The Adsorption, Thermal Desorption and Photochemistry of Methyl Iodide on an Ag-Covered TiO2(110) Surface

Chaochin Su*,a (蘇昭瑄), Chih-Chieng Chenb,c (陳志成), Chih-Song Tsai (蔡枝松), Jong-Liang Linb (林榮良) and Jiing-Chyuan Lin*,c,d (林景泉)

aInstitute of Organic and Polymeric Materials, National Taipei University of Technology, Taipei 106, Taiwan, R.O.C.
bDepartment of Chemistry, National Cheng Kung University, Tainan 701, Taiwan, R.O.C.
cInstitute of Atomic and Molecular Sciences, Academia Sinica, P. O. Box 23-166, Taipei 106, Taiwan, R.O.C.
dDepartment of Chemistry, National Taiwan Normal University, Taipei 106, Taiwan, R.O.C.

The thermal reactions and photochemistry of monolayer methyl iodide (CH3I) on a silver covered TiO2(110) surface have been studied using combinative techniques of temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS). About ~ 60% of CH3I at monolayer coverage on Ag/TiO2(110) dissociates between 130 and 200 K yield adsorbed CH3 and I, with the rest desorbing molecularly at a peak temperature of 200 K in a TPD study. Photochemistry of CH3I on Ag/TiO2(110) is wavelength dependent. Irradiation of monolayer CH3I by 404 nm photon causes C-I bond dissociation and CH3 desorption. Upon 290 nm, UV irradiation, the depletion of CH3I(a) is dominated by photodesorption of molecular CH3I.

Keywords: TiO2(110); CH3I; Adsorption; Photochemistry.

INTRODUCTION

Photochemical reactions catalyzed by semiconductors are being investigated in decomposition of organic pollutants present in the environment, in organic synthesis, and in energy storage.1-4 It is a potential technique in various industries. In these reactions, photogenerated electrons and holes migrate to the semiconductor surfaces where they can induce reduction and oxidation of adsorbed molecules. Titanium dioxide (TiO2), due to its strong oxidizing power of its holes, high photostability and redox selectivity, has been used most extensively as a photocatalyst.1,5-8 However, the quantum efficiency of bare TiO2 catalyst is low because of the fast recombination of photogenerated electrons and holes. Many studies have been devoted to improve the photocatalytic efficiency of TiO2.9,10 It has been found that the presence of metal atoms or clusters may help the electron-hole separation by trapping photoelectrons and thereby facilitating the photooxidation. Among the various metals that have been utilized for increasing the photocatalytic activity of TiO2, silver (Ag) is particularly suitable for industrial applications due to its low cost and easy preparation. The focus of this work is the effect of silver on modifying the adsorption and reaction of methyl iodide (CH3I) occurring on TiO2. CH3I is chosen for thermal and photochemistry studies at adsorbate/surface interfaces due to the weak C-I bond and its high photosensitivity.

The adsorption and reaction of methyl iodide on the TiO2(110) surface have been extensively studied by Kim et al.11-14 and Garrett et al.15,16 The complex desorption TPD spectra suggest the coexisting of several distinct coverage regimes. The dissociatively (~ 5%) adsorbed I atoms remain chemisorbed at 220 K. For photochemistry, it was found that the photodesorption of CD3I follows the substrate mediated mechanism in the monolayer regime. No significant photodissociation of CD3I was observed on TiO2(110). For multilayers of CD3I on TiO2(110), the photodissociation was concluded to be initiated by direct ad-
sorbate excitation mechanism.

