In situ surface Raman spectroscopy studies on the interaction between oxygen and ethanol on electrolytic silver catalyst

Jingfa Deng, Jinhai Wang, Xinhua Xu
Department of Chemistry, Fudan University, Shanghai 200433, PR China

Yuanyan Liao and Bifeng Hong
State Key Laboratory for Physical Chemistry of the Solid Surface, Xiamen University, Xiamen 361005, PR China

Received 10 April 1995; accepted 19 July 1995

In situ Raman spectroscopy is employed to investigate the oxidation of ethanol on the electrolytic silver catalyst under catalytic conditions. Over the temperature range of 300–873 K, the configuration of the surface intermediates is detected. The ethoxide species, acetate species, adsorbed acetaldehyde and surface hydroxide exist on the silver surface. The mechanism for the oxidation of ethanol on the silver surface under industrial conditions is discussed and compared with that obtained in ultrahigh vacuum systems.

Keywords: in situ Raman spectroscopy; ethanol oxidation; electrolytic silver

1. Introduction

Electrolytic silver is a well-established commercial catalyst in the classical process for the manufacture of formaldehyde by the oxidation of methanol [1,2]. Deng et al. observed that electrolytic silver was not only effective for methanol oxidation to formaldehyde [3,4], but also for ethanol oxidation to acetaldehyde [5,6]. Although it is not investigated as intensively as the oxidation of methanol, the molecular mechanism of ethanol oxidation on various metal surfaces has been studied by some researchers. Wachs and Madix [7] examined the interaction between oxygen and C_2H_5OD on both Ag(110) and Cu(110) surfaces preadsorbed with $^{18}O_2$ by the TPRS method. They observed that the surface O enhanced the dissociative chemisorption of ethanol, and ethanol was selectively oxidized by adsorption at 180 K to give $D_2{}^{18}O$ and adsorbed ethoxide, $C_2H_5O(a)$. Yates et al. [8] investigated by the deuterium kinetic isotope effect (DKIE) method the surface reaction of ethanol on Ni(111) and observed the formation/decomposition of ethoxy species. The temperature-programmed reaction spectra for the oxidation and decomposition of ethanol on Cu(100) [10], Cu(110) [11] and Pt(111) [12] surfaces were also reported. The molecular mechanism of ethanol oxidation on metal surfaces has been suggested [7–12] to occur by, first, formation of an ethoxide species (I), followed by further decomposition of this intermediate via different channels yielding the products. The configuration of the ethoxide species has been confirmed by IRAS experiments on Ni(111) [9] and by HREELS on Cu(100) [10] surfaces.

However, it is clear that the conditions for the above molecular mechanism studies are quite different from those for the industrial process, and the results from the practical catalytic reaction cannot be understood completely. For instance, the results from the industrial process [5] showed that methane (CH_4) was an important by-product, to which the molecular mechanism gave no satisfying explanation. Therefore, it would be particularly valuable to carry out the studies of this reaction with in situ technology under practical conditions, since the previous works [7–12] are accomplished in ultrahigh vacuum systems. In order to settle the speculations of the reaction directly, in situ surface Raman spectroscopy is employed to investigate the oxidation of ethanol on the electrolytic silver catalyst under industrial conditions.

2. Experimental

The apparatus constructed for Raman spectroscopy studies was described in our previous papers [13,14]. Raman spectra were obtained on a Jobin Yvon U-1000 laser Raman spectrometer with a specially designed Raman sample cell for in situ catalysis studies. The sample was put in a quartz tube. With an electric furnace around the tube, the sample could be heated up to 973 K, accuracy ± 1 K. Temperature of the sample was controlled by a temperature-programmer and measured by a Ni–Cr/Ni–Si thermocouple inserted in the sample. The experimental conditions of Raman spectra measurements are listed below: $\lambda_0 = 514.5$ nm, laser power: 150 mW, resolution: 2 cm^{-1}, time constant: 0.2 s. The electrolytic silver of 99.999% purity (employed as industrial catalyst) was obtained by means of triple electrolytic refining of silver [3,4]. The grain size was 40–60 mesh. Before the experiments of Raman spectroscopy, the silver sample was first heated to 973 K and kept at this temperature for 30 min in a mixed oxygen/nitrogen ($O_2/N_2 = 1/4$) flow. Then the oxygen was cut off, the sample was kept in pure N_2 flow at 973 K for another 30 min and finally cooled to room temperature. After the above treatment, the Raman spectra of the silver sample showed no obvious vibrational bands. The oxygen/nitrogen flow mentioned above was employed as oxygen source, and ethanol was carried onto the surface of the silver sample by bubbling pure nitrogen through reagent-grade liquid ethanol at 60°C.

