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In situ Raman studies on the interaction of oxygen and methanol with an iodine-modified electrolytic silver catalyst

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In situ Raman spectroscopy was used to study the interaction of iodine-modified electrolytic silver with oxygen and methanol at atmospheric pressure at temperatures between 25 and 500 °C. It is shown that the presence of iodine inhibits the formation of surface oxygen species corresponding to deep oxidation and reduces the vibrational wavenumber of the modes corresponding to surface oxygen species. Moreover, it is found that methanol can be adsorbed and reacted on the surface of the modified silver without the co-adsorption of oxygen, resulting in iodine-induced adsorption of methanol. The intermediates at various temperatures were identified as methoxy and formate groups. According to the results, the reaction pathways in the practical process were proposed and compared with the conclusion obtained from the system without iodine modification, and remarkably close agreement was observed. The detailed mechanism of the oxidative reaction of methanol and the promotion effect of iodine modifier on the working catalyst is also discussed. Copyright © 2002 John Wiley & Sons, Ltd.

INTRODUCTION

Silver is widely used as an industrial catalyst for the production of formaldehyde via methanol oxidation and for ethylene epoxide via ethylene oxidation.[1,2] Many researchers have devoted studies to the improvement or the mechanisms involved in these processes owing to the great importance of these two chemicals.[3–15] Recently, we reported a promising CH₃I promoter that showed significant promoting effects in partial oxidation of methanol, where it was found to achieve an excellent yield of formaldehyde as high as 93% at 98% conversion of CH_3OH over an iodine-modified electrolytic silver catalyst in contrast to 85% at 94% conversion without iodine modification.[16] To gain an insight into the nature of the iodine promoter in the partial oxidation of methanol to formaldehyde, x-ray/ultraviolet photoelectron spectroscopy (XPS/UPS) studies on the basic interaction of iodine with a commercial electrolytic silver catalyst were performed in previous work.[17] It was shown that the chemisorbed iodine was present as AgI on the surface of the electrolytic silver catalyst and the valence electronic shell of the silver catalyst was modified by

the formation of AgI species on the silver surface, which resulted in a change of the surface work function. Therefore, we assumed that the appearance of AgI on silver surface would inhibit the formation of the atomic oxygen species corresponding to a deep oxidation pathway. However, our previous studies were all conducted in an ultra-high vacuum (UHV) system, with low exposure of molecular oxygen. Considering the very different conditions between the UHV system and the industrial process, the states of adsorbed oxygen and the reaction intermediates when exposed to methanol on iodine-modified electrolytic silver under reaction conditions have not yet been clarified. Also, the detailed molecular mechanism of the partial oxidation of methanol over iodine-modified electrolytic silver has not yet been reported. *In situ* Raman spectroscopy has been proved to be a powerful and highly sensitive method for obtaining surface vibration information, which can now provide unique opportunities to investigate surface species under practical reaction conditions.[18] In the present work, *in situ* confocal microprobe Raman spectroscopy was employed to investigate the nature of oxygen species and the dissociative adsorption of methanol on an iodine-modified electrolytic silver surface in an attempt to elucidate the reaction mechanisms of the selective oxidation reaction of methanol to formaldehyde.

EXPERIMENTAL

The triply refined electrolytic silver catalyst (40–60 mesh, purity >99.999%) was purchased from Shanghai Petroleum Chemical Engineering (Shanghai, China) and used without further purification. *In situ* Raman studies were carried out on a confocal microprobe Raman system (Dilor Labram I)[19] equipped with a holographic notch filter and a CCD detector. The Raman spectra were recorded based on an Olympus BX40 system and by using a $50\times$ working-length objective (8 mm). The exciting wavelength was 632.8 nm with radiation from a He–Ne laser with a power of 20 mW at the surface of the sample and a spot of *ca.* 3 μm on the sample surface. Powdered sample was placed in a specially designed quartz *in situ* Raman sample cell.[20] The surface of the sample was extensively cleaned at 600 °C under a flow of purified air for about 30 min. Methanol (AR) and CH_3I (AR) were used as purchased. Gaseous methanol or CH_3I was introduced into the sample cell by bubbling high-purity N_2 (99.9995%) through their solutions at 25 °C under atmospheric pressure.