Here, we present the results on the study of adsorption, thermal- and photoreaction of CH$_3$I on a Ag-covered TiO$_2$(110) surface (Ag/TiO$_2$(110)). We begin with the characterization of Ag film and its thermal stability using combination techniques of XPS, LEED, LEIS, and STM. Annealing of low temperature grown Ag films to 500 K for the apparent coverage of ~ 2.2 ML would result in the formation of Ag clusters which cover about one half of a TiO$_2$(110) surface (0.5 ML) with ~ 4 ML Ag layers thickness. The thermal- and photo- reactions of CH$_3$I adsorbed on such prepared Ag/TiO$_2$(110) surfaces were then studied using XPS and TPD techniques. The possible photoreaction suggested by the XPS results are discussed.

**EXPERIMENT SECTION**

The experiments were carried out in a two level ultra-high vacuum (UHV) μ-metal chamber with a routine base pressure below ~ 5 x 10$^{-10}$ Torr. A detailed description of the system design has been given previously\textsuperscript{17} but with little modification as shown in Fig. 1. Briefly, the chamber was equipped with low-energy electron diffraction (LEED) optics (VG, RVL-900) for surface structure determination, an auger electron spectrometer (AES) for surface elemental analysis and cleanliness check, an ion sputtering gun (VG EX05) for both TiO$_2$(110) surface cleaning and low energy ion scattering (LEIS), and a quadrupole mass spectrometer (QMS) (UTI, 0-300 amu) for temperature-programmed desorption (TPD) experiments. A quartz window was mounted on the UHV chamber to allow \textit{in situ} irradiation by a 500 W Hg-arc lamp (Oriel 6285) operated at 400 W for study of photochemistry. The QMS was situated in a copper tube and separated from the main chamber by a Mo cone with a 3-mm dia. aperture, and differentially pumped with two ion pumps (20 and 60 Ls$^{-1}$). Computer software was employed to linearly control the TiO$_2$ temperature between 100 and 1000 K and to record multiple QMS signals simultaneously for TPD study. The typical He$^+$ ion energy used in LEIS measurements was 1 KeV with a current about 30 nA. The incident angle was about 10° from the surface normal, and the scattering angle was fixed at 30°.

The chamber also contains a VG dual anode X-ray source (Mg/Al) for taking X-ray photoemission spectra (XPS). XPS spectra were acquired using the Mg K$_\alpha$ x-ray source (hv = 1253.6 eV) operated at 300 W (15 KV, 20 mA) with a constant analyzer pass energy of 10 eV. All XPS spectra were calibrated by fixing the binding energy of the Ti 2p photoelectron peak at 460 eV.

The sample is a polished 10 x 4 x 1 mm$^3$ TiO$_2$(110) single crystal (rutile, Commercial Crystal Laboratories). The sample assembly as well as treatment procedures after insertion into vacuum chamber have been described in previous work.\textsuperscript{18} The stoichiometric TiO$_2$(110) surface used in this study was prepared by annealing the Ar$^+$ sputtered clean surface at 1000 K for 3 min in 2 x 10$^{-6}$ Torr of O$_2$ followed by cooling down to room temperature (10 min) in the same oxygen pressure. After this treatment, a (1 x 1) LEED pattern with sharp diffraction spots was obtained (see below).

The Ag-covered TiO$_2$(110) surface (Ag/TiO$_2$(110)) was prepared by vapor deposition of Ag from a home-made metal evaporator source. The evaporator was made of a Ta sheet encircled with one end closed and spot-welded to the feedthrough in order to be connected to a power supply. A bunch of small Ag wires was packed into such a Ta crucible. Evaporation of Ag was obtained by resistively heating the Ta crucible. Temperatures of the evaporator were read by an optical pyrometer (Optex, Thermo-Hunter, Model 804).
VF-1600S °C, 0.7-1.1 μm wavelength). The structure of the Ag/TiO$_2$(110) surface during different stages of preparation was carefully monitored by LEED (see below).

