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The adsorption and reactions of methyl iodide on powdered Ag/TiO_2

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This paper is dedicated to Professor Kwang-Ting Liu of National Taiwan University on his 65th birthday.

Abstract

The adsorption, thermal reaction, and photoreaction of methyl iodide on powdered Ag-covered TiO_2 (Ag/TiO_2) were studied using Fourier transform infrared spectroscopy. The Ag was deposited on TiO_2 by photoreduction of $AgNO_3$. The resultant Ag/TiO_2 was analyzed by TEM, ESCA, and AA. Evolution of methane was observed in the absence of oxygen for thermal reaction at temperature above 623 K. Photoreaction showed the enhancement in CH_3I dissociation due to the presence of Ag on TiO_2 surface. In this reaction, methyl radicals produced were recombined to form ethane molecules over the Ag/TiO_2. The same reactions in the presence of oxygen change their pathways completely yielding oxygen-containing products. In thermal reaction, $CO_{(g)}$, $CO_{2(g)}$, $CH_2O_{(g)}$, $(CH_3)_2O_{(g)}$, and $H_2O_{(g)}$ were observed. On the other hand, in the photochemical reactions, $CO_{2(g)}$, $H_2O_{(g)}$, and surface formate groups were produced. Possible pathways for present thermal and photochemical reactions are discussed and the results were compared with that obtained using bare TiO_2.

Keywords: Adsorption; Thermal reaction; Photoreaction; Ag/TiO_2; ESCA

1. Introduction

Photochemical reactions catalyzed by semiconductors are of interest in photosynthesis, energy storage and in conversion of organic pollutants into harmless molecules [1,2]. In these reactions, the photogenerated electrons and holes migrate to the semiconductor surfaces where they can reduce and oxidize the adsorbates present on the surface. TiO_2 has been extensively used as a photocatalyst due to its strong oxidizing power, high photostability and redox selectivity. However, the quantum efficiency of bare TiO_2 catalyst is low because of the fast recombination of photogenerated electrons and holes. Many studies have been devoted to improve the photocatalytic efficiency of TiO_2 by depositing noble metals on it [3,4]. The presence of metal atoms or clusters may help the electron–hole separation by trapping photoelectrons and thereby facilitating the photooxidation. Many transition metals also increase the absorption of the light and thereby the carrier concentrations. Among the various metals viz. Pt, Pd, Ag, Au, Rh, etc. that have been utilized for increasing the photocatalytic activity of semiconductors, silver (Ag) is particularly suitable for industrial applications due to its low cost and easy preparation.

The effects of Ag dopants on the lattice or surface of TiO_2 have been examined [5–15]. Ilisz et al. investigated the photodecomposition of phenol in near-UV-irradiated TiO_2 aqueous suspensions [9]. They have found that Ag ion can act as an efficient electron acceptor to yield a significantly enhanced photodegradation rate. Tada et al. studied the TiO_2 photocatalytic reduction of bis(2-dipyridyl)disulfide to 2-mercaptopyridine by H_2O [16]. With the incorporation of Ag nanoclusters on TiO_2, the reduction rate was found to be increased markedly. It has been stressed that the reaction-promoting effect of the Ag loading can be attributed to the selective adsorption as well as the increases in the adsorption amount and the efficiency of charge separation. Daohui et al. studied the photocatalytic decomposition of amides on the surface of Ag-modified TiO_2 particles [17]. Their studies revealed that the photocatalytic activity of Ag/TiO_2 is much higher than that of the unmodified TiO_2. Selective reduction of nitric oxide (NO) by ethane in the presence of excess oxygen was investigated

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by Shiba et al. using a Ag supported on TiO_2 catalyst [18]. Ag/TiO_2 showed high catalytic activity reducing NO to N_2 and N_2O. Lee et al. photochemically Ag deposited on TiO_2 films and the photocatalytic activity in degradation of salicylic acid was found to be higher than that obtained for bare TiO_2 films [19]. Most studies investigating the effect of deposition of Ag on photocatalytic activity of TiO_2 focused on the reaction kinetics and the parameters governing the kinetics (mass of catalyst, wavelength, initial concentration, temperature, and radiant flux). These works are mostly the solution phase studies and do not provide sufficient mechanistic understanding. Su et al. have studied the growth of Ag on the $TiO_2(1\,1\,0)$ single crystal [20] and also compared the thermal- and photoreactions of methyl iodide on Ag/$TiO_2(1\,1\,0)$ with that on bare $TiO_2(1\,1\,0)$ [21,22]. The adsorption and reaction of methyl iodide, due to the weak bonding of C–I bond, has been studied as a “model system” to investigate the reactions of hydrocarbon fragments which have been thought to play important role both in Fischer–Tropsch synthesis and in the transformation of methane into other hydrocarbons. Moreover, the photosensitivity of methyl iodide makes it suitable for photochemical study at adsorbate/surface interfaces. From the result of post-irradiated temperature programmed desorption (PITPD) study in a monolayer CH_3I adsorbed on Ag/$TiO_2(1\,1\,0)$, two products, ethane and dimethyl ether, were observed to evolute from substrate surface. In this work, the catalytic activity of Ag/TiO_2 on decomposition and reactions of methyl iodide was investigated in situ using IR spectroscopy in the absence as well as in the presence of oxygen. The results were compared with those obtained by using bare TiO_2. It was found that the presence of deposited Ag showed significant enhancement in the efficiency to decompose CH_3I and resulted in catalysts that can photodegrade methyl iodide to ethane.

