The role of iodide promoter in selective oxidation of methanol to formaldehyde

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The interaction of a CH_3I promoter and a commercial electrolytic silver catalyst was investigated using XPS, UPS and *in situ* confocal microprobe Raman spectroscopy. XPS and UPS results show evidence for formation of AgI on the surface of the silver catalyst. Interestingly, XPS results show no evidence for formation of any carbon species on the silver catalyst at room temperature, implying that CH_3I can be used as a "pure" I-modifier in the catalytic oxidation of CH_3OH to HCHO. UPS results show a positive work function change ($\Delta\phi > 0$) for the I-modified catalysts. *In situ* Raman studies show that both the adsorption and reaction of methanol were promoted on the modified silver surface. The present experimental results provide not only an understanding of the surface chemistry of the silver catalyst but also a further understanding of the promotion effect of CH_3I in the selective oxidation of CH_3OH to HCHO.

Keywords: iodine, promoter, oxidation of methanol, XPS/UPS, *in situ* Raman spectroscopy

1. Introduction

It is well known that silver catalysts are extensively used in the industrial synthesis of ethylene oxide and formaldehyde [1,2]. The huge product capacity as well as the great economic profits of the two products has motivated continuous studies for purpose of improving the characteristics of the catalysts [3–15]. In the commercial ethylene epoxidation process, it is routine that traces of organic chloride are continuously added to the feed to enhance the selectivity toward the formation of the desired ethylene oxide product, but at the cost of decreasing the overall reaction rate [1,16]. Intensive studies have been carried out for better understanding of the promoting effect of Cl in the epoxidation process, and it is described that chlorine inhibits the dissociative adsorption of oxygen by poisoning dissociative sites of ensembles of more than one Ag atom [1,17]. In the partial oxidation of methanol to formaldehyde, most investigations were focused on the addition of various metal elements or oxides in silver catalysts for improved catalyst characteristics [3–17]. Various mechanisms concerning the modifying action were proposed, such as variations in O_2 adsorption [3], mechanical block of the catalyst surface [9], and change of the electronic work function and electron density in the silver catalyst [11,12]. Nevertheless, very few reports have mentioned the addition of trace promoters in the feed for improved performance of the catalysts. Fliol [18] reported the promoting effects of HCl and HBr on the silver catalysts, however, these two additives were just too erosive to be used in the commercial process. Very recently, we reported a promising CH_3I promoter which showed significant promoting effects in the partial oxidation of methanol, where both the overall reactivity and the selectivity toward formaldehyde were substantially enhanced [19]. For a better insight into the nature of the iodine promoter in the partial oxidation of methanol to formaldehyde, it is important to study the basic interaction of CH_3I with the commercial electrolytic silver catalyst.

The present paper reports a surface characterization of the interaction of CH_3I with the electrolytic silver catalyst by using X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), and *in situ* Raman spectroscopy. The XPS and UPS studies showed only evidence of AgI formation on the CH_3I-exposed silver surface whereas no deposited carbon species were observed on the surfaces of the catalysts, implying CH_3I can be used as a "pure" I-modifier in the catalytic oxidation of methanol to formaldehyde. UPS results also show a positive work function change ($\Delta\phi > 0$) for silver catalysts upon CH_3I exposure. *In situ* Raman studies show that both the adsorption and reaction of methanol were promoted on the modified silver surface, suggesting improved catalytic activity on I-modified catalysts. The present experimental results not only provide an understanding of the surface chemistry of CH_3I on silver catalysts but also provide a better understanding of the promotion effect of CH_3I in catalytic oxidation of methanol to formaldehyde on CH_3I-modified silver catalysts.

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2. Experimental

The triply refined electrolytic silver catalyst (40–60 mesh, purity >99.999%) was purchased from Shanghai Petroleum Chemical Engineering Co. Ltd (China). The sample was formed by pressing the powered electrolytic silver catalyst into pellet form prior to insertion into the UHV system (base pressure of $<5\times10^{-10}$ Torr). Sample heating up to 600 °C was achieved using an electric resistance heater through two tantalum rods spot-welded to the sample. Temperature was measured by a Ni–Cr/Ni–Si thermocouple attached to the sample. The sample surface was thoroughly cleaned by cycles of argon bombardment (~2 kV) and oxidation-annealing [20]. Exposure to CH_3I and O_2 was performed by backfilling the UHV chamber. The spectroscopic investigations were performed in a Perkin–Elmer PHI 5000C ESCA System equipped with facilities for XPS and UPS analysis. The XPS data were collected using Al Kα (1486.6 eV) radiation at 14 kV voltage and 18 mA emission current; the spherical capacitor energy analyzer (SCA) was operated in the retarding mode using a pass-energy of 23.5 eV to collect the high resolution spectra. The UPS spectra were taken using the He I line with fixed analyzer transmission (FAT) and fixed retard ratio (FRR) modes. The absolute work function of the sample was measured from the low kinetic energy threshold of the secondary electron emission of He I UPS spectra.