Methyl iodide, CH$_3$I (99.5%, Aldrich), shielded from light by aluminum foil, was purified by several cycles of freeze-pump-thaw and admitted to the UHV chamber without further treatment via a leak valve. During dosing, the Ag/TiO$_2$(110) surface was held at a temperature of (120 ± 3) K and routinely flashed to > 900 K after each data acquisition. In this way, all the C and I residues produced from the thermal- and photoreaction, and the Ag overlayer were completely removed. Since surface defects are known to strongly influence the adsorption behavior of TiO$_2$, a stoichiometric TiO$_2$(110) surface was carefully prepared before another Ag deposition and exposure to CH$_3$I.

The experiment of scanning tunneling microscopy (STM) was carried out in another UHV system (base pressure ~ 1 × 10$^{-10}$ Torr) which was equipped with Omicron VT SPM, AES, LEED, and a Ag source. A detailed description of this chamber can be found in other work. STM data were typically collected at sample biases of 1-2 V with tunneling currents of 0.4-0.5 nA.

RESULTS AND DISCUSSION

Characterization of Ag Films and Thermal Stability on a TiO$_2$(110)–(1×1) Surface

Ag deposition was monitored using combination techniques of low-energy ion scattering (LEIS), x-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and scanning tunneling microscopy (STM). Some discussion can be found in the early stage of this study for Ag deposition on TiO$_2$(110). The LEIS technique, due to its high sensitivity to the top-layer surface composition, was used to calibrate the coverage of surface vacant sites on TiO$_2$(110) after Ag deposition. The lower curve in Fig. 2 shows the LEIS spectra of a clean TiO$_2$(110) surface with a Ti peak appearing at 746 eV and O at 427 eV. Upon Ag deposition, an additional peak due to Ag appears at 894 eV (Fig. 2, upper curve). The integrated He$^+$ signal of Ti and O obtained for a clean and Ag-covered TiO$_2$(110) surface were denoted as (I$_{\text{clean}}^{\text{Ti}}$, I$_{\text{clean}}^{\text{O}}$) and (I$_{\text{Ag}}^{\text{Ti}}$, I$_{\text{Ag}}^{\text{O}}$). The ratio of I$_{\text{Ag}}^{\text{Ti}}$/I$_{\text{clean}}^{\text{Ti}}$ or I$_{\text{Ag}}^{\text{O}}$/I$_{\text{clean}}^{\text{O}}$ thus represents the fraction of uncovered surface bare sites on the Ag deposited TiO$_2$(110) surface.

The growth of Ag layers and their thermal stability on TiO$_2$(110) was monitored by XPS and AES after Ag vapor deposition at about 125 K followed by annealing to various surface temperatures with increments of 100 K. The spectra were recorded after the crystal was cooled down to 110 K. The coverage and temperature dependent variation of Ag intensity are in excellent agreement between XPS and AES measurements and hence only XPS results are presented. Fig. 3 shows the Ag 3d XPS integrated intensity for different annealing temperatures as a function of Ag coverage. It can be seen that for the substrate temperature of 125 K, the Ag signal (solid circles) increases as Ag coverage increases and gradually approaches a plateau at high coverage regime. As mentioned in previous work, to calibrate Ag exposure in terms of ML, we have assumed a pseudo layer-by-layer growth (Frank-van der Merwe, FM mode) model with the escape length for Ag 3d probed by Mg Kα radiation being taken equal to 14.5 Å. The coverage dependent Ag signal is then calculated (open triangles in Fig. 3) and compared with experimental data. As shown in Fig. 3, within the experimental error, the XPS result for deposition at 125 K shows good agreement with the theoretic values. As the sample temperature was raised beyond 500 K, the Ag signal intensities decreased dramatically between ~ 2 ML to ~ 6 ML. The decrease of Ag XPS signal can be attributed to the 3D clustering of Ag upon annealing. Similar temperature-dependent clustering behavior has been ob-
served when 1.5 ML Pt film was deposited on TiO2(110). Formation of Ag 3D clusters upon heating is also supported by temperature programmed desorption (TPD) of Ag layers from the TiO2(110) surface. As shown in Fig. 4, only a single desorption peak with a peak temperature shift to higher temperatures (from 850 to 930 K) at higher Ag coverages was observed. Moreover, from the leading-edge analyses of these spectra, we have found that the Ag desorption from TiO2(110) follows the zeroth order desorption kinetics with a desorption energy of 60 kcal/mol, which is very close to the Ag sublimation energy of 67 kcal/mol. Recently, Luo et al. studied the Ag growth on TiO2(110)-(1×1) at 300 K using XPS, LEIS, LEED, and STM techniques. The growth was shown to be 3D and the Ag clusters are stable on the TiO2 surface. No significant chemical interaction between Ag and TiO2 is observed.