3. Results

The electrolytic silver sample was exposed sequentially to an oxygen/nitrogen (1/4) flow and a nitrogen/ethanol (saturated vapor) flow at room temperature for a long time. Then a pure N_2 flow was introduced into the sample tube and the residual gaseous ethanol was driven away. By heating this sample to various temperatures, the Raman spectra for the interaction between oxygen and ethanol molecules on the silver surface were recorded. Fig. 1 shows the Raman spectrum of ethanol adsorbed on the silver surface preadsorbed with oxygen at room temperature (~300 K). The vibrational bands occur at 463, 610, 708, 814, 907, 1007, 1080, 1290, 1340, 1477, 1500, 1692, 1750, 1864, 1992, 2072, 2640, 2760, 2868, 2973,

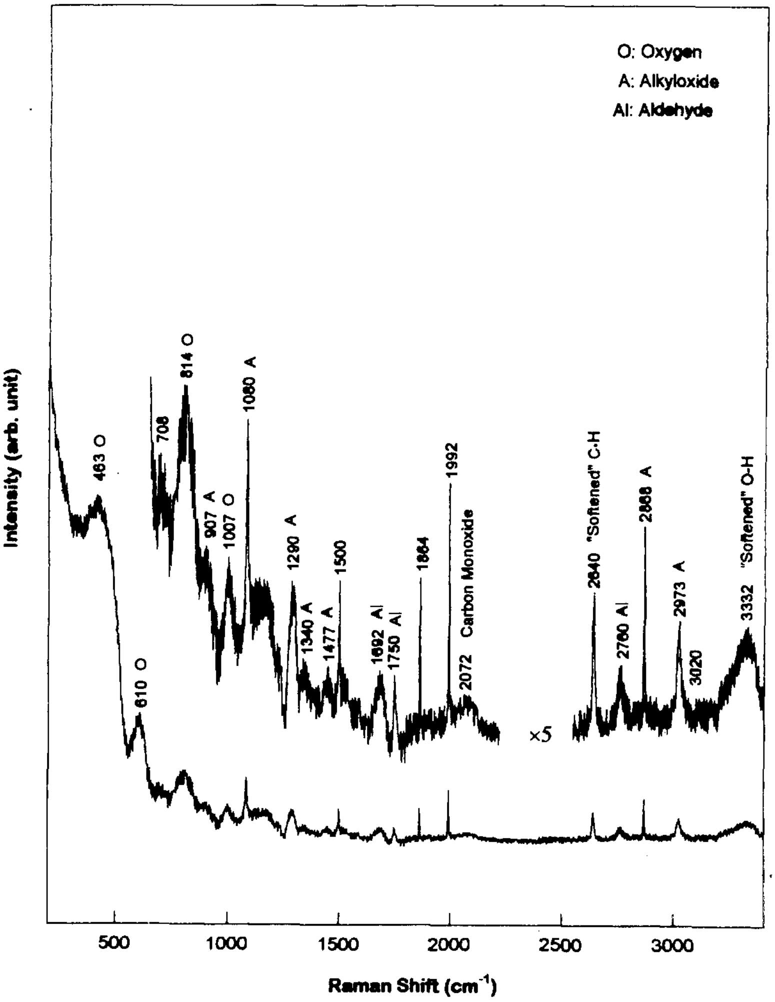


Fig. 1. The Raman spectra of the interaction between ethanol and oxygen on electrolytic silver at room temperature (~300 K).

3020 (weak), and 3332 cm^{-1}, respectively. The bands at 463, 610, 814 and 1007 cm^{-1} are assigned to the vibrations of a variety of adsorbed oxygen species on the electrolytic silver, which are investigated and discussed in our previous works [13]. The other bands apparently arise from the interaction between ethanol molecules and the adsorbed oxygen on the silver surface.

It has been proved that ethoxide species (I) is an important surface intermediate while the adsorption of ethanol occurs on the metal surfaces. The vibrational modes and frequencies for ethoxide (I) on various metal surfaces are listed in table 1, as well as those of liquid ethanol. Relying upon the agreement of the vibrational bands in fig. 1 with those in table 1, assignment can be made as follows: ν(C–C): 907 cm^{-1}, ν(C–O): 1080 cm^{-1}, CH_2 wag: 1290 cm^{-1}, $\delta(CH_2, CH_3)$: 1340/1477 cm^{-1}, and $\nu(CH_2, CH_3)$: 2868/2973 cm^{-1}. The other bands are also determined according to the literature. For instance, Trautmann et al. [16] observed the vibrational bands at 1650 and 1720 cm^{-1}, which were assigned to the stretching mode ν(C=O) of the carbonyl group. The bands at 1699 and 1720 cm^{-1} for the ν(C=O) mode were also detected by Horr et al. [17]. Therefore, the band at 1750 cm^{-1} in fig. 1 is ascribed to the stretch vibrations of the carbonyl group of adsorbed acetaldehyde on silver, and the band at 1692 cm^{-1} is the indication of weakening of the C=O bond by adsorption. The existence of adsorbed acetaldehyde on the surface is also verified by the appearance of the vibrational band at 2760 cm^{-1}, which is characteristic of the ν(CH) mode of aldehyde species [18]. The band at 2072 cm^{-1} is ascribed to the vibration of carbon monoxide adsorbed on impurities. The band at 3332 cm^{-1} is the stretching vibration of a "softened" O–H bond of the surface hydroxide on the silver surfaces, which has been observed by