In situ Raman investigations were conducted on a confocal microprobe Raman system (Dilor Labram I) [21] equipped with a holographic notch filter and a CCD detector. The Raman spectrum was obtained based on an Olympus BX40 system and by using a 50× long working-length objective (8 mm). The exciting wavelength was 632.8 nm from a He–Ne laser with a power of 20 mW and a spot of ca. 3 μm on the sample surface. The powdered sample was put in a specially designed quartz *in situ* Raman sample cell [22]. The surface of the sample was extensively cleaned at 600 °C under flowing atmosphere for about 30 min. Methanol and CH_3I were purified by a series of freeze–pump–thaw cycles before being dosed to the catalyst. Gaseous methanol or CH_3I was introduced into the sample cell by high purity N_2 (99.9995%).

3. Results and discussion

3.1. Reaction of CH_3I with silver on the surface

Figure 1 presents the I 3d XP spectra obtained from the as-prepared sample as a function of CH_3I exposure at

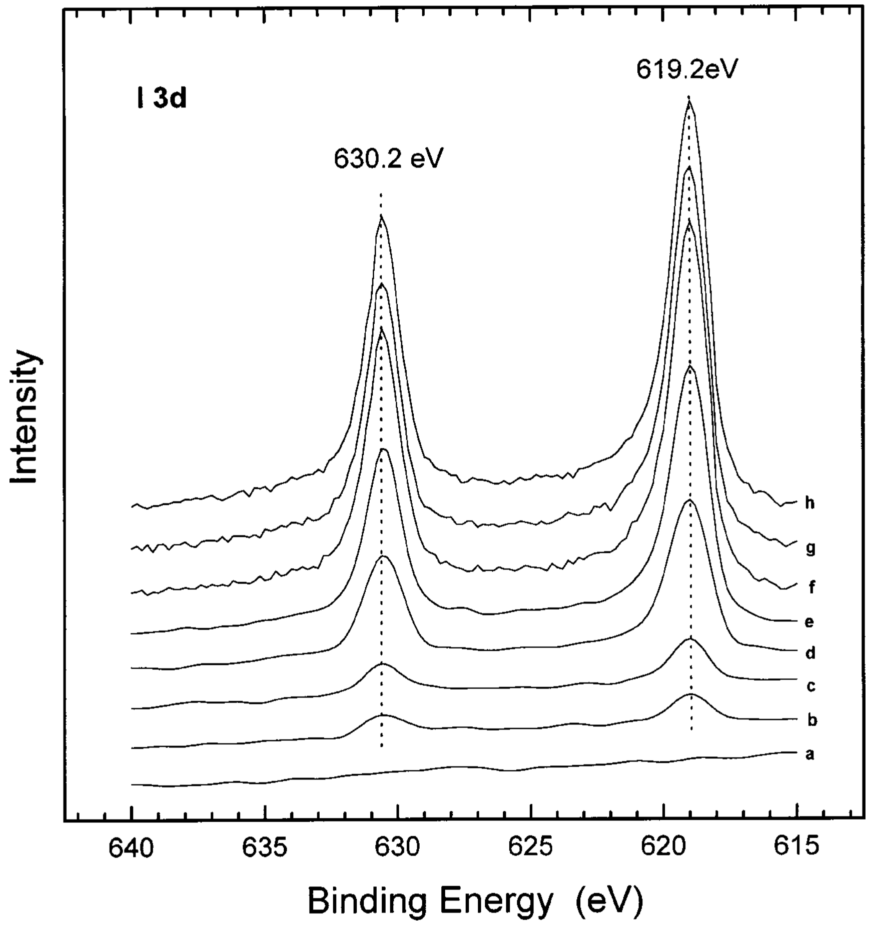

Figure 1. I 3d XP spectra as a function of CH_3I exposure: (a) clean surface, (b) 0.1 L, (c) 0.2 L, (d) 1 L, (e) 2 L, (f) 10 L, (g) 50 L and (h) 100 L.

room temperature. Two well-defined features at 619.2 and 630.2 eV corresponding to I $3d_{5/2}$ and I $3d_{3/2}$ are observed in the spectra. The I 3d features grow with increasing exposure. The chemical state of iodine can also be readily determined from figure 1. The binding energy (BE) of the I $3d_{5/2}$ under all CH_3I exposures is 619.2 eV, which is in good agreement with the XPS data for a silver iodide electrode by Strydom et al. [23]. By reference to the binding energy for molecular iodine at 619.9 eV [24], there is a down shift of about 0.7 eV for the chemisorbed iodine on the surface of the silver catalyst. Thus, the chemisorbed iodine is assigned as AgI on the surface of the catalyst.

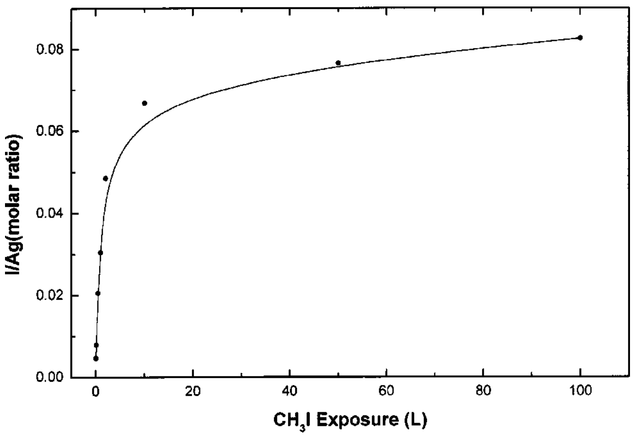

Figure 2. The atomic ratio of I/Ag as a function of CH_3I exposure.