Of important note is that at the initial coverages of ~2.2 to 6 ML (Fig. 3), the Ag XPS signals decrease after annealing to 500 K (solid squares) and 620 K (open squares) and remain relatively constant. As discussed in the previous work without STM measurements, the constant XPS intensity was explained by forming 3D needle-like Ag islands on top of a 2D metastable (2×1) Ag overlayer upon annealing. Another possibility is the formation of Ag clusters, sitting on top of part of the bare TiO2 surface, with sufficient thickness to completely attenuate the photoelectrons emitted from the underlayers of Ag clusters. Based on the study of LEIS, deposition of 2.2 ML Ag on TiO2(110) at 125 K, i.e., the onset coverage of XPS plateau at 500 K, followed by a subsequent annealing at 500 K for 1 min results in ~0.5 ML of uncovered sites on TiO2(110) which corresponds to Ag clusters with at least 4 atomic layers. To resolve this issue, we thus performed the scanning tunneling microscopy (STM) experiments. The STM images were acquired after annealing the Ag/TiO2(110) surface at 500 K followed by cooling to 110 K. As shown in Fig. 5, ~one half of the TiO2(110) surface is covered by Ag clusters, and this is consistent with LEIS result. Furthermore, the clusters are 5-7 nm in diameter with heights of 1-2 nm, corresponding to approximately five atomic Ag layers, which is in agreement with the predicted value from a combination of XPS, LEIS, and theoretic calculation as discussed above.

The structure of the Ag-covered surface was also monitored by LEED. Fig. 6a is a typical (1×1) LEED pattern for a stoichiometric TiO2(110) surface. Deposition of 2.2 ML Ag film at 125 K led to a strong diminution in LEED spots intensity (Fig. 6b), indicating a disordered 2D Ag film grown on the surface. Upon annealing to 500 K, a reasonably clear (1×1) pattern is retrieved, but with weaker spots intensity and a more diffuse background as compared...
to the clean surface (Fig. 6c). This can be explained by the fact that upon annealing, the 2D disordered film would ball up and occupy only part of the surface. Such prepared Ag film can be stable up to 620 K based on XPS results and therefore was used for the temperature-programmed desorption (TPD) and XPS studies of CH$_3$I chemistry on the Ag-covered TiO$_2$(110) surface presented below.

**Thermal Chemistry of CH$_3$I on the Ag-covered TiO$_2$(110)-(1×1) Surface**

XPS Study: Adsorption and Dissociation of CH$_3$I on Ag/TiO$_2$(110)