Table 1
Vibrational frequencies (cm^{-1}) and mode assignments for the ethoxide species on Ag(110), Cu(100), Ni(111) surfaces and C_2H_5OH in liquid, in comparison with the bands in fig. 1

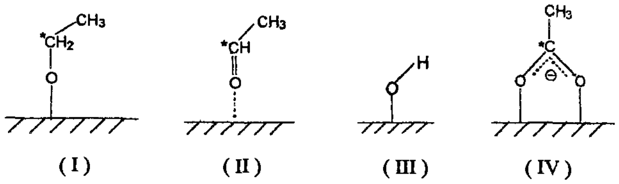
Mode	C_2H_5OH(liq.) [15]	C_2H_5O/ Ag(110) [15]	C_2H_5O/ Cu(100) [10]	C_2H_5O/ Ni(111) [9]	Polycrystalline Ag surface [this work]
ν(Ag–O)	–	270	270	–	–
CH_3 twist	270	270	–	–	–
δ(CCO)	427	475	470	–	–
ν(OH)	674	–	–	–	–
CH_2 rock	775	–	–	–	–
ν(C–C)	877	890	870	–	907
ν(C–O)	1060	1060	1030	–	1080
CH_2 wag	–	1290	–	–	1290
δ(CH)	1405	1370	1380	–	1340
	1472		1450		1477
ν(C–H)	2834	2915	2880	2875	2868
	2980		2965	2964	2973
ν(O–H)	3360	–	–	–	–

Bao et al. [19] and Wu [20] in their HREELS studies of methanol oxidation on silver surfaces. Thus, we can conclude that at room temperature (~300 K), the dominant configuration of the adsorbed ethanol on silver pre-adsorbed with oxygen is an ethoxide species (I). In addition, further reaction occurs at this temperature and adsorbed acetaldehyde (II) and surface hydroxide (III) are formed as products. These surface species are shown schematically as I, II and III in scheme 1.

As the sample was heated up to 473 K, the Raman spectra of the interaction between ethanol and adsorbed oxygen changed. This is shown in fig. 2. The vibrational band at 1080 cm^{-1}, which is due to the stretching mode of the C–O bond, disappears. This phenomenon indicates that there are no ethoxide species on the surface at 473 K. Meanwhile, new bands at 1406 and 1560 cm^{-1} appear. This implies that some new types of surface species are formed. In combination with the other bands in fig. 2 at 969, 1292, 1328, 2900 and 2997 cm^{-1}, we suggest that an acetate species (IV) is formed. The configuration of this species (IV) can be represented schematically as intermediate (IV). The vibrational bands are assigned to be: ν(C–C): 969 cm^{-1}, $\delta(CH_3)$: 1328 cm^{-1}, ν_s(O–C–O): 1406 cm^{-1}, ν_{as}(O–C–O): 1560 cm^{-1} and ν(C–H): 2900/2997 cm^{-1}. These assignments are consistent with those in literature, which are collected in table 2. Besides these, there are vibrational bands at 1667/1794 and 2756 cm^{-1} in fig. 2, which are ascribed to the vibrations of adsorbed acetaldehyde. The band at 2025 cm^{-1} seems to be evidence that there is carbon monoxide on the surface. Therefore, at 473 K the dominant configuration of adsorbed ethanol is an acetate species (IV), which is formed obviously from further reaction of ethanol with adsorbed oxygen species.

The Raman spectrum obtained after heating the sample further to 673 K is shown in fig. 3. In comparison with those in figs. 1 and 2, we can see the disappearance of the vibrational frequencies at 907, 1080, and 969, 1406/1565 cm^{-1}, respectively. As mentioned above, these bands are ascribed to the vibrational modes of the C–C and C–O bonds in ethoxide species and the C–C and O–C–O groups in acetate species. Therefore, it can be suggested that, at 673 K, there is no ethoxide or acetate species on the surface, and the adsorbed ethanol molecule fragmentizes to C_1 products, e.g. CO(ad): 2053 cm^{-1}, CH_x(ad): 1287, 1434(δ), 2553, 2665 and 2839 cm^{-1} (γ) etc. Since there is no vibrational band for the C–C bond in fig. 3, the bands at 1658/1736 cm^{-1} might be due to the ν(C=O) of the adsorbed formaldehyde.

The Raman spectra (not shown in this paper) of interaction between ethanol



Scheme 1.