Figure 2 displays the atomic ratio of chemisorbed iodine to Ag as a function of the CH_3I exposure measured by the XPS I/Ag peak-to-peak ratio. At low CH_3I exposure (<10 L), it is clear that the surface concentration of iodine grows almost linearly with the CH_3I exposure. When the exposure exceeds 10 L, the increment of the I 3d peak intensity turns slowly. At high exposure of 100 L, the adsorption of CH_3I is saturated. The atomic ratio of I/Ag is about 0.083 at saturation exposure, suggesting the formation of AgI islands on local sites of the silver catalyst. The growth behavior of AgI is quite similar to the case of the formation of AgCl islands on a Ag(111) surface [25].

The C 1s XPS spectrum taken from the CH_3I-modified catalyst is not shown here for the extremely weak C 1s peak intensity, suggesting an extremely low surface concentration for the carbon species on a CH_3I-modified silver catalyst. This unexpected observation indicates that only chemisorbed iodine is present on a CH_3I-modified silver catalyst, implying that CH_3I has been used as a “pure” I-modifier in catalytic oxidation of methanol to formaldehyde [19]. We note that this is consistent with the TPD data for CH_3I adsorbed on Ag(111) at 110 K [26], which will be discussed in detail below.

The determination of the chemical state of silver from Ag $3d_{5/2}$ peaks has always been shown to be very difficult [27,28]; there remains much controversial for the interpretation of these results. We do not observe binding energy shifts for Ag $3d_{5/2}$ peaks on the CH_3I-exposed sil-

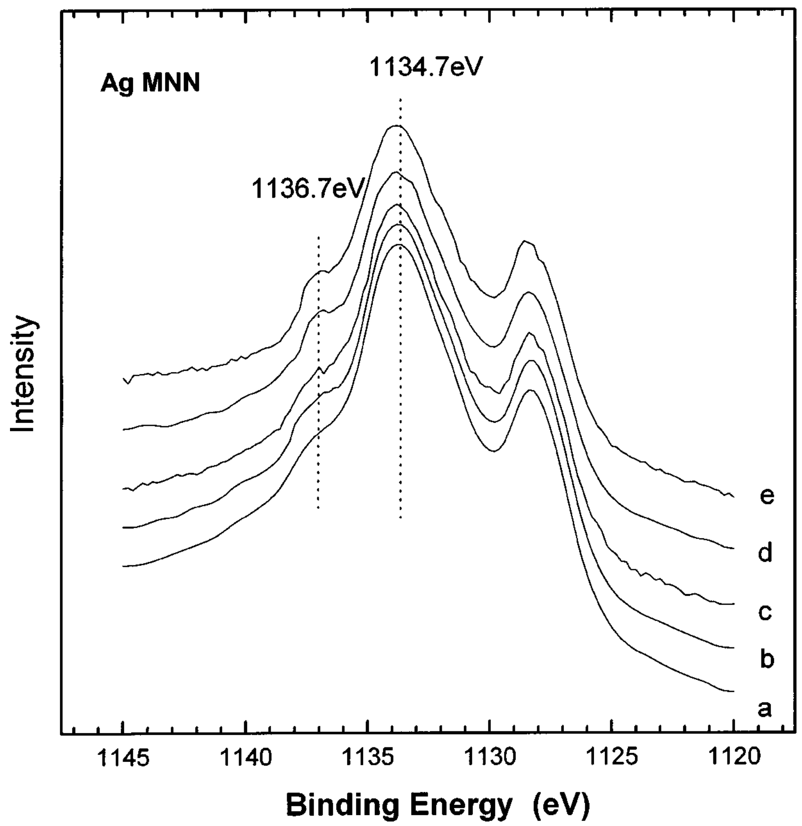

Figure 3. XPS Ag MNN spectra acquired at different exposures of CH_3I: (a) clean surface, (b) 0.2 L, (c) 1 L, (d) 10 L and (e) 100 L.