RESULTS AND DISCUSSION

Interaction of oxygen with iodine-modified electrolytic silver catalyst

It was found that fresh electrolytic silver usually exhibited very weak Raman features after thermal treatment at 450 °C under an oxygen flow followed by a pure N_2 flow. A typical Raman spectrum in the 400–1300 cm^{-1} region is displayed in Fig. 1(a). Four Raman features at 403, 677, 857 and 1018 cm^{-1} are present. Based on the literature, these bands are assigned to subsurface oxygen, O_2^{2-}, atomic oxygen and O_2^{-} species, respectively.[21,22] After the sample had been exposed to flowing O_2/N_2 and subsequently swept with highly pure N_2 at room temperature, the intensity of the Raman band at 857 cm^{-1} increased significantly while both bands at 677 and 1018 cm^{-1} shifted to lower wavenumber values and the intensity of the former decreased, as shown in Fig. 1(b). In addition, the band at 403 cm^{-1} was split into two bands at 415 and 460 cm^{-1}. The results are in good agreement with that from Boghosian *et al.*,[23] who also observed strong Raman signals at 815 and 870 cm^{-1}, where 815 cm^{-1} appeared as a shoulder band, similar to the shape of the Raman peak from our atomic oxygen. Because the appearance of the strong atomic oxygen Raman band was probably due to the surface-enhanced Raman spectra (SERS) effect in Boghosian *et al.*'s system, it can be suggested that the same SERS effect is also present on the surface of iodine-modified silver in the present work. A typical Raman spectrum of pre-oxidized electrolytic silver on exposure to CH_3I is shown in Fig. 1(c). The band at 857 cm^{-1} changes from a wide band to a much stronger, sharp, symmetrical band, indicating that iodine modification reduces the kinds of surface atomic oxygen species. On the other hand, the sub-surface oxygen species changes from double bands to a single band at 459 cm^{-1} again suggesting

that the kinds of the sub-surface oxygen species are also reduced with iodine modification. According to the practical catalytic reaction data, the surface of the iodine-modified electrolytic silver was favorable for the dehydrogenation reaction of methanol, resulting in an increase in the yield of formaldehyde, which may be ascribed to the excellent unitary of the kinds of the surface oxygen species.

The change of the Raman vibration bands of oxygen species on the iodine-modified silver catalyst surface with temperature under a pure N_2 flow is shown in Fig. 2. The Raman band obtained at 100 °C [Fig. 2(b)] shows that the intensity of the 856 cm^{-1} band is decreased compared with that at 25 °C, indicating that the atomic oxygen species is not stable and its vibration intensity decreases with increase in temperature. A new band at 929 cm^{-1}, and also a shoulder band at 838 cm^{-1} attributed to atomic oxygen species, appear at 100 °C. Also, the intensity of the bands at 403 cm^{-1} due to subsurface oxygen species and at 667 cm^{-1} belonging to O_2^{2-} species decrease dramatically. Subsequent heating to 200 °C [Fig. 2(c)] causes the reappearance of subsurface and O_2^{2-} species. These could result from the dissolution of atomic oxygen in the bulk and re-population on the surface region. Further heating to 400 °C, as shown in Fig. 2(d), caused a substantial decrease in atomic oxygen species responsible for the 856 cm^{-1} band. Also, the Raman bands at 403 and 667 cm^{-1} still exist in the spectrum, indicating that the subsurface and O_2^{2-} species are very stable at elevated temperature.
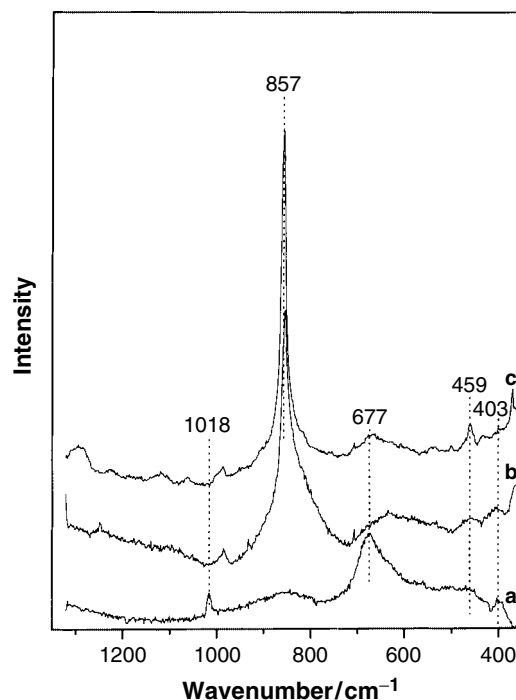

