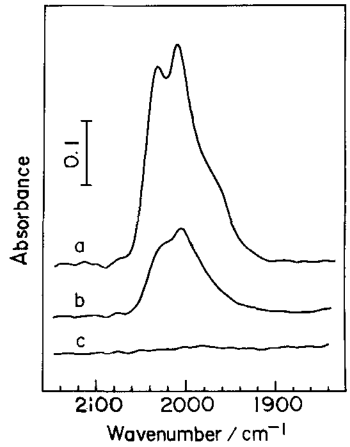

Figure 1 IR spectra of $Fe(CO)_5$ adsorbed on TiO_2 outgassed at room temperature for 1 h: (a) after exposure to 0.05 Torr of $Fe(CO)_5$; (b) after photolysis; (c) after evacuation of the gas phase for 1 h.

RESULTS AND DISCUSSION

When TiO_2 outgassed at 200 °C for 1 h was exposed to $Fe(CO)_5$ at room temperature, the adsorption isotherm indicated that a monolayer coverage is achieved at *ca* 0.03 Torr of $Fe(CO)_5$. The adsorption amount of $Fe(CO)_5$ for the monolayer coverage is estimated to be *ca* 1.0×10^{-4} mol g^{-1}, which corresponds to *ca* 1.2 molecules nm^{-2}. The amount of $Fe(CO)_5$ adsorbed was strongly dependent upon the outgassing temperature of TiO_2. On the sample outgassed at room temperature, the amount adsorbed is less than 1×10^{-5} mol g^{-1} even at 0.10 Torr of $Fe(CO)_5$. Hydration of the TiO_2 surface may cause a significant decrease in the amount of $Fe(CO)_5$ adsorbed at room temperature, since large amounts of hydroxyl groups as well as water adsorbed on the surface are observed by IR spectroscopy.

Figure 1, curve a, shows the IR spectrum of $Fe(CO)_5$ adsorbed on TiO_2 outgassed at room temperature. Two intense absorption bands were observed at 2029 and 2008 cm^{-1} in the C—O stretching region. These bands disapeared after brief pumping of the gas phase, indicating that $Fe(CO)_5$ is weakly physisorbed on TiO_2. When adsorbed $Fe(CO)_5$ was illuminated by near-UV light (250–400 nm) using a band-pass filter, the color of the sample changed to gray and the IR spectrum of adsorbed $Fe(CO)_5$ decreased in intensity (Fig. 1, curve b). After the photolysis, a significant amount of CO was detected in the gas phase by mass spectroscopy. No photolysis products were observed in the IR spectrum after removing unreacted $Fe(CO)_5$ by pumping at room temperature (Fig. 1, curve c). This result indicates that $Fe(CO)_5$ adsorbed on TiO_2 is photodecomposed to IR-nondetectable species such as iron metal or iron oxides without any intermediate species such as $Fe(CO)_4$ remaining on the surface. Since the sample outgassed at room temperature is covered with hydroxyls and adsorbed water, the products could react with hydroxyls or adsorbed water to form iron hydroxide or iron oxides.

On the sample outgassed at 200°C, on the other hand, a very small amount of $Fe_3(CO)_{12}$ was detected as a photolysis product. This result is consistent with the previous conclusion that $Fe_3(CO)_{12}$ is photoproduced at acidic or neutral sites on the substrate surfaces,[9] since TiO_2 surfaces have weak acid properties. However, the fact that most of the photolysis products on dehydrated TiO_2 are still IR-nondetectable is quite different from the results obtained for SiO_2 and Al_2O_3. It is well known that band-gap excitation of semiconductors gives rise to photocatalytic reactions.[14] Especially, illuminated TiO_2 exhibits a powerful ability to oxidize CO as well as organic compounds in the presence of oxygen,[15] and in the absence of oxygen olefins undergo isomerization, metathesis and decomposition reactions.[16] The lack of IR detectable products on TiO_2, therefore, may be attributable to band-gap excitation of TiO_2. This was examined by measurements of the wavelength dependence on the photolysis rate.

Figure 2 shows the time course of CO evolution during $Fe(CO)_5$ photolysis on TiO_2 outgassed at 200°C. In the dark a trace amount of CO was evolved, probably because of the catalytic effect of the TiO_2 surface. The CO evolution rate depended on the wavelength of light; the CO evolution rate at 433 nm was greater than at 366 nm, though the 366 nm light from the mercury lamp is greater in intensity than the 433 nm light. This result implies that the decomposition of $Fe(CO)_5$ on TiO_2 mainly occurs, not because of band-gap excitation, but because of photoexcitation of adsorbed $Fe(CO)_5$ itself, since the absorption edge of TiO_2 is much shorter than 433 nm. The initial CO evolution rate at 433 nm was estimated to be *ca* 1.1×10^{-5} mol min^{-1}.