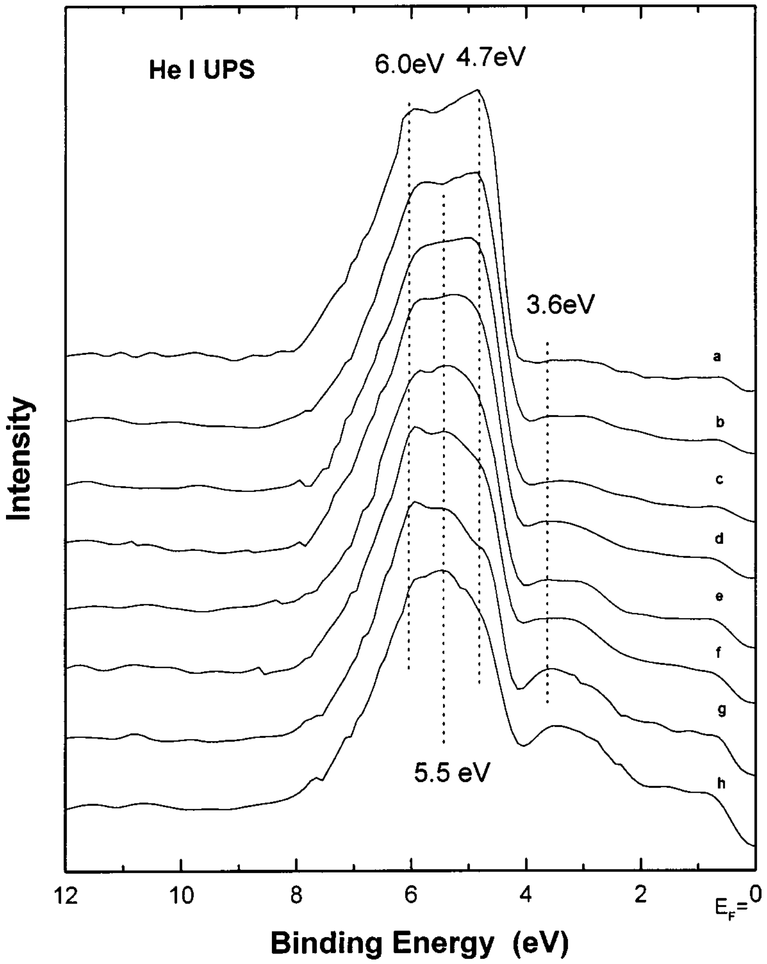

Figure 4. He I UP spectra for electrolytic silver as a function of CH_3I exposure: (a) clean surface, (b) 0.1 L, (c) 0.2 L, (d) 0.5 L, (e) 1 L, (f) 2 L, (g) 5 L and (h) 10 L.

ver surface. However, the MNN Auger transitions of silver are sensitive to the formation of ionic bonds between Ag and other elements [28]. The XAES spectra of Ag(MNN) obtained from the sample with varying CH_3I exposure is shown in figure 3. With increasing CH_3I exposure, the Ag XAES peaks become broader. A shoulder at 1136.7 eV (pure silver: 1134.7 eV) gradually turns stronger along with the increase of CH_3I exposure. The shift is well consistent with the AES spectra of a Cl-exposed Ag(111) surface, where the peak shift of ∼2 eV was assigned to Ag(I) [25]. Further, the Auger parameter (α), which can be used to determine the chemical states of surface elements primely [29], is calculated as: $\alpha = E_{\mathrm{k(A)}} + E_{\mathrm{b(P)}}$, where $E_{\mathrm{k(A)}}$ represents the kinetic energy of Ag MNN, $E_{\mathrm{b(P)}}$ represents the binding energy of Ag $3d_{5/2}$. The value of α for I-modified silver is 726.0 eV, while that for pure silver is 724.0 eV. The difference between them is also ∼2 eV, which not only agrees well with the standard values [29], but also accords with the reference mentioned above [25].

Figure 4 presents the He I UP spectra for the electrolytic silver catalyst as a function of CH_3I exposure. The spectrum from the clean silver catalyst is shown in figure 4(a); two features at 4.7 and 6.0 eV are clearly observed. The two dominant features are consistent with the valence photoemission spectrum for metallic Ag by Rodriguez et al. [30], and are therefore assigned to the Ag 4d band. Upon CH_3I exposure, a significant spectral change is observed. Exposure to CH_3I induces attenuation in the 4.7 and 6.0 eV features. With increasing CH_3I exposure, two additional features at 3.6 and 5.5 eV are gradually intensified. The feature at 5.5 eV is assigned to AgI by reference to the valence band spectrum for AgI by Mason [31], while the peak at 3.6 eV is attributed to I 5p according to Nunes et al. [32]. This interpretation is consistent with the XAES data. Therefore, the UPS results along with the XAES data show further evidence for formation of AgI on the surface of the catalyst.

It is interesting to find that the AgI formed on the sample surface is not stable on the surface under UHV conditions even at room temperature. The I $3d_{5/2}$ peak for the 12000 L CH_3I-pre-exposed sample as a function of temperature is shown in figure 5. After 12 h in the UHV chamber (figure 5(b)), the single peak of I $3d_{5/2}$ splits into double peaks, corresponding to atomic (618.9 eV) and molecular iodine (619.7 eV) respectively. When the sample is heated to 100 °C, the double peaks merge into a single peak again while the peak position shifts to 618.9 eV, indicating that all