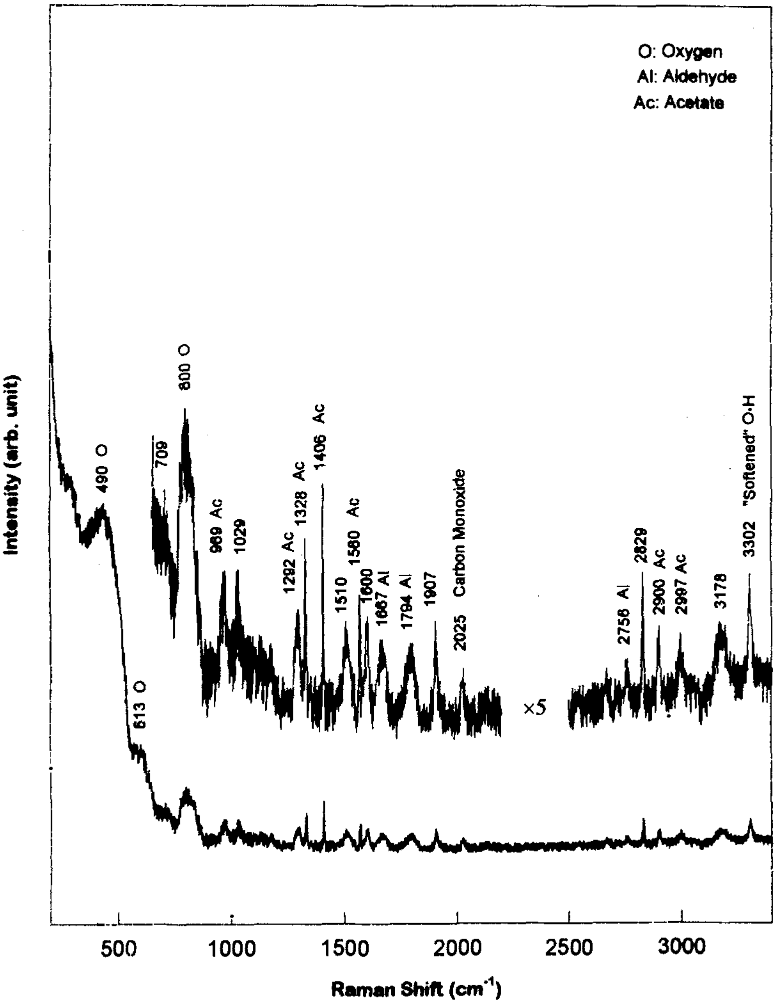


Fig. 2. The Raman spectra of the interaction between ethanol and oxygen on electrolytic silver at 473 K.

Table 2

Vibrational frequencies (cm^{-1}) and mode assignments for acetate species on various catalysts and for CH_3COO^- in sodium salt, in comparison with those in fig. 2

Mode	Ag film [21]	Pd/Al_2O_3 [16]	MoO_3 [22]	CH_3COONa [23]	Polycrystalline Ag surface [this work]
ν(C–H)	–	2941/3021	–	–	2900/2997
ν_{as}(O–C–O)	1539	1579	1530	1560	1560
ν_s(O–C–O)	1400	1470	1420	1410	1406
$\delta(CH_3)$	–	1331/1396	1350	1381	1328
ν(C–C)	931	–	–	–	969