2. Experimental

2.1. Preparation of Ag/TiO_2

Silver can be deposited on TiO_2 by photocatalytic reduction or thermal decomposition of silver salt solutions, or by vapor deposition [19,23]. We have prepared the Ag/TiO_2 samples by depositing Ag on Degussa P25 TiO_2 powders through photoreduction of aqueous $AgNO_3$. The $AgNO_3$ solution (3.1×10^{-2} M) containing suspended TiO_2 powders (1.5 g, Degussa P25 TiO_2) was irradiated with 200 W Hg arc lamp (Oriel Corp.). During the irradiation, nitrogen was bubbled vigorously through the reaction mixture. The color of the reaction mixture was observed to be changed from white to violet-brown indicating the reduction and deposition of Ag on TiO_2. The irradiated mixture was then centrifuged for 2 h and the recovered Ag/TiO_2 precipitate was washed by deionized water. The obtained Ag/TiO_2 was characterized by transmission electron microscopy (TEM, Hitachi, H-7100) for particle morphology and electron spectroscopy (ESCA, VG Scientific ESCALAB 250) for chemical composition. Silver metal deposited was analyzed by atomic absorption spectroscopy (AA). The final 3% by weight of Ag was determined by AA.

2.2. Reaction of methyl iodide on Ag/TiO_2

The experiments of methyl iodide reaction with Ag/TiO_2 were carried out in a stainless steel IR cell, having two ZnSe windows for IR transmission and connected to a gas manifold pumped by a $60\,\mathrm{l\,s^{-1}}$ turbomolecular pump to reach a base pressure of $\sim 1 \times 10^{-6}$ Torr. The powdered Ag/TiO_2 was supported on a tungsten (W)-mesh which was held by two stainless steel clamps for sample heating. The samples were prepared by spraying the suspension of the above-prepared Ag/TiO_2 powder redispersed in the solvent water/acetone (15 ml/135 ml) onto the both sides of W-mesh. The W-mesh is held at a temperature of ∼50–60 °C by a home-made temperature programmed heating system. The solvents are flash evaporated leaving behind the uniform Ag/TiO_2 layer coated on the tungsten. Fig. 1 shows the SEM micrographs (scanning electron microscopy, Hitachi 3000) of Ag/TiO_2 coated W-mesh. The holes of the W-mesh were observed to fill up evenly from all sides as the Ag/TiO_2 suspension is sprayed onto it. This “slurry” technique for uniform deposition of powder sample on tungsten grid was originally designed by Yates’s group for studying the dehydroxylation of Al_2O_3 [24]. It has been applied extensively for the studies of adsorption and desorption of organic molecules on high area solids [21,25–27]. No tungsten participation in the reaction has been reported so far, nevertheless, we have no direct proof to exclude this possibility. The Ag/TiO_2 sample was then mounted onto the IR cell for in situ monitoring the reaction processes using FTIR (ABB Bomem MB104). The temperature measurement was done using the C-type thermocouple spot-welded on the center of W-mesh. Before each run of the experiment, the Ag/TiO_2 sample was subjected to UV pre-illumination at 373 K under the oxygen back-filled condition for 2 h so as to remove the possible hydrocarbons adsorbed on the Ag/TiO_2 surface. The IR data was determined in separate experiments using the newly prepared Ag/TiO_2 samples which were subjected to photoreduction and coating and/or pre-annealed at various temperatures. At least two sets of IR spectra were taken from different Ag/TiO_2 samples and the most typical sets were reported (Section 3). The values for peak intensity are subject to about 20–25% variability.

Fig. 2 shows the schematic presentation of the reaction apparatus (side view), including the vacuum system, gas manifold, UV-light source, and IR beam direction. In the photoreaction experiments, both, the irradiating light source and the IR beam, were 45° to the normal of the W-mesh position so that the photochemical reactions can be induced and detected simultaneously. The geometry of W-mesh relative to UV irradiation and IR detection is shown in Fig. 3. De-

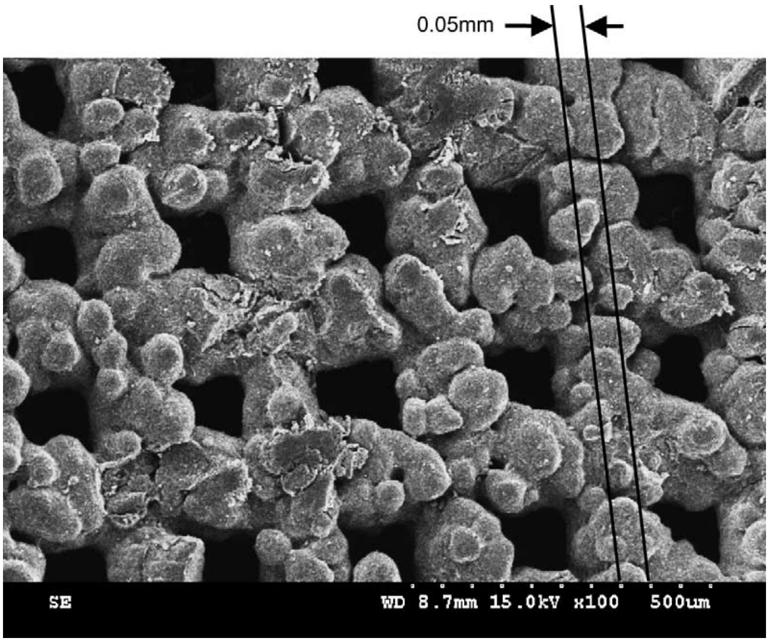

Fig. 1. Micrograph of uniform deposition of powder samples on tungsten mesh after slurry deposition as observed by scanning electron microscopy (SEM).