X-ray photoelectron spectroscopy (XPS) was used to characterize the adsorption behavior of methyl iodide on Ag/TiO$_2$(110). Since the x-ray induced chemical effect was noted in alkyl halide films, and at least 6 min was required to complete a XPS scan, we had to first examine the stability of the monolayer CH$_3$I on Ag/TiO$_2$(110) with respect to x-ray irradiation. The as prepared Ag/TiO$_2$(110) surface (previous section) was exposed to 2 L of CH$_3$I at 110 K. A series of XPS spectra were then recorded at increasing irradiation time. As shown in Fig. 7a, in the initial XPS measurements, the binding energy (BE) for I 3d is shown at about 621.8 eV. With extended x-ray irradiation, I 3d peaks broaden toward lower BE. The I 3d XPS peaks in all spectra can be satisfactorily fitted with two Gaussian peaks using the built-in analysis program of VGX900X, one at 621.6 and the other at 620 eV. The BE and width of each peak can be varied independently in each fit. In the previous XPS study of CH$_3$I on Ag(111), Zhou et al. have observed that the BE of I 3d shifts from 620.5 to 618.5 eV as CH$_3$I is thermally dissociated on the surface. Liu et al. have studied the photodissociation of CH$_3$I on Pt(111) using XPS and found that I 3d shifts from 620.8 to 619.9 eV. Therefore, in agreement with the two previous findings, the observed two peaks in Fig. 7a should correspond to the BE of I in molec-
ular CH$_3$I$_{(a)}$ (621.6 eV) and I$_{(a)}$ atomically adsorbed on TiO$_2$(110) (620 eV), respectively. Obviously, the adsorbed CH$_3$I is sensitive to x-ray irradiation under this condition. Such dissociation is possibly caused by the secondary and hot electrons from the substrate subject to x-ray illumination. As shown in the inset of Fig. 7a, while the intensity of the 621.6 eV peak for molecular CH$_3$I$_{(a)}$ decreases as a function of x-ray irradiation time, the 620 eV peak intensity for atomic I$_{(a)}$ increases. Such electron induced dissociation for alkyl halide film has been reported previously by White et al. In contrast, for CH$_3$I on TiO$_2$(110), the I 3$d$ signal decays rapidly and vanishes entirely after 35 minutes x-ray irradiation (Fig. 7b). In addition, no noticeable photodissociation was observed on the bare TiO$_2$(110) surface. Based on the results in Fig. 7a, the estimated uncertainty in the I 3$d$ intensity during a typical XPS scan in this study is expected to be less than 4% and therefore will not significantly affect the results presented below. In order to minimize the x-ray effect, a fresh CH$_3$I/Ag/TiO$_2$(110) sample was always prepared before each new XPS experiment.

To investigate the thermal reaction of CH$_3$I monolayer on Ag/TiO$_2$(110), XPS experiments were performed after heating the crystal to desired temperatures. The results for I 3$d$ XPS spectra are presented in Fig. 8. The BE of I 3$d$ photoelectron prior to annealing is at 622.0 eV. After heating, changes in the I 3$d$ peaks were observed. As shown in the 164, 176, and 200 K traces, the peaks become broader toward the lower BE and can be decomposed into two peaks similar to those in Fig. 7a. The observed small variation in I binding energy at higher annealing temperatures is attributed to surface charging and XPS resolution. Obviously, the cleavage of the C-I bond occurs to form adsorbed I$_{(a)}$ during thermal process at temperatures as low as 164 K. At temperatures above 240 K, the I 3$d$ peak corresponding to CH$_3$I$_{(a)}$ vanishes completely and only atomic I$_{(a)}$ is left on the surface. This is consistent with the fact that the molecular desorption of CH$_3$I occurs at Ag/TiO$_2$(110) (see below). The intensity of I$_{(a)}$ remains constant up to 700 K and desorbs accompanying the Ag desorption from Ag/TiO$_2$(110) at higher temperatures. Due to the low sensitivity of the C

---

**Fig. 7.** I 3$d$ core level peaks for monolayer CH$_3$I on the (a) Ag/TiO$_2$(110) and (b) TiO$_2$(110) surfaces recorded at increasing x-ray irradiation time. The inset shows the integrated peak area as a function of irradiation time.
photoelectron, it is difficult to distinguish any change in C peak (around 284.7 eV, not shown) through the heating procedure. However, when crystal was heated to above 300 K, the 284.7 eV peak vanished completely indicating the complete desorption of C-containing products at this temperature.