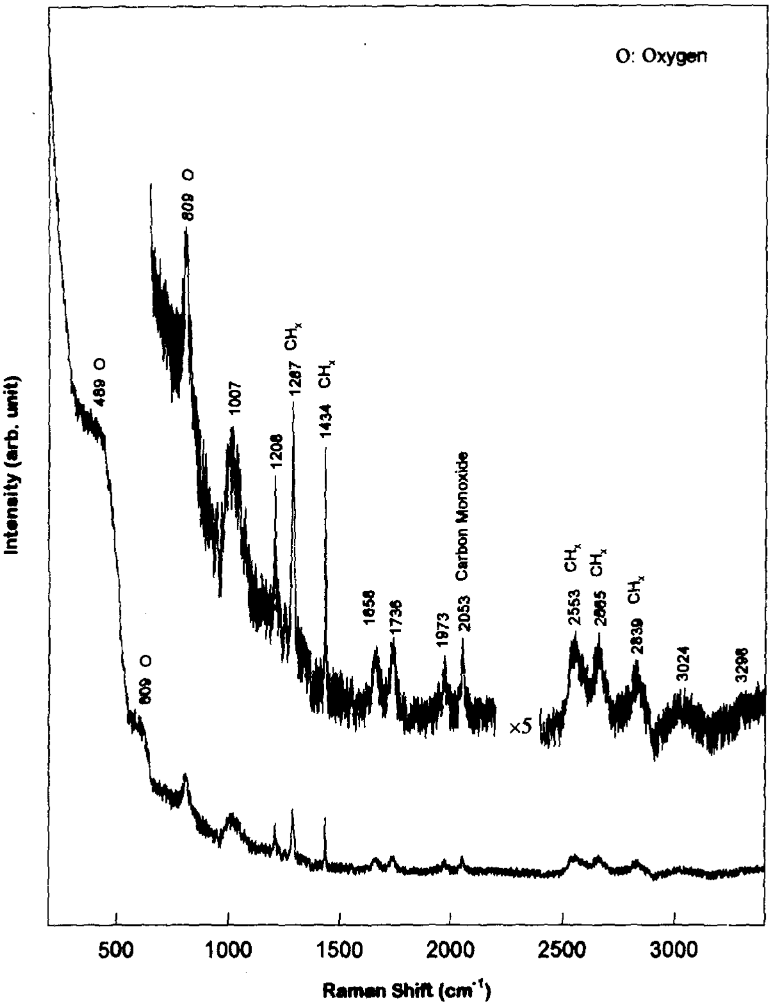


Fig. 3. The Raman spectra of the interaction between ethanol and oxygen on electrolytic silver at 673 K.

and oxygen on electrolytic silver surface heated to 873 K show no obvious bands except adsorbed carbon monoxide around 2000 cm^{-1}.

According to the results from the industrial process [5,6], the oxidation of ethanol on the silver catalyst is carried out over the temperature range of 773–873 K. In order to settle this contradiction, a Raman spectroscopy experiment under practical conditions is performed. After passing the mixed C_2H_5OH/O_2 flow through the sample at 873 K, the obvious bands can be observed (fig. 4). In fig. 4, the bands at 851/892, 1098, 1467 and 1525 cm^{-1} are present, which are assigned to the stretching modes of ν(C–C), ν(C–O), ν_s(O–C–O) and ν_{as}(O–C–O). In combination with the other vibration bands, we can conclude that there are both ethoxide and acetate species on the surface. Besides these, there are also adsorbed acetaldehyde,

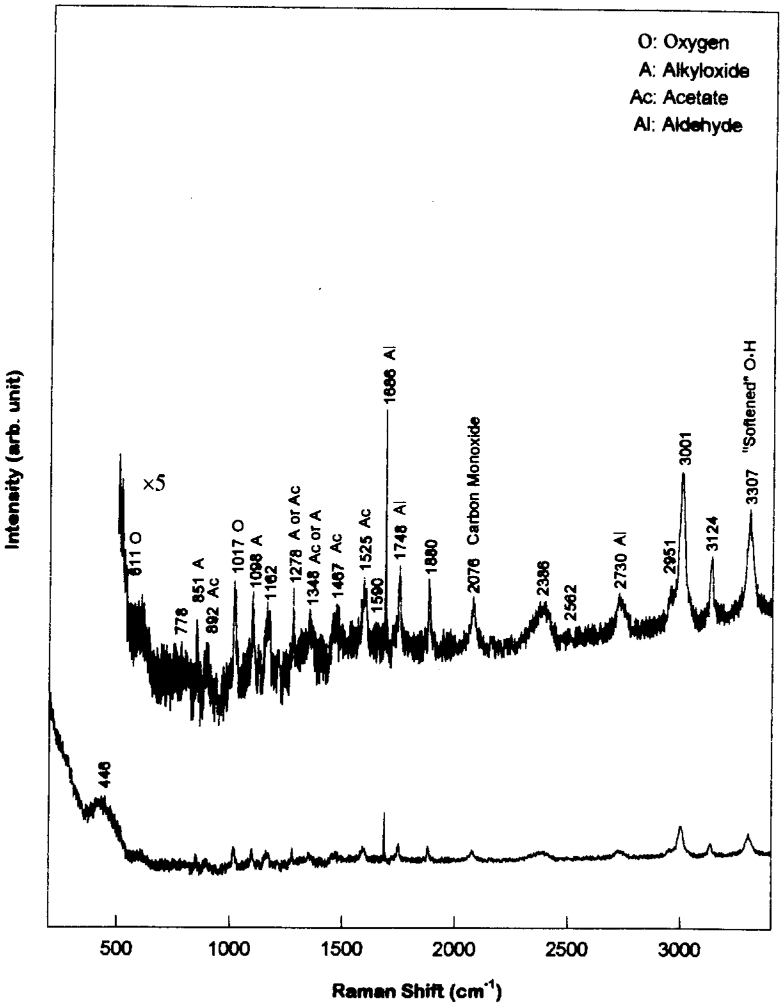


Fig. 4. The Raman spectra of the interaction between ethanol and oxygen on electrolytic silver at 873 K in an ethanol/oxygen flow.

CO and surface hydroxide species etc. Clearly, the continuous flow of ethanol/oxygen supplies the consumption and decomposition of the surface intermediates, which is demonstrated by Raman bands at 873 K.