Figure 1. Raman spectra of O_2 adsorption on an iodine-modified electrolytic silver catalyst. (a) Background; (b) treatment with O_2/N_2 at room temperature; (c) exposure to 10 Torr CH_3I.
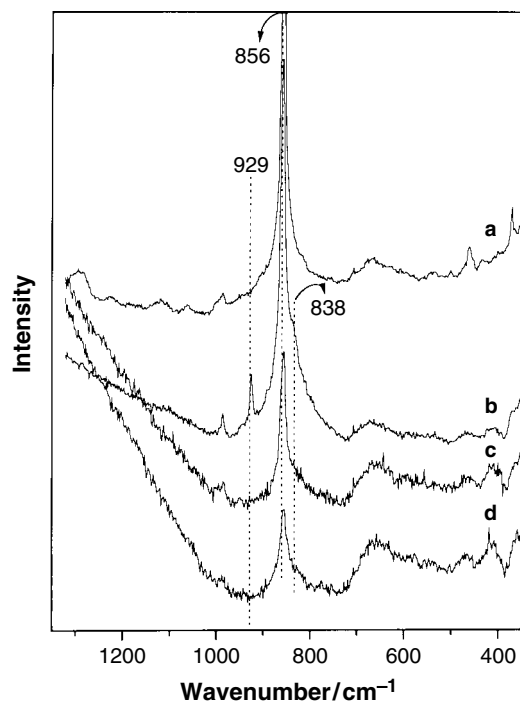
Figure 2. Variation of Raman spectra of the O species with treatment temperature on an iodine-modified electrolytic silver catalyst. (a) 25; (b) 100; (c) 200; (d) 400 °C.

Figure 3. Raman spectra of the interaction of CH_3OH with an iodine-modified electrolytic silver catalyst at central wavenumber 800 cm^{-1}. (a) Background; (b) 25; (c) 100; (d) 300; (e) 500 °C.

Interaction of iodine-modified electrolytic silver catalyst with methanol

The interaction of iodine-modified electrolytic silver with CH_3OH was also investigated by introducing gaseous CH_3OH with a pure N_2 flow. The sample was exposed to a $CH_3OH–N_2$ mixture at room temperature, and no obvious changes in the Raman spectra were observed except that the band at 403 cm^{-1} decreased, which can be ascribed to the chemisorption of CH_3OH. The Raman spectra of iodine-modified silver at various temperatures with pre-adsorption of CH_3OH are illustrated in Fig. 3. Heating the sample to 100 °C results in the appearance of both the 1088 and 1159 cm^{-1} bands. Based on the vibrational wavenumbers of methoxy species on different metal surfaces as listed in Table 1,[24] these two bands can be assigned to $v(CO)$ and $\rho(CH)$ vibrations. Both bands disappear upon heating the catalyst to 300 °C under a pure N_2 flow. At the same time the intensity of the 860 cm^{-1} band decreases whereas the 658 cm^{-1} band increases. Further heating to 500 °C causes an increase again of the intensity of 860 cm^{-1} band and a decrease in the band at 658 cm^{-1}.