CO evolution rates during the $Fe(CO)_5$ photolysis as well as in the dark were also measured on Al_2O_3 and SiO_2, which were used in the previous work.[6,8,9] As shown in Fig. 3, CO evolution in the dark is almost the same for the three samples. After illumination, CO evolution from Al_2O_3 and TiO_2 becomes faster than from SiO_2 and, after illumination for 1 h, the CO evolution from Al_2O_3 gradually levels off. In the previous paper we assumed from the IR spectrum of adsorbed $Fe(CO)_5$ a stronger interaction of $Fe(CO)_5$ with Al_2O_3 surfaces than with SiO_2 surfaces.[9] If $Fe(CO)_5$ is adsorbed on a substrate with some molecular distortion, then the photodecarbonylation of adsorbed $Fe(CO)_5$ would occur at a higher rate. A relatively high rate of CO evolution from the Al_2O_3 surface is, therefore, ascribed to strong adsorption of $Fe(CO)_5$ on the Al_2O_3 surface, and the decrease in the rate after 1 h is attributable to the formation of $Fe_2(CO)_9$, which is stable under illumination.[9] The IR spectrum of $Fe(CO)_5$ adsorbed on TiO_2 is rather similar to that on SiO_2, suggesting a relatively weak interaction between $Fe(CO)_5$ and the TiO_2 surface. However, CO photo-evolution from the $Fe(CO)_5$-adsorbed TiO_2 is comparable with that from the Al_2O_3 surface. Complete decarbonylation of $Fe(CO)_5$ leads to the formation of five CO molecules per photo-excited $Fe(CO)_5$, while the formation of $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ produces one or two CO molecules per photo-excited $Fe(CO)_5$ molecule since $Fe(CO)_4$ or $Fe(CO)_3$ is a precursor for the oligomers. Therefore, complete decarbonylation on the TiO_2 surface may be responsible for the relatively high rate of CO photo-evolution.

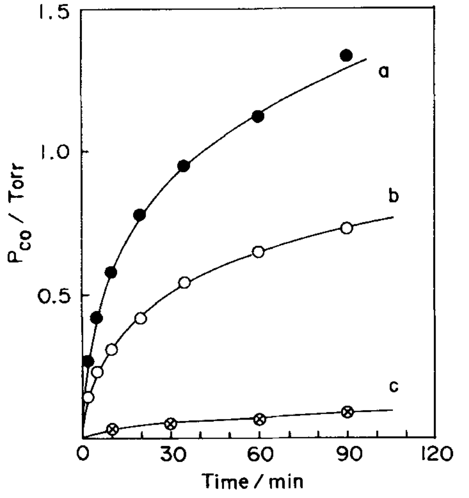

Figure 2 Time course of CO evolution during photolysis of $Fe(CO)_5$ at 0.05 Torr on 50 mg of TiO_2 outgassed at 200°C: (a) 433 nm light; (b) 366 nm light; (c) dark.

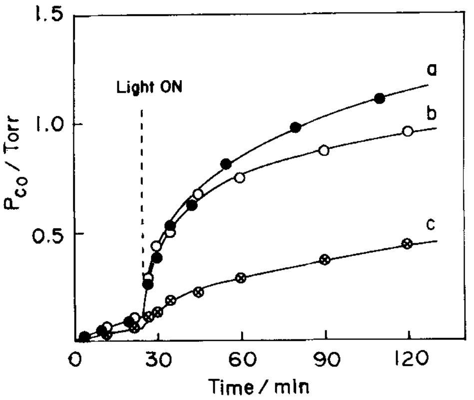

Figure 3 Time course of CO evolution during the photolysis of $Fe(CO)_5$ at 0.07 Torr under illumination of 366 nm light on various substrates (100 mg) outgassed at 200°C: (a) TiO_2; (b) Al_2O_3; (C) SiO_2.

It is noteworthy that photolysis of $Fe(CO)_5$ on silicon surfaces has been reported to give rise to photodecomposition to iron metal.[10–12] The photodecomposition reaction occurs under illumination with UV light of wavelength shorter than 350 nm and is attributed to direct excitation of molecular electronic transitions of $Fe(CO)_5$, metal–ligand charge transfer and *d–d* transitions.[12] These results lead us to assume that complete photodecomposition of $Fe(CO)_5$ preferably takes place on semiconductor surfaces. On insulators such as SiO_2, PVG or Al_2O_3, the intermediate species such as $Fe(CO)_4$ or $Fe(CO)_3$ are so stable and mobile[4,5,7] that oligomerization reactions occur easily. As observed on silicon surfaces,[12] partially decarbonylated $Fe(CO)_x$ species appear to be unstable on semiconductor surfaces and undergo further decarbonylation even in the dark, probably because of an electronic interaction between the semiconductor and unsaturated iron carbonyls. We suppose that an electron transfer from the substrates to $Fe(CO)_x$ species plays an important role in the $Fe(CO)_5$ photolysis and the thermal decarbonylation of $Fe(CO)_x$ on semiconductor surfaces. With this connection, we have found that $Fe(CO)_5$ adsorbed on platinized TiO_2 readily releases CO to the gas phase even in the dark, resulting in a detectable amount of $Fe_3(CO)_{12}$-like species. To investigate such an interaction further, spectroscopic studies of adsorption states of $Fe(CO)_5$ adsorbed on TiO_2 and metal surfaces are under progress in our laboratory.[17]

CONCLUSION

$Fe(CO)_5$ adsorbed on TiO_2 is photodecomposed to iron metal or iron oxides by illumination of visible and near-UV light. The direct photoexcitation of adsorbed $Fe(CO)_5$ is more effective for the photodecomposition reaction than the band-gap excitation of TiO_2. The decomposition process seems to involve the photoliberation of CO from adsorbed $Fe(CO)_5$, followed by thermal decarbonylation of coordinatively unsaturated species.

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