**Temperature Programmed Desorption**

While XPS was utilized to explore the adsorption and dissociation processes, the temperature programmed desorption (TPD) was performed to elucidate the thermal desorption behavior when methyl iodide was adsorbed on the Ag/TiO$_2$(110) surface. At the beginning of each experiment, the Ag/TiO$_2$(110) surface was exposed to methyl iodide of different exposures at 120 K. The surface was then heated linearly at 2 K/s to 900 K. Heating CH$_3$I/Ag/TiO$_2$(110) to such a high temperature not only desorbs CH$_3$I and Ag but also generates oxygen vacancy on the surface. Therefore, for each TPD experiment, a fresh Ag/TiO$_2$(110) surface was prepared by performing oxidation and Ag deposition/annealing procedures. Desorbing species were detected by QMS which allows multiple ions to be detected simultaneously. Fig. 9 shows TPD spectra of methyl iodide molecular desorption monitored at m/e = 142 for adsorbed CH$_3$I on the Ag/TiO$_2$(110) surface. At 2 L exposure, the TPD curves show a saturate single desorption peak (denoted as $\alpha$) at ~ 202 K. Assuming first order kinetics, an activation energy of 12 kcal/mol for CH$_3$I molecular desorption from Ag/TiO$_2$(110) is obtained by the Redhead formula. Further increase of CH$_3$I exposure, new desorption states develop with new $T_p$ appearing at lower temperatures, as shown in the upper curve of Fig. 9 for 10 L exposure. Based on the overlap feature of the $\alpha$ peak in these two desorption spectra, we assign these low temperature desorption peaks to more weakly bonded adsorption states or CH$_3$I multilayers. The appearance of this lower temperature feature is thus used to define the exposure for completion of the adsorbed monolayer exposure of CH$_3$I. Our TPD result shows that the multilayer formation begins around 2
In comparison, for CH$_3$I adsorption on Ag-free TiO$_2$(110), as shown in the inset of Fig. 9, monolayer CH$_3$I desorbs as a single peak maximized at ~ 204 K. Zhou et al. also detected a single peak for monolayer CH$_3$I thermally desorbing from the Ag(111) surface at ~ 212 K. The similarity of the desorption behavior hampers the analysis of Ag effect on CH$_3$I thermal desorption. It is noted, however, that the signal intensity of the parent molecule desorbing from the Ag/TiO$_2$(110) surface is noticeably lower than that from the clean TiO$_2$(110) surface for the same exposure of 2 L. This is due to the thermal dissociation of CH$_3$I on Ag/TiO$_2$(110) during the TPD process as indicated by XPS study. In contrast, for a monolayer of CH$_3$I on TiO$_2$(110) surface, no thermal dissociation was found. The calibrated ratio of CH$_3$I TPD signals from the bare and the Ag-covered surfaces, against the ratio of molecular 13d XPS signals from the Ag-covered and the TiO$_2$(110) surfaces, yields the undissociated fraction of CH$_3$I on the Ag/TiO$_2$(110) surface. The maximum thermal decomposition probability is found to be 60% for 1 ML CH$_3$I on the Ag/TiO$_2$(110) surface. The thermal dissociation is thought to predominantly take place on the surface Ag nanoclusters. Zhou et al. have investigated the thermochemistry of methyl iodide on Ag(111) and found that ~ 35% of monolayer CH$_3$I dissociates between 130 and 200 K to yield adsorbed CH$_3$ and I. The higher activity for CH$_3$I thermal dissociation on Ag/TiO$_2$(110) might be due to the more sparsely distributed Ag clusters and hence stronger reactivity as compared to the compact structure of a Ag single crystal surface.

As shown by XPS study, the adsorbed iodine is formed by thermal dissociation of methyl iodide on Ag/TiO$_2$(110). Iodine remains on the surface up to at least 700 K and desorbs at higher surface temperatures as indicated by the appearance of QMS signal of m/e at 127. The desorption behavior (not shown) is complicated by the co-desorption of Ag at temperatures above 700 K. Based on the studies of halogens adsorbed on metal surfaces, iodine may either desorb in atomic form or as metal halides. We have not, however, been able to detect any I-containing desorbing species since the masses of AgI and I$_2$ are beyond the range of our mass spectrometer.