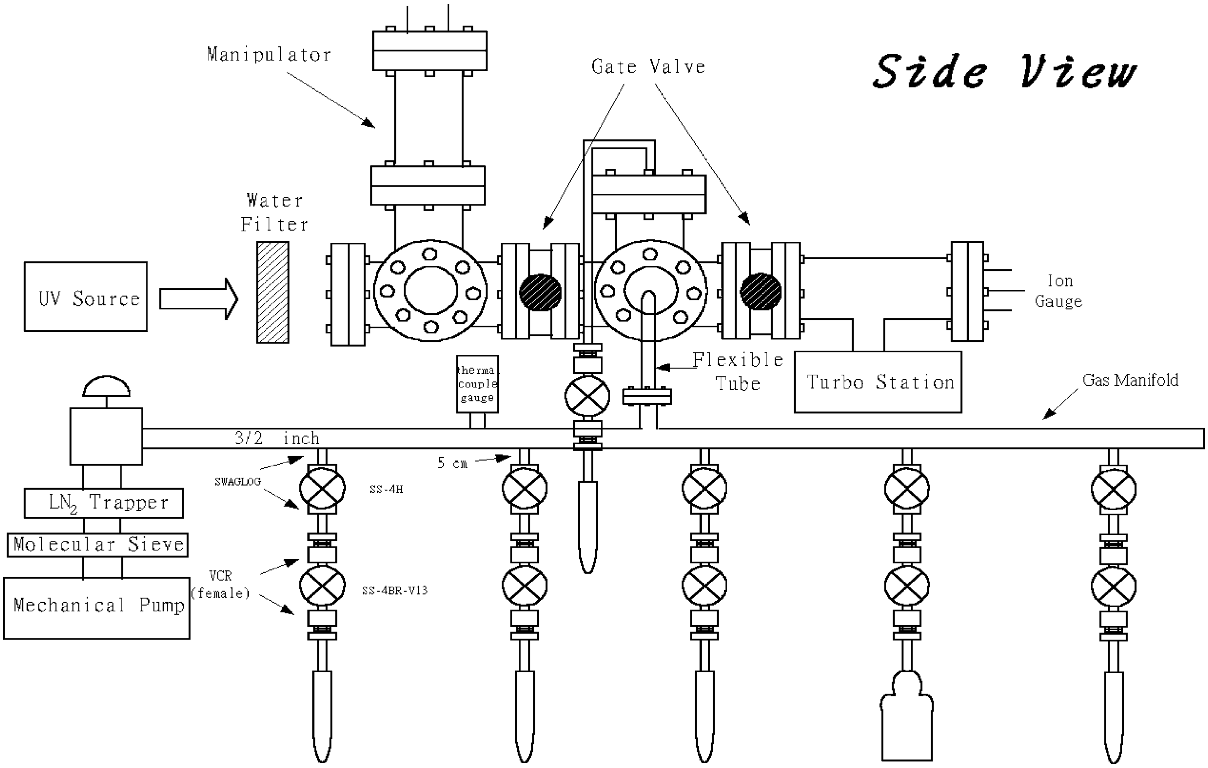

Fig. 2. Design of temperature variable infrared cell for in situ study of gas–powder catalyst interaction.

tailed description of this system can be found in the Yate's work [24].

Methyl iodide purchased from Aldrich (99.5%) was protected from light by alumnia foil and purified by cycles of freeze–pump–thaw before introducing into the IR cell.

3. Results and discussion

3.1. Characterization of Ag/TiO_2

To present the results of thermal- and photochemistry of CH_3I on Ag/TiO_2, we begin with the characterization of Ag

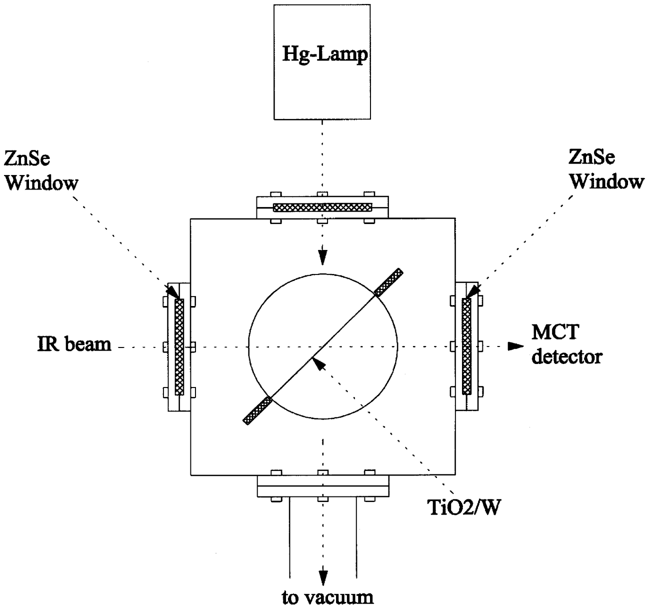

Fig. 3. The 45° geometry of W-mesh relative to UV irradiation and IR detection.

clusters deposited by photoreduction and its thermal stability. TEM is the useful technique for the observation of the size and shape of ultrafine particles. Fig. 4 shows the TEM micrographs of Ag/TiO_2 at various growing stages corresponding to irradiation time: (a) 0 min (before deposition), (b) 30 min, and (c) 90 min. The samples used for TEM analysis were prepared by placing a drop of the Ag/TiO_2 suspension (diluted 10-fold with ethanol) onto a 150-mesh Cu grid. The Degussa P25 TiO_2 particles are polygonal in shape (Fig. 4a). From Fig. 4b, it can be seen that the deposited Ag clusters were localized individually on the surface of the TiO_2 after the photoreduction. The shape of Ag/TiO_2 particles appeared in nebulous and conglomerated upon irradiation. The size of Ag/TiO_2 may be as large as 90 nm (Fig. 4c), which is larger than that of bare TiO_2 particles (∼13 nm). No isolated Ag nucleus off the TiO_2 substrate was observed, indicating that the Ag^+ ions were initially adsorbed on the reaction sites of TiO_2 and were then reduced by the surface trapped electrons to form nuclei as well as cluster of silver. The reduction of Ag^+ was accompanied by a decrease in the pH, indicating the replacement of surface protons by silver ions to form TiO–Ag bond on the TiO_2 surface ($TiOH + Ag^+ \rightarrow TiO\text{–}Ag + H^+$) [28]. Then the adsorbed Ag^+ ions were reduced/deposited on TiO_2 by the following stoichiometry: $4Ag_{ads}{}^+ + 2H_2O \rightarrow 4Ag^0 + 4H^+ + O_2$ [9,28]. Due to the existence of protons, the surface hydroxyl groups may be protonated to form $Ti\text{–}OH_2{}^+$ which then combines readily with another Ti–OH to form Ti–O–Ti oxygen bridge by eliminating a water molecule [29] and simultaneously releasing one proton ion. Such condensation process may pull together the primitive TiO_2 particles into a larger mass by building up further oxide network. Similar phenomenon has been observed in the preparation of Au/TiO_2 [30] and Pt/TiO_2 [31]. Wang et al. found that during the irradiation of a $HAuCl_4$ solution in the presence of TiO_2 colloid, the deposited Au clusters were localized on the surface of TiO_2 particles and the substrate part of Au/TiO_2 was larger than that of an individual TiO_2 before photodeposition [30].