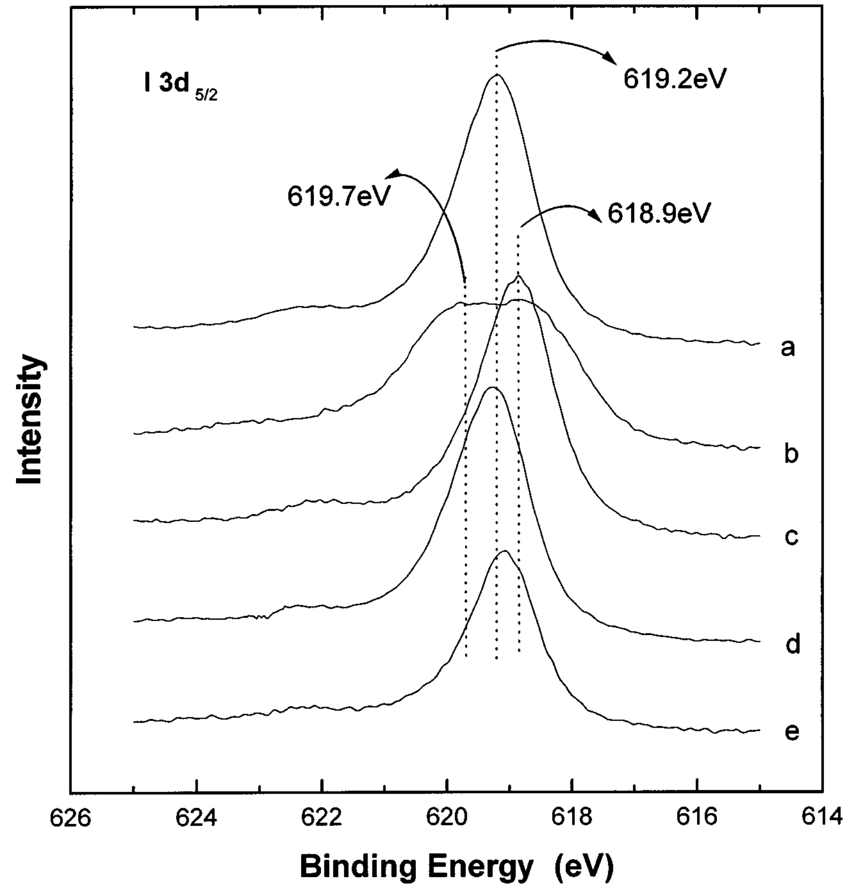

Figure 5. I $3d_{5/2}$ XP spectra at different treating conditions: (a) exposing to 12000 L CH_3I, (b) after 12 h in UHV chamber, (c) heating to 100 °C, (d) heating to 200 °C and (e) heating to 400 °C.

iodine species converse to be atomic [24]. When the sample is heated to 200 °C the iodine atoms react with silver to form AgI again, which is shown in figure 5(d). When the sample was heated up to 400 °C, the peak area of I $3d_{5/2}$ is gradually attenuated, indicating the desorption of chemisorbed iodine from the silver surface. There were no I $3d_{5/2}$ signals observed on the sample surface after the sample was heated at 600 °C for 2 h, indicating that the silver iodide on the silver surface would undergo decomposition at elevated temperatures. The present observation agrees well with the modification case in the catalytic reaction, where the CH_3I promoter must be continuously added to the feed for lasting improved performances [19].

The reaction of CH_3I with silver results in an increase of the work function of the silver catalyst. The change of work function as a function of CH_3I exposure is shown in figure 6. According to figure 6, $\Delta\phi$ increases rapidly with increasing CH_3I exposure. When the silver surface is exposed up to 7 L of CH_3I, further exposure could only change the work function very little. The absolute value of $\Delta\phi$ saturates at +0.5 eV. This value is almost the same as that obtained from an oxygen exposing experiment [33], but much smaller compared with that for Cl adsorption (1.3 eV) [30]. Upon the adsorption of gas molecules on a metal surface, the work function changes are usually associated with electron transfer between adsorbate and metal, and the value represents the extent of the electron transfer. The sameness of work function change value between CH_3I and oxygen exposure suggests that these two systems may have a similar valence electron structure. Hence it is reasonable to observe the similar adsorption and reaction behavior with methanol on iodide- and oxygen-preadsorbed silver surfaces in the partial oxidation of methanol

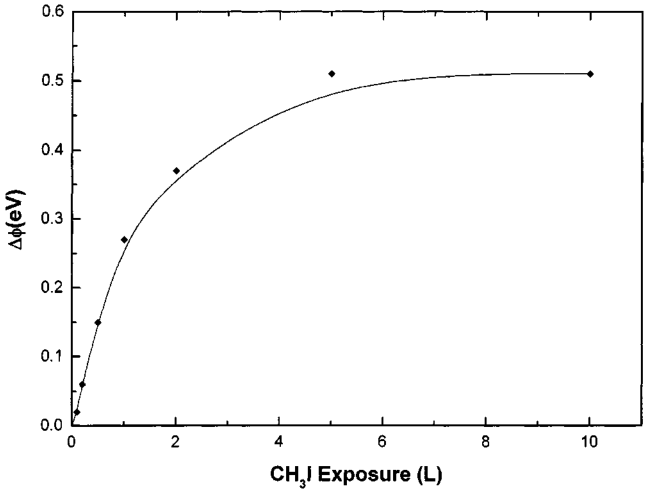

Figure 6. The work function change ($\Delta\phi$) for the catalyst as a function of CH_3I exposure.