**Photochemistry of CH$_3$I on the Ag-covered TiO$_2$(110)- (1×1) Surface**

In this section, the interaction of UV light with monolayer CH$_3$I adsorbed on the Ag/TiO$_2$(110) surface was studied. XPS was used to examine the changes in I 3d and C 1s on CH$_3$/Ag/TiO$_2$(110) subject to irradiation at various wavelengths: 290 and 403 nm. The maximum surface temperature measured by thermocouple attached to the crystal edge was ~ 130 K during prolonged irradiation, substantially less than the onset desorption temperature (~ 180 K) of the monolayer CH$_3$I from Ag/TiO$_2$(110) (Fig. 9). Considerable thermal-dissociation of CH$_3$I on Ag/TiO$_2$(110) at such low temperature regimes also seems unlikely. Fig. 10 shows the representative 13d (a) and C 1s (b) XPS results for 1 ML CH$_3$I adsorbed on Ag/TiO$_2$(110) at 120 K following irradiation at 403 nm for 0, 30, and 120 min. With increasing irradiation time, there is noticeable broadening of the I 3d peaks to the lower binding energy side. The I 3d peaks were fitted to the sum of two Gaussian peaks with equal widths of ~ 2 eV located at ~ 621.6 and ~ 620 eV corresponding to CH$_3$I(a) and I(a), respectively. In order to obtain a best fit, the peak position and width used is varied within 10% from one spectrum to another. Obviously, the surface chemical changes induced by Hg-lamp irradiation also result in the dissociation of CH$_3$I on Ag/TiO$_2$(110) to form I(a). Similar changes of XPS feature of I 3d upon irradiation at 290 nm were observed (not shown). The C 1s peak broadens slightly and decreases in area with increasing irradiation time for both wavelengths studied. No discernible shift for C 1s peak was observed. All C 1s spectra were fitted with a single Gaussian peak. The C 1s intensity remains constant after a period of irradiation.

Fig. 11(a) summarizes the intensity of I 3d XPS peaks (two individual Gaussian components and the sum) as a function of irradiation time, which has been converted to photon flux, for the monolayer CH$_3$I adsorbate upon irradiation at: 403 nm (upper panel) and 290 nm (lower panel). The results for 621.6 eV peak are shown in solid circles and that for 620 eV peak are shown in open circles. The open triangles in Fig. 11(a) are the summation of areas from two I 3d peaks. The loss of I 3d intensity due to decreasing CH$_3$I(a) is accompanied by the growth of intensity due to I(a). At 403 nm, the total I intensity stays fairly constant through the entire range of irradiation. In addition, while the intensity of CH$_3$I(a) decreases with increasing of irradiation time, the I(a) intensity increases with the same rate. These observations suggest either no or minor photodesorption of molecular CH$_3$I or I atoms during CH$_3$I photo-irradiation at 403 nm. The total depletion of CH$_3$I(a) can be attributed to pure photo dissociation. In contrast, at 290 nm, the total I 3d intensity decreases after irradiation, indicat-
Fig. 10. The XPS peaks of (a) I 3d and (b) C 1s for 1 ML CH₃I adsorbed on Ag/TiO₂(110) at 110 K following irradiation at 403 nm for 0, 30, and 120 min.