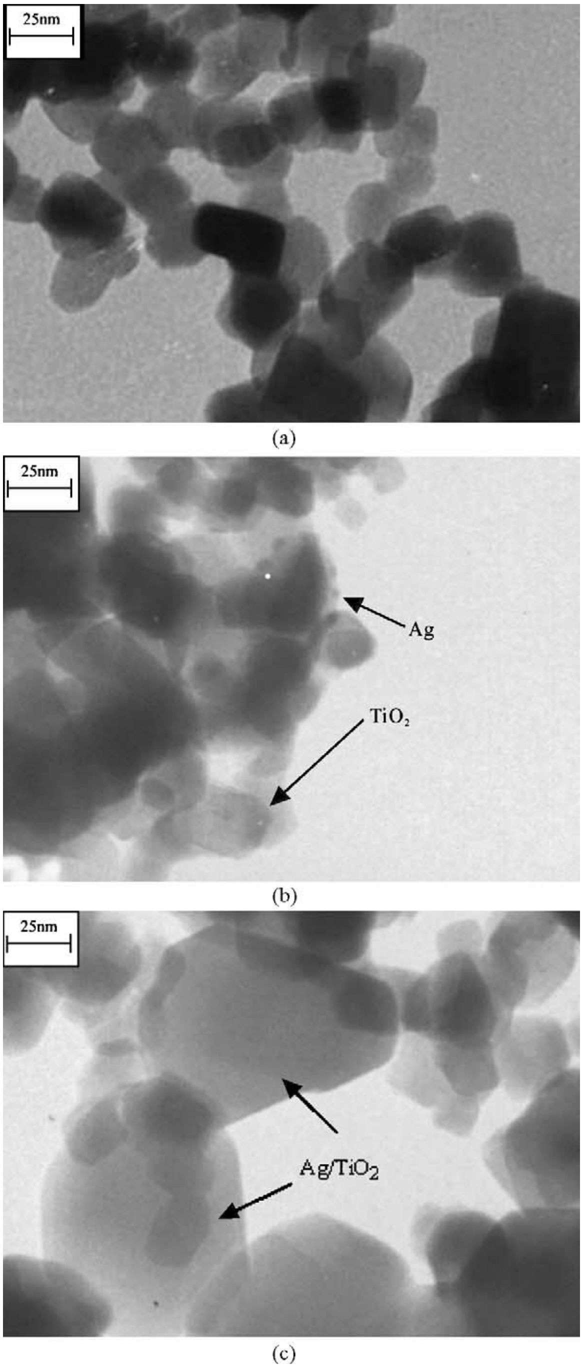

Fig. 4. TEM micrographs of (a) Degussa P25 TiO_2, (b) Ag/TiO_2 after photoreduction time of 30 min, and (c) 90 min.

According to TEM analysis, Ag was deposited on the surface of TiO_2. To confirm such deposition, ESCA measurement was performed. The ESCA spectra for O 1s peak, Ti 2p doublet, and Ag 3d doublet were observed (Fig. 5a-c). These

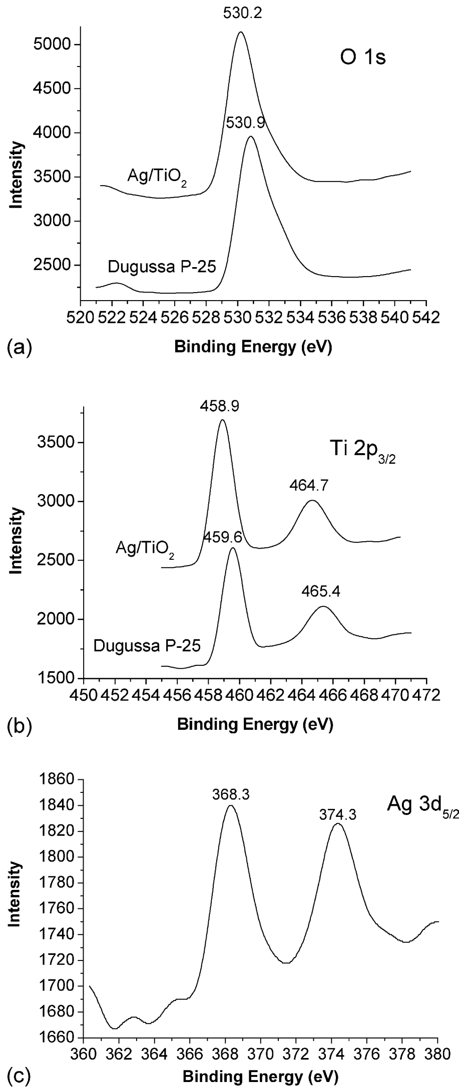

Fig. 5. ESCA spectra of Ag/TiO_2 for (a) O 1s, (b) Ti $2p_{1/2}$, and (c) Ag $3d_{5/2}$.

spectra confirmed the Ag deposition onto TiO_2. Only a small shift (∼0.7 eV) in the binding energy of Ti and O peaks was observed in Ag/TiO_2 from those of bare TiO_2 indicating no significant electronic interaction within the ESCA resolution between Ag and TiO_2. Su et al. have prepared Ag films on TiO_2(1 1 0) by thermal evaporation [20]. They have not observed any change in Ag binding energy, suggesting electron transfer does not occur in the Ag–TiO_2 interface. The small binding energy shift of Ti and O are attributed to the polarization effect.

The thermal stability of Ag on TiO_2 was monitored by AA upon loading Ag/TiO_2 sample into the IR cell and annealing to various temperatures (T_a). Thus the thermal stability was measured under the similar conditions that were used for studying adsorption and reactions. As shown in Fig. 6, the amount of Ag on TiO_2 diminished gradually after T_a exceeded 550 K. This result was vindicated by the weak interaction between Ag and TiO_2 as shown from ESCA study.