Focusing on the band region centered at 1600 cm^{-1}, as shown in Fig. 4, no obvious vibrational bands appear in the region below 100 °C. Upon heating to 200 °C, two weak vibrational features at 1430 and 1555 cm^{-1} appear. Further heating to 300 °C results in an increase in both bands and heating to 400 °C eventually results in uniting of the two bands into one broad band. The intensity of the broad band
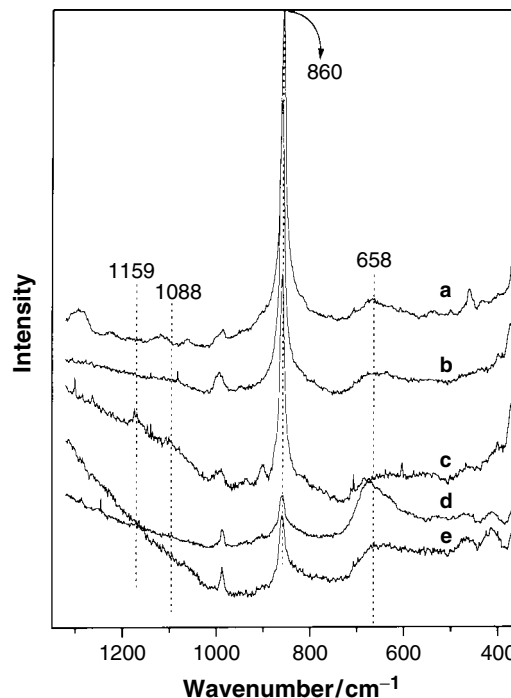
decreases greatly on heating to 500 °C. Compared with the results of vibrational wavenumbers of formate species as listed in Table 2,[24] these two bands can be assigned to stretching modes of $v_s(OCO)$ and $v_{as}(OCO)$ from formate species, respectively.

It can be concluded that methanol may be chemisorbed and dissociated to methoxy groups on the surface of iodine-modified electrolytic silver. Since methanol cannot be chemisorbed on a clean surface of silver, this conclusion gives direct evidence of the promoting effect of iodine on the adsorption and reaction of methanol over an electrolytic silver catalyst. It is commonly accepted that oxygen can promote the adsorption of methanol on a silver surface, and this phenomenon is called as 'oxygen-induced adsorption.'[2] In our system, a similar phenomenon also exists and 'iodine-induced adsorption' of methanol may play an essential role in the enhancement of the activity and selectivity for the oxidative dehydrogenation of methanol.

Interaction of iodine-modified silver catalyst with oxygen and methanol

In situ Raman studies of CH_3OH with an electrolytic silver catalyst under an oxidative atmosphere were also conducted under a $CH_3OH–air$ flow. Figures 5, 6 and 7 show the resulting spectra centered at 800, 1600 and 3100 cm^{-1}, respectively. The vibrational bands that occur at room temperature at 1020, 1352, 1430, 1580, 2844 and 2940 cm^{-1}

Table 1. Vibrational wavenumbers (cm^{-1}) and mode assignments for methoxy species on various surfaces

Mode	Pt(111)	Pd(100)	Rh(100)	Ru(100)	Fe(100)	Ni(100)	Cu(100)	Zn(0001)	Ag(110)
ν_{as}(CH)	2910	2905	2960	2955	2895	2910	2910	2995	2915
ν_s(CH)	—	—	2890	2810	—	2790	2830	2885	—
δ(CH)	1430	1455	1440	1435	1430	1440	1450	1485	1450
δ(CO)	—	—	1115	1140	—	1150	—	—	1150
ν(CO)	1000	997	1005	1005	1020	1030	1010	1030	1040
ν(M−OMe)	370	—	400	325	405	400	290	510	330

Table 2. Vibrational wavenumbers (cm^{-1}) and mode assignments for formate species on various surfaces and for HCOO$^-$ in sodium salt