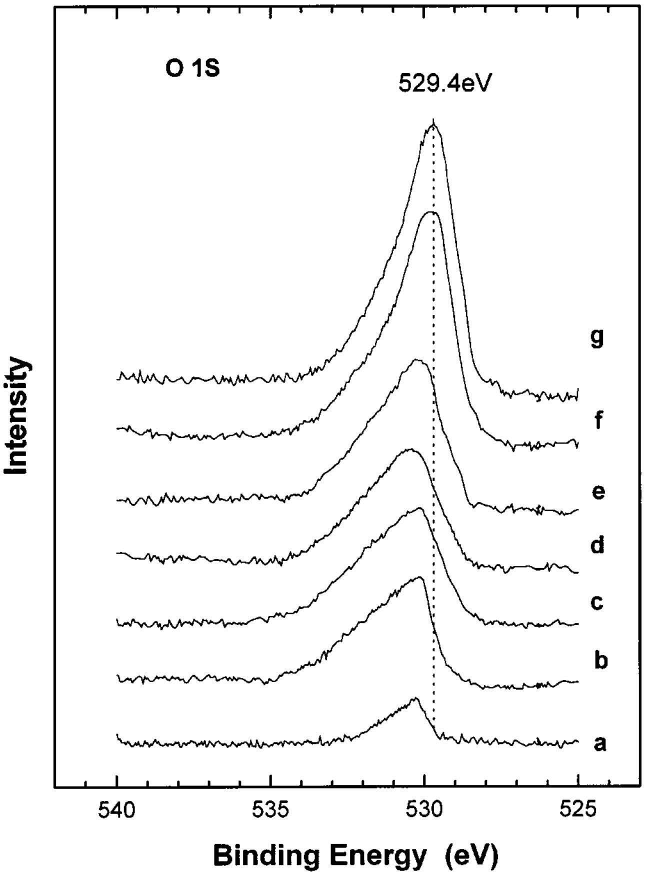

Figure 7. O 1s XP spectra for exposure to 12500 L O_2 of 50 L CH_3I-pre-dosed silver surface as a function of temperature: (a) background, (b) 25 °C, (c) 100 °C, (d) 200 °C, (e) 400 °C, (f) 500 °C and (g) 600 °C.

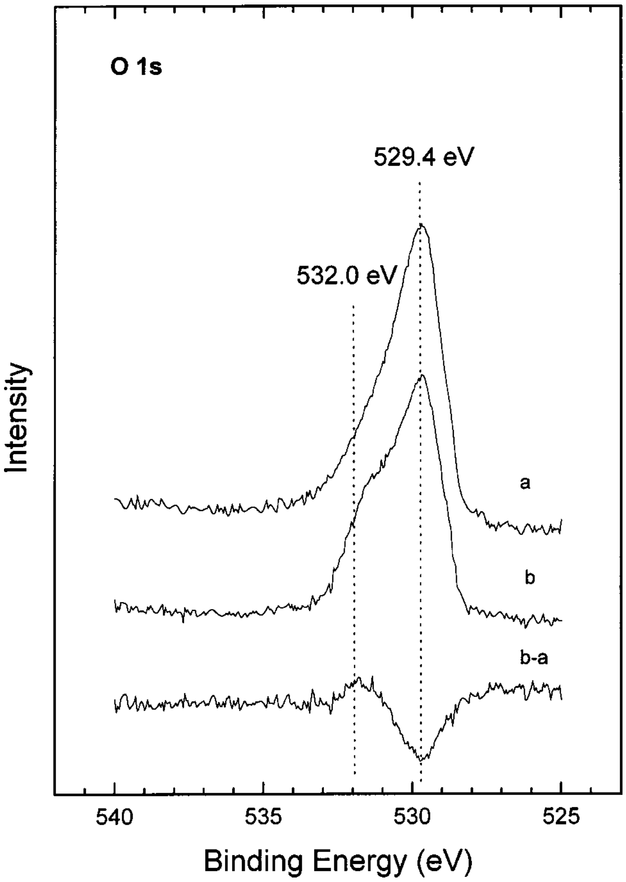

Figure 8. O 1s XP spectra before and after exposure to 12500 L CH_3I: (a) the same as (g) in figure 7, (b) after exposure to 12500 L CH_3I, (b) − (a) difference spectra.

to formaldehyde. We propose that iodine plays a similar role as oxygen in the oxidation of methanol to formaldehyde. Since iodine itself will not take part in the oxidation of methanol but can promote the adsorption of methanol at the same time, this interpretation is well consistent with the enhancement of both the selectivity and the overall activity in the CH_3I-promoted reaction [19].

3.2. Effects of iodine on the adsorption of oxygen

Figure 7 displays the temperature dependence of O 1s XP spectra for exposure to 1.2×10^4 L O_2 of a 50 L CH_3I-pre-exposed silver surface. The O 1s peak intensity gradually increases with increasing adsorption temperature. This result is similar to that on clean silver surface, but the intensity of O 1s peak under this condition is relatively smaller, implying that iodine atoms may have replaced some oxygen adsorption sites. This conclusion was further confirmed by exposing an O_2-pre-covered silver surface to CH_3I (figure 8). Figure 8(a) shows the O 1s XP spectrum for 1.2×10^4 L oxygen exposed silver surface, the O 1s peak has a binding energy at 529.4 eV and is assigned to the strong adsorbed atomic oxygen [34]. Subsequent exposure to 1.2×10^5 L CH_3I produces significant spectral changes for the O 1s peak (figure 8(b)). The peak at 529.4 eV is weakened along with the appearance of a shoulder at 532.0 eV. To illustrate the spectral change more clearly, the difference spectrum is displayed also in figure 8. A strong negative peak at 529.4 eV corresponding to the strongly adsorbed atomic oxygen [34] indicates that certain adsorbed oxygen species have been replaced by iodine, while the weak positive peak at 532.0 eV suggests the appearance of molecular oxygen species [34]. It is noted that the present observation is quite similar to the adsorption of chlorine on Ag(111) [35]. It is noted that the relative intensity ratio of the negative peak to the positive one reflects the decrease of the total amount of adsorbed oxygen upon the subsequent exposure to CH_3I.