From the Raman spectra in figs. 1–4, the configurations of the intermediates in the oxidative reaction of ethanol are detected. The dominant surface species vary over the temperature range of 300–873 K. At room temperature (300 K), ethoxide (I) species is the dominant intermediate on the surface. The dominant configuration of the surface intermediate at 473 K becomes an acetate-like species (IV). At temperature above 673 K, both the C–C bonds and the C–O bonds are broken and there are only decomposed pieces, e.g. CH_2(ad), CH_3(ad), on the surface. In the ethanol/oxygen flow at 873 K, both ethoxide and acetate-like species are detected.

The characteristics of these intermediates over the range of 300–873 K are listed in table 3.

4. Discussion

Ethoxide species has been determined to be formed at first on the metal surfaces, resulting from the bond scission of the O–H bond of the hydroxyl group in ethanol. Wachs et al. [7] observed the formation of ethoxide on Ag(110) and Cu(110) surfaces at 180 K. The ethoxide species on Cu(110) was further investigated by means of XPS and UPS by Bowker et al. [11] at about 250 K. The vibrational features of ethoxide on Ag(110) were detected by Dai et al. [15] with HREELS at 250 K. In addition, formation of ethoxide on Ni(111) at 250 K [8,9], Cu(100) at 370 K [10], Pt(111) below 350 K [12], Pd(111) below 250 K [24] and Si(111) at 300 K [25] were also observed. These results reveal that the ethoxide species (I) is formed and stable at about room temperature (~300 K), which is in agreement with the results from the Raman spectroscopy experiments in this work (fig. 1). Therefore, the mechanism of ethanol oxidation at room temperature on electrolytic silver does not seem different from that on single-crystalline metal surfaces, though the electrolytic sil-

Table 3
Characteristics of the surface intermediates from the interaction between ethanol and adsorbed oxygen over the temperature range of 300–873 K

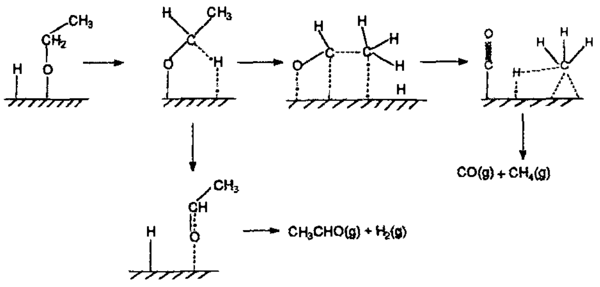
Temperature (K)	Frequency (cm^{-1})	Mode	Assignment	Characterization
300	907	ν(C–C)	ethoxide species	diminishes over 473 K
	1080	ν(C–O)		
	1340/1477	$\delta(CH_2, CH_3)$		
	2868/2973	$\nu(CH_2, CH_3)$		
473	969	ν(C–C)	acetate species	decomposes over 673 K
	1328	$\delta(CH_3)$		
	1406/1560	$\nu_{s,as}$(O–C–O)		
	2900/2997	$\nu(CH_3)$		
673	1434	δ(C–H)	CH_2, CH_3 pieces	desorbs over 873 K
	2839	ν(C–H)		
873	none	none	none	–
873 K in ethanol/ oxygen flow	851/892	ν(C–C)	ethoxide and acetate species	–
	1098	ν(C–O)		
	1348/1467	δ(C–H)		
	1467/1525	ν(O–C–O)		
	2951/3001	ν(C–H)		

ver is revealed to acquire special surface structure and surface morphology, as presented in our previous works [4,26].

Further reaction of ethoxide species with the surface resulted in the decomposition of the ethoxide species. For instance, the chemical bond activation sequence of ethanol molecule on the Ni(111) surface was observed by Gates et al. [8]. This sequence can be described as

(1) hydroxyl, O–H, bond;
(2) methylene (CH_2), C–H, bond;
(3) carbon–carbon, C–C, bond;
(4) methyl (CH_3), C–H, bond.

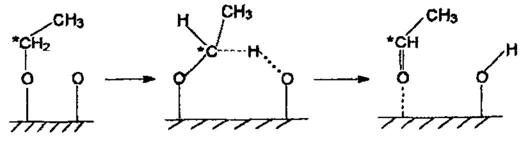
The decomposition of ethoxide on the Ni(111) surface can be represented as



(1)

(2)

The chemisorption and surface reaction of alcohols on the silver surface show features different from those on the nickel surface. For instance, our previous works show that no adsorption of methanol, hydrogen [4] or ethanol (unpublished results) occurred on the clean electrolytic silver surface above room temperature. However, the ability of silver to chemisorb these gaseous molecules mentioned above was greatly enhanced by preadsorbing the surface with oxygen. Wachs and Madix [7] observed that the ability of the Ag(110) and Cu(110) surfaces to dissociatively chemisorb the ethanol was enhanced by surface oxygen species. Madix [27] pointed out that oxygen species adsorbed on the silver surface obtained the ability to abstract hydrogen atom from a variety of molecules. Therefore, the adsorbed oxygen should be considered to have an important effect on the reaction of ethanol on the silver surface. This reaction can be represented as