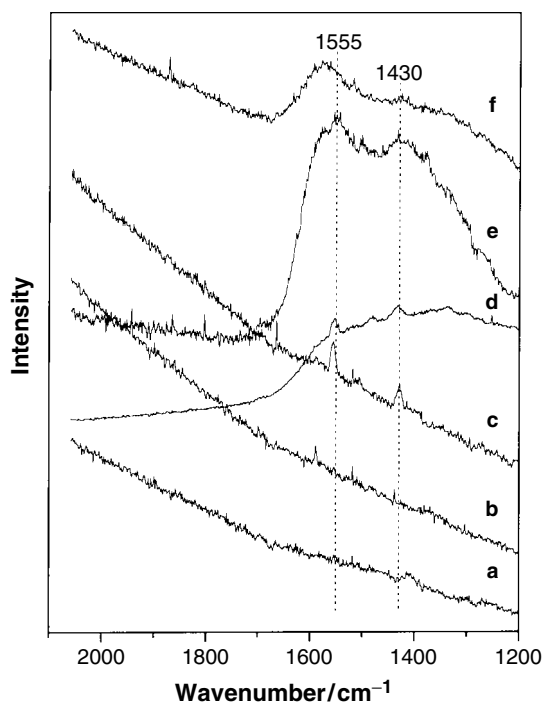| Mode	Ag(110)	Ag(111)	Cu(100)	Cu(110)	Cu/SiO$_2$	HCOONa
ν_{as}(CH)	2900	2970	2910	2940	2935	2841
ν_s(CH)	—	2840	2840	2840	2851	—
ν_{as}(OCO)	1640	1680	1640	1560	1553	1567
δ(CH)	—	1488	—	—	—	1377
ν_s(OCO)	1340	1312	1330	1360	1351	1366
π(CH)	1050	—	—	—	—	1073
δ(OCO)	770	750	760	780	—	772
ν(M−O)	280	—	340	390	—	—

Figure 4. Raman spectra of the interaction of CH$_3$OH with an iodine-modified electrolytic silver catalyst at central wavenumber 1600 cm^{-1}. (a) Background; (b) 25; (c) 200; (d) 300; (e) 400; (f) 500 °C.
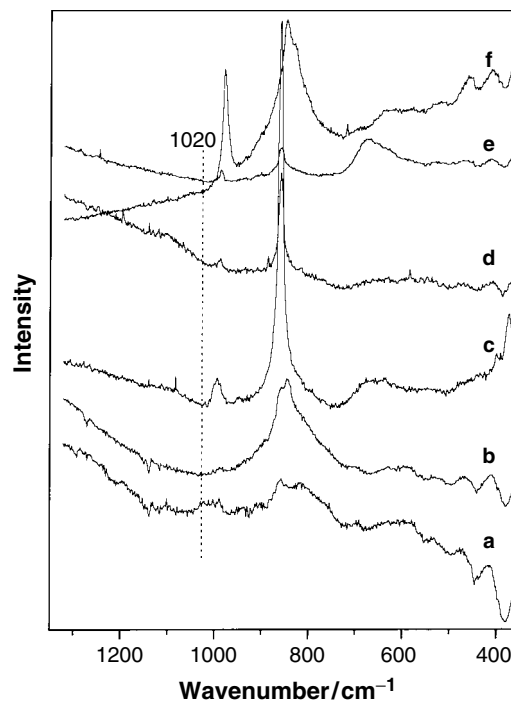

Figure 5. Raman spectra of the interaction of CH$_3$OH and O$_2$ on the surface of an iodine-modified electrolytic silver catalyst at central wavenumber 800 cm^{-1}. (a) 25; (b) 100; (c) 200; (d) 300; (e) 400; (f) 450 °C.

can be divided into two groups. The first group, consisting of 1020, 1430, 2844 and 2940 cm^{-1}, can be assigned to

vibrational modes of adsorbed methoxy species of ν(CO), δ(CH), ν_s(CH) and ν_{as}(CH), respectively. The other two
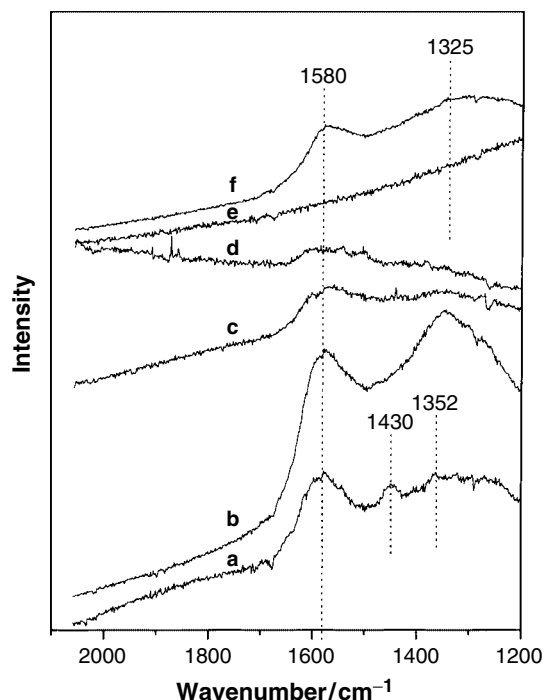
Figure 6. Raman spectra of the interaction of CH_3OH and O_2 on the surface of an iodine-modified electrolytic silver catalyst at central wavenumber 1600 cm^{-1}. (a) 25; (b) 100; (c) 200; (d) 300; (e) 400; (f) 450 °C.