3.3. The adsorption of methanol on CH_3I-modified silver surface

An *in situ* Raman spectroscopy experiment was carried out to investigate the adsorption and reaction of methanol on a AgI-modified silver surface. After the sample was carefully cleaned at high temperature, a N_2 flow mixed with small amount of CH_3I was introduced to the sample cell to mimic the real catalytic reaction. Methanol vapor mixed with N_2 was passed through the catalyst at room temperature. But no Raman signals corresponding to chemisorbed methanol were observed. Upon heating to 100 °C, two

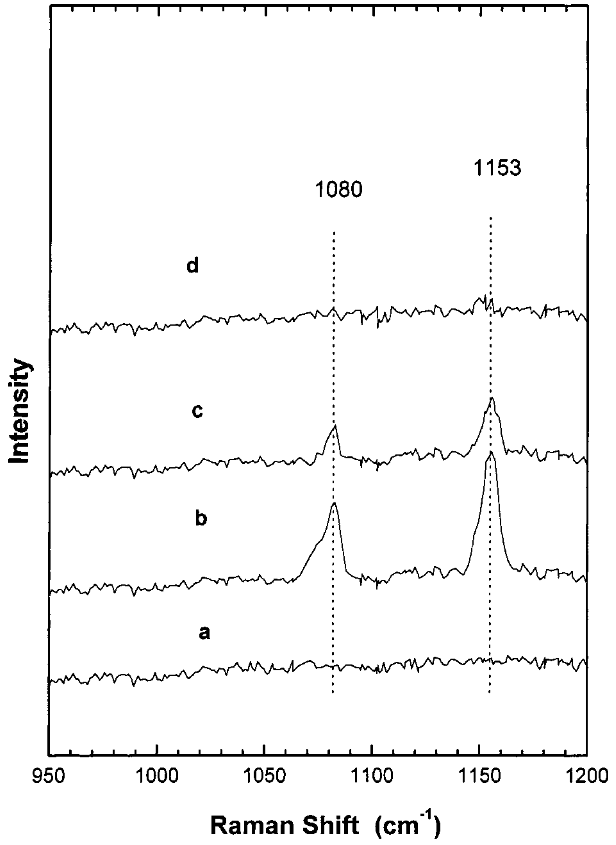

Figure 9. *In situ* Raman spectra of chemisorbed methanol on I-modified surface of electrolytic silver catalyst: (a) 25 °C, (b) 100 °C, (c) 200 °C and (d) 300 °C.

bands are evident at 1080 (ν(CO)) and 1153 cm^{-1} (ρ(CH)) (figure 9), typical for methoxide (CH_3O–) adsorbed on silver surface [36]. Upon heating to 200 °C, these two bands are attenuated and disappeared at 300 °C, indicating that methanol could be adsorbed and decomposed on the iodine-modified silver surface. Since methanol cannot be chemisorbed on the clean surface of silver, this experiment yields direct evidence of the promotion of CH_3I on the adsorption and reaction of methanol over silver catalysts. It is well known that oxygen promotes methanol adsorption, so there goes the so-called "oxygen-induced adsorption" [2]. We suggest that, in our case, the "iodine-induced adsorption" of methanol plays an essential role in the promoting action.

3.4. Discussion

The trace CH_3I promoter has been reported as an excellent modifier in the partial oxidation of methanol to formaldehyde; both the selectivity and activity were profoundly promoted [19]. The XPS/UPS study of the interaction of the CH_3I with electrolytic silver catalysts showed only formation of AgI on the surface of the silver catalysts. The extremely low surface concentration for carbon species on CH_3I-exposed catalyst implies that CH_3I has been used as a "pure" I-modifier in the catalytic oxidation of methanol to formaldehyde. This interesting observation is, however, in excellent agreement with the latest TPD results for CH_3I on Ag(111) by Wu et al. [26]. Their TPD experiments exhibited C_2H_6 desorption at 255 K for CH_3I adsorbed on Ag(111) at 110 K due to the C–C coupling reaction of the surface-bound $CH_3\cdot$ fragments upon thermal activation. In the present case, it is expected that CH_3I would decompose fully upon initial adsorption on the polycrystalline silver catalysts, then the resulted $CH_3\cdot$ fragments undergo a quick C–C recombination and desorb as C_2H_6 from the catalyst at room temperature. Hence, it is reasonable that our XPS C 1s data do not show evidence for the presence of carbon species on CH_3I-modified silver catalysts.