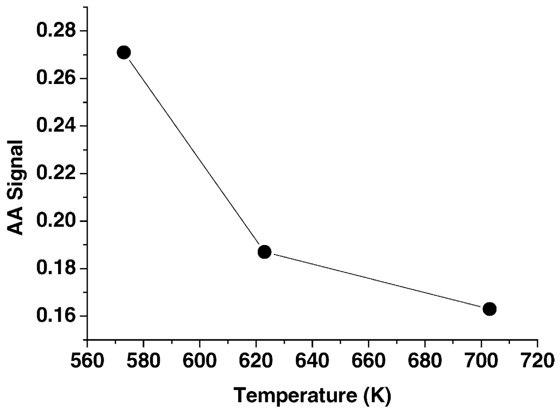

Fig. 6. The variation of Ag loading on Ag/TiO_2 measured by AA intensity as a function of annealing temperature.

3.2. Thermal reaction of CH_3I on Ag/TiO_2

The Ag/TiO_2 used in the thermal- and photoreaction (Section 3.3) with CH_3I was irradiated for 30 min. Fig. 7 shows the IR spectrum of Ag/TiO_2 at 308 K in contact with 20 Torr of $CH_3I_{(g)}$. Four major absorption peaks at 2980, 2958, 1261, and 1240 cm^{-1} are observed. By comparing the peak frequencies and their relative intensities with that from NIST standard reference database [32], it is concluded that the observed peaks are due to $CH_3I_{(g)}$ with the assignment of $CH_3^\bullet$ deformation (1240 and 1261 cm^{-1}), and stretching (2958 and 2980 cm^{-1}). This was also confirmed by CH_3I gaseous IR spectrum (not shown) measured in a separate experiment using the same optical path. Su et al. have previously reported the study of adsorption and reactions of methyl iodide on TiO_2 [21]. It was found that in the adsorption, CH_3I molecules directly bonded to the TiO_2 surface and form surface methoxy groups (OCH_3) with two major IR absorption peaks at 1245 and 2955 cm^{-1}. The absorption due to adsorbed $CH_3I_{(a)}$ are not obvious for Ag/TiO_2 because the amount of Ag/TiO_2 sample used in this exper-

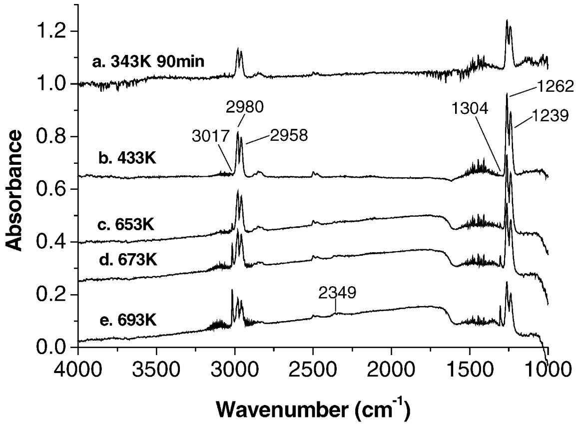

Fig. 7. The variation of IR spectra of Ag/TiO_2, in contact with CH_3I at 308 K, followed by heating to the indicated temperatures without the presence of oxygen.

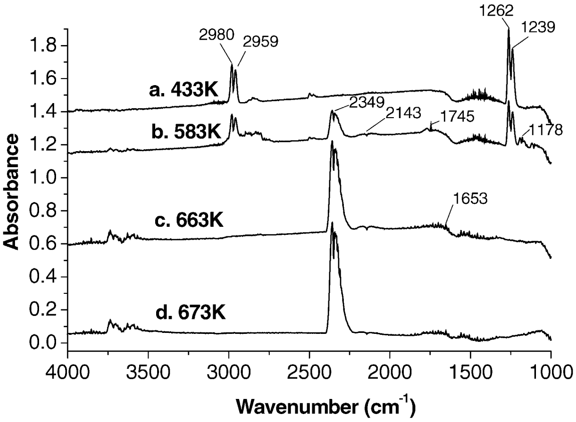

Fig. 8. The variation of IR spectra of Ag/TiO$_2$, in contact with CH$_3$I at 308 K, followed by heating to the indicated temperatures in the presence of oxygen.

iment was small and Ag might block part of the oxygen reaction sites for CH$_3$I adsorption. Therefore, the signal intensity from methoxy, if any of it was formed on the surface, would be difficult to be distinguished from the immense absorption intensity of CH$_3$I$_{(g)}$. Larger amount of catalyst could result in lower IR transmittance which may hamper the acquisition and the analysis of IR spectra. However, since the Ag/TiO$_2$ sample preparation process used in this work cannot completely remove the hydroxyl groups on the surface of Ag/TiO$_2$, the negative bands at 3600–3800 cm^{-1} due to the decrease of surface hydroxyl groups indicate the CH$_3$I adsorption on TiO$_2$. To study the thermal reaction of CH$_3$I with Ag/TiO$_2$, the Ag/TiO$_2$ sample was heated linearly at the rate of 2 K/s from 308 to 693 K in the presence of 20 Torr of CH$_3$I. The IR spectra were taken at various stages of heating. Upon thermal activation, two new peaks appear at 1304 and 3017 cm^{-1} revealing the formation of methane in the gas phase [21]. The reaction was initiated by dehydrogenation of OCH$_3$ groups during the heating process (discussed later). The methane starts to evolve at ~433 K and was the major product detected. A small but observable amount of CO$_2$ was also found at 2349 cm^{-1}.