Figure 7. Raman spectra of the interaction of CH_3OH and O_2 on the surface of an iodine-modified electrolytic silver catalyst at central wavenumber 3100 cm^{-1}. (a) 25; (b) 100; (c) 200; (d) 450 °C.

bands at 1352 and 1580 cm^{-1} can be assigned to $\nu_s(OCO)$ and $\nu_{as}(OCO)$ vibrational modes associated with adsorbed formate species. On heating the silver catalyst to 100 °C, vibrational bands of the first group assigned to methoxyl species decrease greatly. The result is similar to the case for the system without the presence of oxygen, indicating that the methoxy species is unstable on the surface even at 100 °C. In addition, it is obviously found that the Raman intensity of methoxy species without the co-adsorption of oxygen is much stronger than the reverse, suggesting that the methoxy intermediate is much more unstable when methanol is co-adsorbed with oxygen on the silver surface. Subsequent heating to 200 °C only results in an increase in Raman intensity of atomic oxygen species and partial decomposition of formate species. Further heating to 300 °C causes substantial attenuation of both the atomic oxygen and the formate species. After heating to 400 °C, no discernible signals can be observed except for those of oxygen species on the silver surface.

In situ Raman studies of the interaction of CH_3OH with the electrolytic silver catalyst were also conducted under conditions similar to those of the industrial process (a mixture of flowing air and methanol vapor with an oxygen-to-methanol molar ratio of 0.4 at 450 °C) to mimic the practical reaction. No carbonaceous species except for formate species on the catalyst surface were detected, suggesting that a formate species is the unique stable intermediate under the
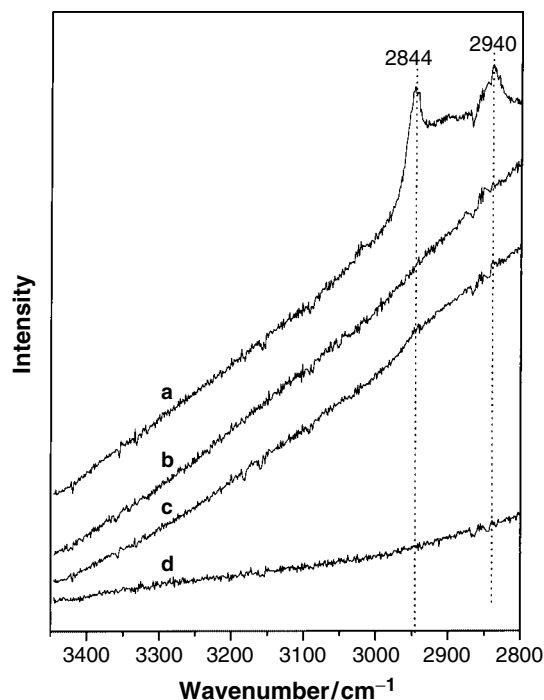
reaction conditions. This result agrees well with that for a similar system without iodine modification as reported previously.[24]
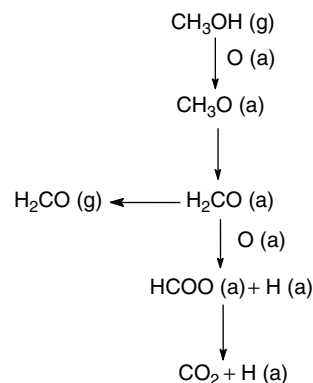
DISCUSSION