The presence of two additional features at 3.6 and 5.5 eV in UPS spectra together with the significant increase of the surface work function reflected that the valence band electron density of the catalyst was significantly changed upon the exposure to CH_3I. The nature of the active sites of the silver catalysts was considered as an intrinsic property of silver, determined by unique characteristics of the valence electronic shell [10]. It was expected that a promoted catalytic silver catalyst could be achieved by appropriate modifying on the valence electronic shell of the silver. This is consistent with the present promoting effects of the iodide additive in the catalytic oxidation of methanol to formaldehyde.

The XPS characterization of the adsorption of oxygen on a CH_3I-pre-dosed silver surface revealed that the formation of AgI on the silver surface would inhibit the following adsorption of O_2 although the temperature dependence behavior was quite similar to that on a clean silver surface. Further study of the XPS O 1s peak for post-exposure to CH_3I of an O_2-pre-dosed silver surface indicated that the O1s peak at 529.4 eV corresponding to strong adsorbed atomic oxygen species was attenuated, while a peak at 532.0 eV associated with the adsorbed molecular oxygen species appeared. It can be concluded that there were variations in oxygen adsorption on the AgI-modified catalyst surface. It is well documented that those different forms of oxygen adsorbed on silver direct the different reaction pathways on silver surface, such as dehydrogenation, partial or deep oxidation [2]. In our case, the formation of AgI on the silver surface would alter the population of different adsorbed oxygen species on the catalyst surface. The I-modified silver surface was found to inhibit certain strongly adsorbed atomic oxygen species corresponding to deep oxidation. It is well known that only atomic oxygen atoms take part in the partial oxidation of methanol to formaldehyde. However, molecular oxygen can also be detected under the reaction conditions, which can be interpreted as a precursor of atomic oxygen [37]. This can well explain the enhancement of the selectivity to formaldehyde in the CH_3I-promoted partial oxidation of methanol to formaldehyde.

Recently, the promoting effects of iodine have also been explored theoretically by performing a bond order conservation Morse potential (BOC-MP) study by our research group [38]. By calculation, we have found that the partial oxidation of methanol to formaldehyde is preferable to the direct dehydrogenation pathway. The promoting effects of CH_3I to the catalyst were interpreted as not only controlling the concentration of surface atomic oxygen, but also promoting the replenishing of surface oxygen during the processing of the reaction. Hence, apart from the equilibrium between the gaseous molecular oxygen and the adsorbed oxygen, there is also another equilibrium between the adsorbed molecular oxygen and the atomic oxygen so that the concentration of atomic oxygen could be controlled. If the atomic oxygen was consumed, it could be replenished faster from the adsorbed molecular oxygen and the adsorbed molecular oxygen was just like a storeroom for atomic oxygen.

Our XPS analysis also shows that the AgI formed by exposing CH_3I to the silver catalyst is unstable even at room temperature under UHV conditions. Upon heating to 600 °C ($\sim$900 K, typical temperature for partial oxidation of methanol), the disappearance of I 3d features indicates the decomposition of AgI and desorption of I_2 from the silver surface. This result indicates that chemisorbed iodine on a polycrystalline silver surface is much more stable than that on a Ag(111) surface, suggesting CH_3I a desirable modifier for high temperature oxidation of methanol to formaldehyde. It is noted that this observation agrees well with our previous analysis for the CH_3I-modified silver catalyst exposed to a clean feed for 2 h [19], where the surface reaction of CH_3I with silver and decomposition of AgI was proposed as:

$$2Ag + 2CH_3I \rightarrow 2AgI + C_2H_6 \qquad (1)$$

$$2AgI \rightarrow 2Ag + I_2 \qquad (2)$$

Again, the gradual loss of the promoting effects under clean feed [19] confirms the essential effects of surface AgI species to the catalyst. Hence, to maintain the improved performance, the promoter must be continuously added into the feed.

The *in situ* Raman study shows evidence for methanol chemisorption on the I-modified electrolytic silver catalyst. Two vibrational features at 1080 and 1153 cm^{-1} were observed, corresponding to chemisorbed methanol on CH_3I-modified silver catalyst. The “iodine-induced-adsorption” of methanol is coincident with the improved total activity in the CH_3I-modified partial oxidation of methanol to formaldehyde.

4. Conclusions

In summary, the promoting effects of CH_3I on the partial oxidation of methanol to formaldehyde have been studied by using XPS, UPS, and *in situ* Raman spectroscopy. XPS and UPS results show only the presence of AgI species on CH_3I-modified silver catalysts, implying that CH_3I has been used as a pure I-modifier in the promotion reaction of methanol to formaldehyde. UPS experiments show a positive work function change ($\Delta\phi > 0$) for I-modified silver catalysts, reflecting the modification of the valence electronic shell of the silver catalyst by the formation of AgI species on the silver surface. The observation of the “iodine-induced-adsorption” of methanol in Raman experiments further implied that the total activity was also improved on the CH_3I-modified silver surface. The present experimental results provide not only an understanding of the surface chemistry of CH_3I on silver catalysts but also a better understanding of the promotion effect of CH_3I in the catalytic oxidation of methanol to HCHO on CH_3I-modified silver catalysts.

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