Fig. 8 shows the IR spectra acquired at the indicated temperatures during heating of Ag/TiO$_2$ at the rate of 2 K/s up to 673 K in the presence of a mixture of 25 Torr of CH$_3$I and 70 Torr of O$_2$. It was clear that when oxygen coexists with CH$_3$I, the IR spectra change dramatically, indicating a completely different reaction pathways. No methane formation was detected in the reaction system from the temperatures 433 to 673 K. However, above 583 K, new IR peaks were observed at 2143, 1745, 1178, and 1653 cm^{-1}. These peaks represent partially oxidized intermediates, including carbon monoxide (CO$_{(g)}$, 2143 cm^{-1}), formaldehyde (CH$_2$O$_{(g)}$, 1745 cm^{-1}), dimethyl ether ((CH$_3$)$_2$O$_{(g)}$, 1178 cm^{-1}), and water (H$_2$O$_{(g)}$, 1653 cm^{-1}). The CH$_3$I declined continuously with increasing temperatures and however CH$_2$O$_{(g)}$ and (CH$_3$)$_2$O$_{(g)}$ showed their maxima at 583 K and beyond this temperature they declined gradually. The formation of dimethyl ether and the formaldehyde in the presence, and methane in the absence, of oxygen indicated C–I bond breaking during the interaction of CH$_3$I with Ag/TiO$_2$ although the adsorbed species was not observed directly. Notably, in this pathway, the fully oxidized product, carbon dioxide (CO$_{2(g)}$, 2439 cm^{-1}), replaced methane and became the major reaction products. The CO$_{2(g)}$ increased monotonically with increase in temperature. The formation of H$_2$O$_{(g)}$ reaches its maximum at ~660 K and then declines with simultaneous increase in surface hydroxyl groups as observed in the range of 3600–3800 cm^{-1}. Presumably, H$_2$O$_{(g)}$ was decomposed on Ag/TiO$_2$ at high temperature.

3.3. Photoreaction of CH$_3$I on Ag/TiO$_2$

The photochemical reaction of CH$_3$I on Ag/TiO$_2$ was first studied in the absence of oxygen. We monitored the reaction by in situ FTIR as the function of irradiation time intervals. Fig. 9 shows a series of IR spectra of Ag/TiO$_2$ in contact with CH$_3$I as a function of irradiation time, at 308 K after annealing the Ag/TiO$_2$ sample at 423 K. We found that following the irradiation, the amount of CH$_3$I decreased as indicated by the peaks at ~1261 and ~2980 cm^{-1}. Two peaks at 1661 and 1445 cm^{-1} revealed the formation of water and ethane ((CH$_3$–CH$_3$)$_{(g)}$). The intensity of C$_2$H$_6$ increases as a function of the photoirradiation time. A separate control experiment was performed to check the absolute effect of heating on reaction products since the Ag/TiO$_2$ temperature increased to ~330 K during the UV irradiation. As seen in the previous section, no significant thermal reaction was observed for CH$_3$I over Ag/TiO$_2$ at temperatures below 400 K. Obviously, the dissociation of CH$_3$I took place upon adsorption/irradiation on Ag/TiO$_2$. The dissociation-formed adsorbate species, presumably CH$_3$$^\bullet$ and/or OCH$_3$$^\bullet$ (see above) do not dehydrogenate, but recombine to give C$_2$H$_6$ and desorb from Ag/TiO$_2$. The coupling of CH$_3$$^\bullet$ to form ethane on metal or oxide surfaces has also been reported by several research groups [33–35]. The assignment of C$_2$H$_6$ is based on the previously reported

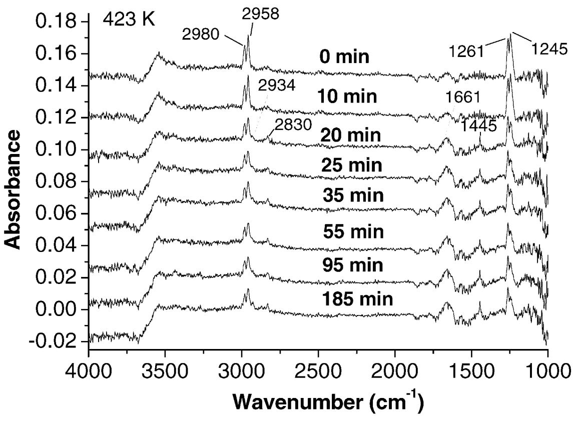

Fig. 9. The IR spectra of annealed (423 K) Ag/TiO$_2$ in contact with CH$_3$I as a function of irradiation time, at 308 K.

results. Cruz and Sheppard have measured the IR spectrum of ethane adsorbed on silica-supported platinum catalyst at 90 K [36]. They observed the strong IR absorption bands at 1463 and 2973 cm^{-1}, corresponding to $CH_3^\bullet$ antisymmetric bending and antisymmetric stretching, respectively. Moreover, Tejada and Eggers have studied the ethane adsorption on CsBr at 64 K using IR spectroscopy [37]. Similar absorption peaks but with significant shift (~15 cm^{-1}) in antisymmetric bending of $CH_3^\bullet$ bond were observed. The adsorption due to $CH_3^\bullet$ stretching is not obvious in our spectra, because under the present experimental conditions, the amount of C_2H_6 produced was much lower than the unreacted CH_3I, and its absorption might be buried in the large absorption bands CH_3I in the gas phase. Su et al. have recently studied the adsorption and reaction of monolayer CH_3I on Ag-covered TiO_2(1 1 0) single crystal surface [22]. They have found that the maximum thermal decomposition probability for 1 ML CH_3I on Ag/TiO_2(1 1 0) is about 62%. In addition to C_2H_6, desorption of a small amount of $(CH_3)_2O$ at temperatures above 280 K was also observed at multilayer coverages. Zhou et al. have investigated the thermochemistry of methyl iodide with Ag(1 1 1) and found that ~35% of monolayer CH_3I dissociates between 130 and 190 K to give adsorbed $CH_3^\bullet$ and I [38]. Post-irradiation of TPD spectra of multilayer CH_3I on Ag(1 1 1) resulted in the evolution of C_2H_6. Therefore, it is not unreasonable to assign ethane to be the photoreaction product of CH_3I with Ag/TiO_2. It is to be noted that for photoreaction of CH_3I on Ag-free TiO_2 powder, C_2H_6 was not observed after extensive illumination (not shown). Since the ethane molecules were produced by the coupling reaction between two methyl radicals, this result suggests that deposition of Ag on TiO_2 may enhance the CH_3I dissociation probably to form higher concentration of methyl radicals on the sample surface. We also noticed that the activity for CH_3I thermal dissociation on Ag/TiO_2(1 1 0) is higher than that on Ag(1 1 1), which might be due to the more free, 3D needle-like Ag structure [20] on TiO_2(1 1 0) compared to the more compact structure of Ag single crystal surface. Therefore, it is expected that the monodistributed and nano-sized Ag particles (Fig. 4b) on TiO_2 may improve the dissociation of CH_3I. Nevertheless, direct observation of CH_3I on Ag/TiO_2 is still unachievable.