Because of the great importance of the role of oxygen during the oxidative dehydrogenation of methanol, intensive investigations have been performed to elucidate the nature of oxygen adsorption behavior on the surface of an electrolytic silver catalyst. It is well established that various kinds of oxygen species on the surface of an electrolytic silver catalyst lead to different reaction pathways such as pure dehydrogenation and partial or deep oxidation reactions. In the present work, the intensity of vibrational bands corresponding to various oxygen species changed significantly because of the re-population of different oxygen species due to the promoting effects of chemisorbed iodine. The band at 856 cm^{-1} relating to the surface atomic oxygen species changes from a very broad to a relative sharp peak and becomes much stronger upon the introduction of CH_3I to the silver surface. CH_3I modifier inhibits the formation of surface oxygen species corresponding to deep oxidation and can be suggested as an important factor for the high selectivity towards formaldehyde for methanol oxidation. At elevated temperatures, such as 200 °C, the population of atomic species decreases and dissolved oxygen in the

bulk of the catalyst can migrate and re-populate in the surface region, resulting in the appearance of bands both at 403 cm^{-1} assigned to subsurface oxygen species and at 677 cm^{-1} corresponding to peroxide species. Further heating to temperatures above 400 °C causes a significant decrease in the surface concentration of the atomic oxygen species. In the present work, modification of the silver surface with iodine altered the population of different surface oxygen species. The surface of the iodine-modified catalyst was found to inhibit those strongly adsorbed atomic oxygen species relevant to deep oxidation of methanol. It was found that only atomic oxygen participated in the partial oxidation of methanol to formaldehyde, while molecular oxygen was shown as a precursor of atomic oxygen.[17] Hence the iodine promoter may enhance the selectivity towards formaldehyde in the oxidation of methanol. This conclusion was also supported by theoretical calculation results obtained by our group.[25]

Previous investigations of the adsorption of methanol on a silver surface by various modern surface techniques have shown that it is difficult for methanol to chemisorb on an oxygen-free silver surface.[26–29] However, the presence of surface oxygen on the silver surface would greatly enhance the dissociative chemisorption of methanol, giving rise to the formation of methoxy groups. If there are excess atomic oxygen species present on the surface, further oxidation of HCHO to CO_2 through a formate intermediate will occur. In our system, the *in situ* Raman studies show direct evidence for methanol chemisorption on the iodine-modified oxygen-free electrolytic silver catalyst and co-adsorption of both oxygen and methanol at room temperature results in the existence of both methoxy and formate surface species. Further oxidative decomposition of methoxy groups gives off HCHO. Compared with Raman features under oxygen-free conditions, the decrease in intensity of bands corresponding to methoxy species was observed, demonstrating that methoxy species are less stable in the presence of excess surface oxygen species. In an oxidative atmosphere, methoxy species tend to be converted to formate species. As a result, formate species dominate the catalyst surface. At elevated temperature, the surface formate species decompose to produce carbon dioxide. The reaction pathway can be summarized as showing in Scheme 1.

The methanol oxidation mechanism on the iodine-modified electrolytic silver catalyst that we propose based on the present data from *in situ* Raman spectroscopy is in agreement with that proposed on commercial electrolytic silver reported in previously.[24] However, in the present case, methanol adsorption on an iodine-modified silver catalyst is promoted predominantly by adsorbed iodine modifiers and surface oxygen species. It is known that the adsorbed oxygen species will inevitably lead to deep oxidation of methanol, while iodine could not take part in the full oxidation of methanol, and an increase in the selectivity towards formaldehyde could be easily established. On the

$$CH_3OH \ (g)$$
$$\downarrow O \ (a)$$
$$CH_3O \ (a)$$
$$\downarrow$$
$$H_2CO \ (g) \longleftarrow H_2CO \ (a)$$
$$\downarrow O \ (a)$$
$$HCOO \ (a) + H \ (a)$$
$$\downarrow$$
$$CO_2 + H \ (a)$$

Scheme 1

other hand, the presence of iodine will also promote the adsorption of methanol, as confirmed by *in situ* Raman spectroscopy, resulting in an increase in the reaction activity. Therefore, the *in situ* Raman studies demonstrated clearly the micro-mechanism of the promoting effect of iodine in the practical reaction of methanol oxidation on a commercial electrolytic silver catalyst.