Fig. 11. (a) The intensity of I 3d XPS peaks as a function of photon impingement for the monolayer CH₃I adsorbed on Ag/TiO₂(110) at 120 K following irradiation at: 403 nm (upper panel) and 290 nm (lower panel). (b) The intensity of C 1s XPS peaks as a function of photon impingement for the monolayer CH₃I adsorbed on Ag/TiO₂(110) at 120 K following irradiation at: 403 nm (upper panel) and 290 nm (lower panel).
ing loss of I from the surface. This could be a result from
the photodesorption of CH₃I and/or the photodissociation
formed I(a). Note that the propensity of decrease in CH₃I(a)
signal is evidently more expeditious than the increase of I(a)
signal, although the XPS sensitivity of I(a) and CH₃I(a) may
not be the same. This result suggests that the desorption of
CH₃I upon irradiation is more likely. As shown previously,
atomic I produced by thermal dissociation of CH₃I on
Ag/TiO₂(110) is strongly bonded to the surface and desorbs
above 700 K. For comparison, I(a) produced by thermal dis-
sociation of CF₃I on Ag(111) desorbs at 830 K.²⁴ In light of
this information, to thermally desorb photodissociation
produced I(a) at temperatures as low as 120 K seems un-
likely. Therefore, we tentatively assume that in the present
study, there is no photodesorption of I(a) produced by
photodissociation of CH₃I(a).

Fig. 11(b) shows the overall changes of C area during
irradiation at: 403 nm (upper panel) and 290 nm (lower
panel). The C decay is rapid in the initial irradiation and be-
comes slow for longer irradiation. Compared to Fig. 11(a),
it is found that the decay of total C 1s signal is more dra-
matic than that of total I(a) 3d signal for both wavelengths.
At 403 nm, where no molecular desorption of CH₃I(a) oc-
curs during irradiation, this result indicates the desorption
of CH₃ fragment from Ag/TiO₂(110). At 290 nm, in addition
to photodissociated CH₃(a) desorption, photodesorption of
CH₃I(a) also contributes to loss of C signal. Therefore, the
maximum drop of total C intensity is higher than that of to-
tal I intensity. Further experiments and more quantitative
analysis are currently under investigation in order to get a
more definitive determination of the mechanism for photo-
reaction pathways of CH₃I(a) on Ag/TiO₂(110).

CONCLUSION

The surface chemistry of methyl iodide on a Ag cov-
ered TiO₂(110) surface shows interesting and complex be-
behavior. We have first characterized Ag film on TiO₂(110).
A quasi-layer-by-layer growth mode was found for Ag
everation deposition on TiO₂(110) at a low temperature
of 125 K. Annealing the Ag-film results in the formation of
3D Ag islands or clustering of Ag. At coverages of ~ 2.2 to
6 ML, the annealing formed Ag clusters occupy a surface
area of ~ 0.5 ML with a thickness of about four Ag layers.

Such prepared Ag film can be stable up to 620 K and
used for the thermal chemistry and photochemistry of
methyl iodide on the Ag/TiO₂(110) surface. Methyl iodide
was dosed molecularly on Ag/TiO₂(110) at 120 K. Upon
heating, the CH₃I dissociates between 130 and 200 K to
give adsorbed CH₃ and I. The maximum thermal dissocia-
tion probability is ~ 0.60 for one monolayer coverage of
CH₃I on Ag/TiO₂(110). The undissociated CH₃I molecule
desorbs at higher temperatures with a maximum desorption
rate at temperature ~ 200 K.

From the variation of I 3d XPS intensity of CH₃I(a)
and I(a) as a function of photon flux, it is found that both
photodesorption and photodissociation were proceeded
upon irradiation. At 403 nm, the depletion of CH₃I(a) is
mainly attributed to pure photo dissociation. While I atoms
presumably remain on the surface, a significant amount of
CH₃ product desorbs during photolysis. On the other hand,
at a wavelength of 290 nm, the photodesorption is the pri-
mary process for CH₃I(a) depletion.

ACKNOWLEDGMENTS

We gratefully acknowledge the financial support of
the National Science Council of the Republic of China
(Grant: NSC-92-2113-M-001-068, NSC-92-2113-M-006-
016, and NSC-92-2113-M-027-001) for this research.

Received October 19, 2005.

REFERENCES

13, 219.