The photoreaction of CH_3I with Ag/TiO_2 which was annealed at different higher temperatures was also carried out. Figs. 10 and 11 show a series of IR spectra of Ag/TiO_2 in contact with CH_3I as a function of irradiation time, at 308 K after annealing the Ag/TiO_2 sample at 523 and 623 K, respectively. We found that at these temperatures, the ethane formation was diminished due to the desorption of Ag from TiO_2. We also observed the changes in the baseline in the IR spectra when Ag/TiO_2 was annealed to the onset of Ag desorption temperature (~550 K) from TiO_2. Since in the present experiment, the IR spectra were obtained upon subtraction of Ag/TiO_2 IR spectrum before photoirradiation, change of substrate condition, i.e., the background spectrum, would vary the final IR spectra. Moreover, ultraviolet photons may create Ti^{3+} surface defects by photodesorption of molecular oxygen from TiO_2 as reported by Shultz et al. [39]. Such defects can be healed through the re-adsorption of oxygen to form Ti^{4+}:O_2^- complex [39], yet, the detected absorption feature would be affected.

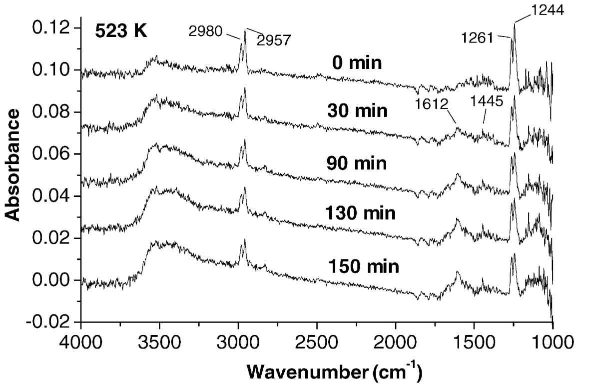

Fig. 10. The IR spectra of annealed (523 K) Ag/TiO_2 in contact with CH_3I as a function of irradiation time, at 308 K.

The photochemical reactions of CH_3I over Ag/TiO_2 were also studied in the presence of oxygen. Fig. 12 shows the IR spectra of the Ag/TiO_2 at 308 K in contact with a mixture of 2 Torr of CH_3I and 10 Torr of oxygen, before (a) and after photoillumination for 3 h (b). The reaction is completely different from that in the absence of oxygen. Instead of C_2H_6, $CO_{2(g)}$, $H_2O_{(g)}$, and surface formate groups (1380, 1551, 1620, and 2870 cm^{-1}) were observed to be the major photoreaction products under these reaction conditions. Moreover, these reaction products are not from thermal activation as discussed in the early section.

3.4. Reaction mechanism of CH_3I on Ag/TiO_2

The reaction mechanisms of thermal- and photoreactions of CH_3I on Ag/TiO_2 in presence as well as in the absence of oxygen are discussed in this section. Kinetically transient intermediates were not detected under the experimen-

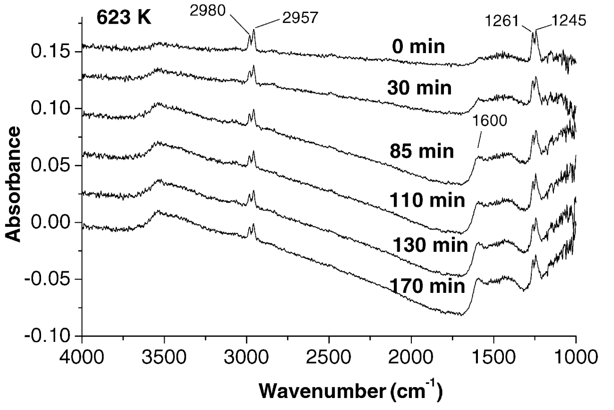

Fig. 11. The IR spectra of annealed (623 K) Ag/TiO_2 in contact with CH_3I as a function of irradiation time, at 308 K.

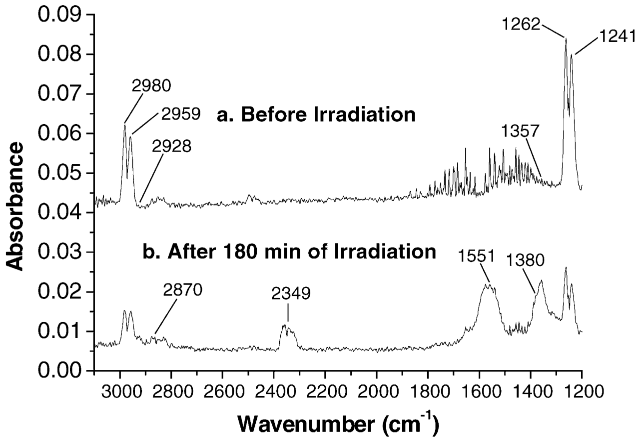

Fig. 12. IR spectra of Ag/TiO_2 in contact with CH_3I and oxygen mixtures (a) before and (b) after 3 h photoillumination.