CONCLUSION

In situ Raman studies on the interaction of iodine-modified electrolytic silver with oxygen and methanol at atmospheric pressure and various temperatures revealed that the presence of iodine inhibits the formation of surface oxygen species corresponding to deep oxidation and reduces the vibrational wavenumbers of the modes corresponding to surface oxygen species. Methoxy and formate groups were identified as two intermediates during the adsorption and reaction of methanol. It was also found that methanol can be adsorbed and reacted on the surface of the modified silver without the co-adsorption of oxygen, resulting in iodine-induced adsorption of methanol. The reaction pathways in the present work were suggested as being the same as those in the system without iodine modification.

REFERENCES

1. Kilty PA, Sachtler WMH. *Catal. Rev.* 1974; **10**: 1.
2. Bartern MA, Madix RJ. In *Chemical Physics of Solid Surface and Heterogeneous Catalysis*, Vol. 4 Elsevier; Amsterdam, 1982; 139.
3. Braylovski SM, Toomkin ON, Trofimova IV. *Probl. Kinet. Katal.* 1985; **19**: 146.
4. Carcia PF, Rao VN. US Patent 4 474 996, 1984.
5. Verbster DE, Rouse IM. UK Patent 1 603 821, 1981.
6. Gerberish HR, Smith ET. US Patent 4 386 014, 1983.
7. Kalia ML, Nechaeva GU, Kulkova NV. *Kinet. Catal.* 1982; **23**: 1287.
8. Fild RM, Krasotkin AE. *Kinet. Catal.* 1962; **3**: 282.
9. Iede R, Mansko E, Ganshow O. *J. Vac. Sci. Technol.* 1985; **3**: 1983.
10. Pestryakov AN, Davydov AA. *Appl. Catal. A* 1994; **120**: 7.

11. Deng JF, Yang J, Zhang S, Yuan XH. *J. Catal.* 1992; **138**: 395.
12. Pestryakov AN. *Catal. Today* 1996; **28**: 239.
13. Graf F, Engelbaeh H, Hupfer L. Ger. Offen. 3 643 469, 1988.
14. Aicher A, Disteldof W, Petri N, Reuss G. *European Patent* 467 169, 1990.
15. Bao X, Deng JF, Dong S. *Acta Chim. Sin.* 1986; **44**: 619.
16. Dai WL, Liu Q, Cao Y, Deng JF. *Appl. Catal. A* 1998; **175**: 83.
17. Dai WL, Cao Y, Deng JF, Liao YY, Hong BF. *Catal. Lett.* 1999; **63**: 49.
18. Wachs IE. *Top. Catal.* 1999; **8**(1–2): 57.
19. Sahronov S, Nabiev I, Chourpa I, Feofanov A, Valsa P, Manfait M. *J. Raman Spectrosc.* 1994; **25**: 699.
20. Long RQ, Huang YP, Wan HL. Chin. Pat. Appl. 96 200851.6, 1996.
21. Deng JF, Xu XH, Wang JH, Liao YY, Hong BF. *Catal. Lett.* 1995; **32**: 159.
22. Wang CB, Goutam D, Wachs IE. *J. Phys. Chem. B* 1999; **103**: 5645.
23. Boghosian S, Bebelis S, Vayenas CG, Papatheodorou GN. *J. Catal.* 1989; **117**: 561.
24. Wang JH, Xu XH, Deng JF, Liao YY, Hong BF. *Appl. Surf. Sci.* 1997; **120**: 99.
25. Shen BR, Chen XY, Fan KN, Deng JF. *Surf. Sci.* 1998; **408**: 128.
26. Wachs IE, Madix RJ. *Surf. Sci.* 1978; **76**: 531.
27. Telter TE, Weinberg WH, Lastushkina GY, Zudan PA, Boreskov GK, Hrbek J. *Appl. Surf. Sci.* 1983; **16**: 351.
28. Bao XH, Deng JF. *J. Catal.* 1986; **99**: 391.
29. Bao XH, Deng JF, Zhai RS, Wang DZ, Guo XX. *Catal. Lett.* 1990; **4**: 25.