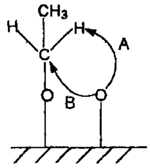


(I) (V) (II) (III)

(3)

The existence of the surface intermediates I, II and III on electrolytic silver at room temperature has been verified by the Raman spectra in this work (fig. 1). As for the intermediate V, we can note a band at 2640 cm^{-1} in fig. 1, which can be ascribed to be "softened' C–H stretch vibrations resulting from the C–H bond pointing towards the Ag surface. This assignment is supported by the following facts: (i) a band at 2600 cm^{-1} was observed for the adsorption of methanol and ethanol on Ag(110) surface, which was due to the "softened" C–H stretch vibrations [15]; and (ii) in the case of cyclopentene on the Pt(111) surface modes at this frequency have been assigned similarly [28]. Thus, it is suggested that the intermediate V is relatively stable on the electrolytic silver surface at room temperature.

According to previous works by work-function measurement and UPS method [26], the adsorption of oxygen on the electrolytic silver results in the electron transfer from silver to oxygen. Thus, there is some negative charge on the chemisorbed atomic oxygen and $O_{ad}^{\delta-}$ species are formed. As for the ethoxide species, they can undergo nucleophilic attack by $O_{ad}^{\delta-}$ on two different positions, shown schematically as follows:



The dehydrogenation of ethoxide can proceed via the β-H elimination reaction without O_a at moderate temperature on Ag surface as well as via the path A. This leads to the formation of acetaldehyde species (II). As the sample is heated up to 473 K, the ethoxide species on the silver surface disappeared completely (fig. 2). In comparison with the oxidation of methanol, it was found that methoxide species was stable around 473 K [14], which means that CH_3O(ad) was more stable than CH_3CH_2O(ad). Wachs and Madix [7] also pointed out that EtO^- was less stable than MeO^- on both Ag(110) and Cu(110) surfaces.

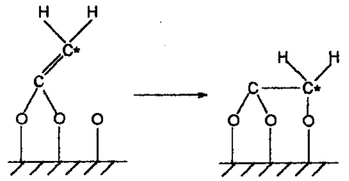
The dominant configuration at 473 K has been shown as an acetate species (IV). It is formed via the nucleophilic attack by atomic oxygen at the C* atom of ethoxide or acetaldehyde, and followed by the β-H elimination reaction. Barteau et al. [29] observed the formation of CH_3CHO_2(ad) (IV) at 160 K on the Ag(110) surface, and this intermediate decomposed at 250 K to liberate H_2 and produce a stable CH_3COO(ad) intermediate species:

$$CH_3CHO(ad) + O(ad) \rightarrow CH_3CHO_2(ad) \tag{4}$$

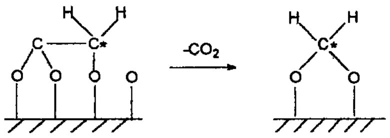
$$CH_3CHO_2(ad) \rightarrow CH_3COO(ad) + H(ad) \tag{5}$$

The Raman spectra in the present work cannot give a distinction between the configuration of the intermediates CH_3CHO_2(ad) and CH_3COO(ad). Since CH_3CHO(ad) was unstable at 473 K [29,30], the acetate species (CH_3COO(ad)) including the O–C–O structure is suggested as the surface intermediate (fig. 2).

The works on Ag(110) [29] also showed that the adsorbed acetate species was a very stable surface intermediate, which decomposed at 640 K to yield CO_2, CH_3COOH, CH_4, H_2CO and C(ad) as major products. In comparison with the Raman spectra at 673 K (fig. 3), we can see that the bands for C–C, C–O and O–C–O bonds disappear completely, and there are only the vibrational bands for C–H bonds and CO(ad), CO_2(ad) species in fig. 3. This is consistent with the works of Barteau et al. [29–31] who pointed out that this decomposition reaction involved removal of a methyl proton from acetate by O_a to form CH_2COO(ad). Further reaction with O_a gave a glycolate intermediate OCH_2COO(ad):

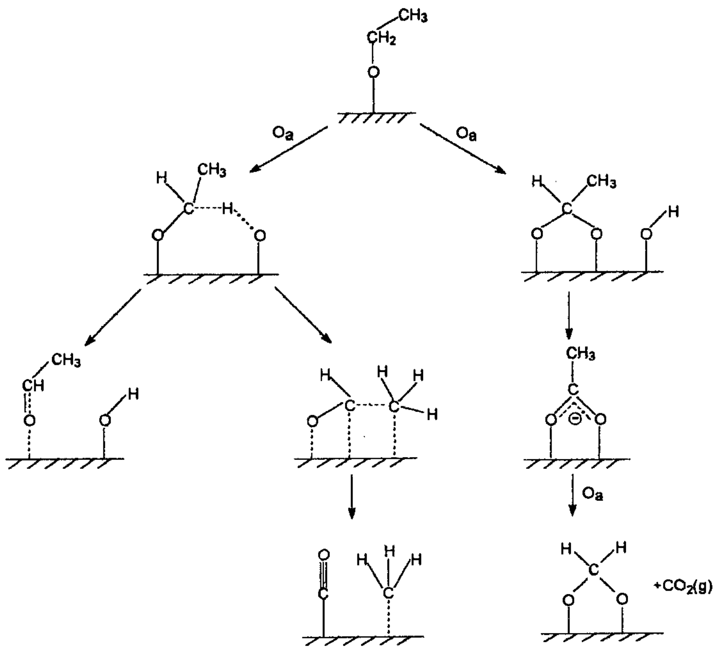


(6)