tal conditions hence the reaction pathways proposed are based on the results published by several researchers. The IR study presented above for thermal reactions of CH_3I with Ag/TiO_2 in the absence of oxygen shows that only methane molecules were generated. Methane formation might be initiated by dissociation of CH_3I to form methoxy ($OCH_{3(a)}$), presumably on the TiO_2 [21], or methyl ($CH_{3(a)}$), on the Ag [40] of Ag/TiO_2. The methoxy groups may diffuse to oxygen-deficient defect sites on the TiO_2 and proceed C–O scission to form $CH_3^\bullet$ accompanying by the filling of surface oxygen vacancies [41,42]. A portion of the $CH_3^\bullet$ species might be dissociating to generate surface hydrogens (dehydrogenation) that react instantaneously with the remaining methyl groups to form methane molecules desorbing from Ag/TiO_2. In the presence of oxygen, $CO_{2(g)}$ was the major product and methane formation was not observed. In this reaction, three partially oxidized intermediates viz. $CH_2O_{(g)}$, $(CH_3)_2O_{(g)}$, and $CO_{(g)}$ were observed. Surface process followed completely different and relatively complicated reaction pathways. It is proposed that the methoxy groups formed by the decomposition of CH_3I onto the TiO_2 surface may dehydrogenate and incorporate with oxygen molecules to form formaldehyde (HCHO) desorbing from Ag/TiO_2. The formaldehyde may further react with TiO_2 to produce surface formates ($HCOO^-$) that upon heating might be easily decomposed to form $CO_{(g)}$ and $CO_{2(g)}$. Similar observations can be found in the study of adsorption and transformation of formaldehyde on various oxide surfaces [41]. The coupling of two methoxy groups and/or one methoxy group with one methyl group results in the formation of dimethyl ether, $(CH_3)_2O_{(g)}$. Similar products were observed in the thermal reactions of CH_3I with bare TiO_2. However, it is to be noted that the temperatures at which evolution of products occurs are different, i.e. in the absence of oxygen, the onset temperature for methane molecule is ∼623 K which is much higher than that of 433 K for same reaction on Ag/TiO_2. The similar difference in onset temperatures for thermal reactions in the presence of oxygen was observed. This can be explained by the salt effect in which the strong I–Ag interaction may expedite the dissociation probability of CH_3I to form $CH_3^\bullet$ on Ag/TiO_2 surface.

Photoreaction of CH_3I on Ag/TiO_2 yielded C_2H_6 and H_2O as the major products. The C_2H_6 might be formed through the direct coupling of two methyl ($CH_3^\bullet$) groups and the surface hydrogens resulting from C–H bond scission might be attacking the surface hydroxyl groups to form water molecules. Methyl radical is an important species in the catalytic oxidative coupling of CH_4 to form C_2H_6 and subsequently C_2H_4. Keller and Bhasin proposed that the formation of C_2H_6 is resulted from the surface coupling of adsorbed $CH_3^\bullet$ [33]. In contrast to this mechanism, Lunsford and co-workers proposed that a homogeneous gas-phase coupling of $CH_3^\bullet$ radicals, formed by the surface abstraction of H-atoms from CH_4, was the primary pathway for C_2H_6 formation [43,44]. This mechanism was further vindicated by Campbell et al. using the MIESR (matrix isolation electron spin resonance) technique [45]. Nevertheless, in the present study, no ethane formation was found in the absence of Ag/TiO_2 and/or bare TiO_2. Over the bare TiO_2 powder, the photoreaction of CH_3I in absence of oxygen is negligible. However, over the Ag/TiO_2 powders photoreaction produced C_2H_6. This clearly indicates that the dissociation of CH_3I to form $CH_3^\bullet$ was enhanced due to the Ag deposition on the TiO_2 surface.

Upon irradiation of CH_3I with Ag/TiO_2 in the presence of oxygen the major products formed were CO_2, H_2O, and surface formats. Oxygen (O_2), due to its high electron affinity, is able to capture the photoelectron generated from band-gap excitation and thereby form superoxide ion (O_2^-). Other oxide species, such as O_3^- and O_3^{3-} may be produced as well during the UV irradiation. According to the EPR (electron paramagnetic resonance) study, O_2^- is the only species that can be stable at room temperature [46]. On the other hand, the surface methoxy groups may receive photoholes from TiO_2 band-gap excitation, following the decomposition to form $–OCH_2^\bullet$ radical (dehydrogenation) which then incorporates with O_2 to form peroxy radicals, $–OCH_2COO^\bullet$. The proton (H^+) formed by dehydrogenation may recombine with O_2^- to form $HOO^\bullet$ radicals which is believed to be formed in close proximity to $–OCH_2COO^\bullet$ on the catalyst surface [26]. Therefore, the $–OCH_2COO^\bullet$ and $HOO^\bullet$ may recombine to produce cyclic $–OCH_2OOOOH$ tetraoxides and at last decompose to produce $HCOO_{(a)}$ and H_2O. Part of formates may decompose to form $CO_{2(g)}$ [25].

4. Conclusion

Transmission infrared spectroscopy has been employed to study the adsorption and reactions of CH_3I, methyl iodide, over Ag/TiO_2. First we have characterized the Ag/TiO_2 prepared by photoreduction. The Ag/TiO_2 is nebulous in shape and conglomerated upon irradiation. Weak interactions, probably due to the polarization-induced electric bilayer between Ag and TiO_2, with partial charge formed on the sides of the TiO_2. In the thermal reactions, in the absence of oxygen, $CH_{4(g)}$ and in the presence of oxygen, $CO_{2(g)}$ is the major product. In presence of oxygen reactions yielded other oxygen-containing products, including $CO_{(g)}$, $CH_2O_{(g)}$, $(CH_3)_2O_{(g)}$, and $H_2O_{(g)}$. Dissociation of CH_3I to form $CH_3^{\bullet}$ in photoreaction was observed to be enhanced due to the deposited Ag on the TiO_2 surface. Thus the Ag/TiO_2 facilitates formation of ethane by combining $CH_3^{\bullet}$ in the absence of oxygen. However, in the presence of oxygen, $CO_{2(g)}$, $H_2O_{(g)}$, and surface formate groups were formed. More experimental data is required to vindicate the proposed mechanisms for thermal and photoreaction of methyl iodide with Ag/TiO_2.

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