(7)

Heating up to 873 K caused complete desorption of the surface species.



Scheme 2.

The Raman spectrum at 873 K in an ethanol/oxygen flow becomes complicated again (fig. 4). The bands for C–C, C–O and O–C–O structures appears, as well as the vibrational bands for adsorbed acetaldehyde, surface hydroxide, CO and even CO_2(ad) at 2390 cm^{-1}. This is evidence that all of the reactions mentioned above occur simultaneously on the electrolytic silver at 873 K. The whole reaction can be described as in scheme 2.

Acknowledgement

This work was supported by grants from State Key Laboratory for Physical Chemistry of the Solid Surface at Xiamen University and National Natural Sciences Foundation of China.

References

[1] C.L. Thomas, in: *Catalytic Processes and Proven Catalysts* (Academic Press, New York, 1970) p. 208.
[2] M.A. Barteau and R.J. Madix, in: *Chemical Physics of Solid Surface and Heterogeneous Catalysis*, Vol. 4 (Elsevier, Amsterdam, 1982) p. 139.
[3] J.F. Deng, Y.F. Xiang, L.Y. Ye and X.Z. Zhu, J. Catal. (China) 4 (1983) 266.
[4] X. Bao and J.F. Deng, J. Catal. 99 (1986) 391.
[5] Fudan University, Petrochem. Tech. (China) 7 (1978) 323.
[6] Y.F. Xiang, Z.M. Cai, J. Zhu and J.F. Deng, Petrochem. Tech. (China) 13 (1984) 70.
[7] I.E. Wachs and R.J. Madix, Appl. Surf. Sci. 1 (1978) 303.
[8] S.M. Gates, J.N. Russell Jr. and J.T. Yates Jr., Surf. Sci. 171 (1986) 111.
[9] J. Xu, X. Zhang, R. Zenobi, J. Yoshinobu, Z. Xu and J.T. Yates Jr., Surf. Sci. 256 (1991) 288.
[10] B.A. Sexton, Surf. Sci. 88 (1979) 299.
[11] M. Bowker and R.J. Madix, Surf. Sci. 116 (1982) 549.
[12] B.A. Sexton, K.D. Rendulic and A.E. Hughes, Surf. Sci. 121 (1982) 181.
[13] J.F. Deng, X. Xu and J. Wang, Catal. Lett. 32 (1995) 159.
[14] Y. Liao and P. Hong, *Proc. 7th Chinese Light Scat. Conf.*, Yichang, 1993, p. 218.
[15] Q. Dai and A.J. Gellman, Surf. Sci. 257 (1991) 103.
[16] S. Trautmann and M. Baerns, J. Catal. 136 (1992) 613.
[17] T.J. Horr, J. Ralston and R.St.C. Smart, Colloid. Surf. 63 (1992) 21.
[18] L.J. Bellamy, in: *The Infrared Spectra of Complex Molecules* (Chapman and Hall, London, 1975) p. 151.
[19] X. Bao, J.F. Deng, R. Zhai, D. Wang and X. Guo, Catal. Lett. 4 (1990) 25.
[20] K. Wu, PhD Thesis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, PR China (1991).
[21] S. Fujii, Y. Misono and K. Itoh, Surf. Sci. 277 (1992) 220.
[22] C. Martin, I. Martin and V. Rives, J. Mol. Catal. 73 (1992) 51.
[23] L.J. Bellamy, in: *The Infrared Spectra of Complex Molecules* (Chapman and Hall, London, 1975) p. 199.
[24] J.L. Davis and M.A. Barteau, Surf. Sci. 187 (1987) 387.
[25] Z. Ying and W. Ho, Surf. Sci. 198 (1988) 473.

[26] X. Bao, S. Dong and J.F. Deng, Surf. Sci. 199 (1988) 493.
[27] R.J. Madix, Science 233 (1986) 1159.
[28] N.R. Avery, Surf. Sci. 146 (1984) 363.
[29] M.A. Barteau, M. Bowker and R.J. Madix, J. Catal. 67 (1981) 118.
[30] A.G. Sault and R.J. Madix, Surf. Sci. 172 (1986) 598.
[31] A.G. Sault and R.J. Madix, J. Phys. Chem. 90 (1986) 4723.