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In situ surface Raman spectroscopy studies of oxygen adsorbed on electrolytic silver

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In situ Raman spectroscopy has been employed to investigate oxygen adsorption on electrolytic silver catalyst under industrial conditions for methanol oxidation to formaldehyde. Both adsorbed atomic and molecular oxygen species are shown to exist on the silver surface in O_2 flow above 870 K. The peroxide species is determined to be a precursor to atomic adsorbed oxygen. In consideration of the industrial process, the molecular mechanism of the partial oxidation of methanol and the adsorption mechanism of oxygen on electrolytic silver surface are discussed.

Keywords: in situ Raman spectroscopy; oxygen adsorption; electrolytic silver; methanol oxidation

1. Introduction

Electrolytic silver is widely used as an industrial catalyst for the oxidation of methanol to formaldehyde [1,2]. The surface properties of electrolytic silver and the interaction between oxygen and the silver surface have been investigated in detail in our laboratory [3–6]. It was revealed that there were much more surface defects on electrolytic silver than on a single crystalline silver surface. Compared with other kinds of silver catalysts investigated, the adsorption behavior of oxygen on electrolytic silver was quite unique. Unfortunately, the previous researches were done in an ultra-high vacuum (UHV) system, with low exposure of molecular oxygen. With regard to the very different conditions between the UHV system and the industrial process, the states of adsorbed oxygen on electrolytic silver under reaction conditions are not clear yet. In order to investigate the interaction between

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oxygen and silver in the industrial process, we employ in situ surface Raman spectroscopy to study the adsorption behavior of oxygen on electrolytic silver under industrial conditions.

2. Experimental

The apparatus constructed for Raman spectroscopy study is shown in fig. 1. Raman spectra are obtained on a Jobin Yvon U-1000 laser Raman spectrometer with a specially designed Raman sample cell for in situ catalyst studies. The sample is put in a quartz tube. With an electric furnace around the tube, the sample can be heated to 973 K. Temperature of the sample is controlled by a temperature programmer and measured by a Ni–Cr/Ni–Si thermocouple inserted in the sample. The experimental conditions of the Raman spectra measurements are listed below: $\lambda_0 = 514.5$ nm; laser power: 150 mW; resolution: 2 cm^{-1}; time constant: 0.2 s. Electrolytic silver of 99.999% purity is obtained by means of triple electrolytic refining of silver [2,4]. The size is 40–60 mesh. The sample is pretreated as follows: in a mixed oxygen/nitrogen ($O_2 : N_2 = 1 : 4$) flow, the sample is heated to 973 K and kept at this temperature in pure nitrogen flow for 30 min. Then the sample was cooled to room temperature. After the above pretreatment, the Raman spectra of the sample show no obvious vibrational bands.

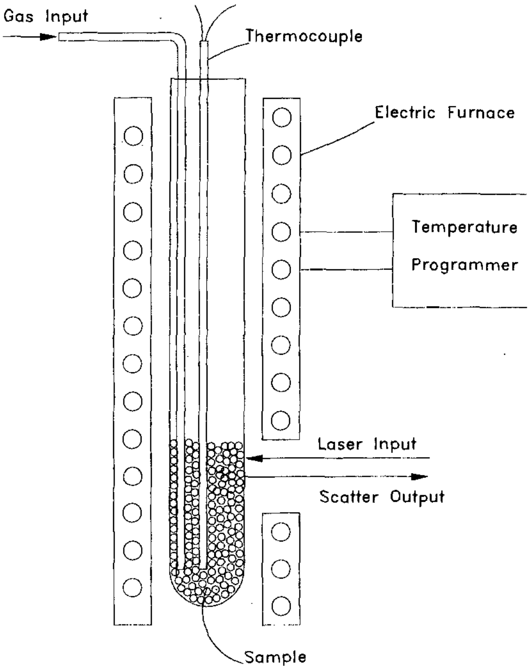

Fig. 1. Diagram of the apparatus constructed for the Raman spectroscopy study.

3. Results

The mixture of O_2/N_2 passed through the sample at room temperature until the adsorption of oxygen was saturated. Then a pure N_2 flow was introduced to the sample instead of the oxygen/nitrogen flow and Raman spectroscopy experiments were performed at given temperature. Fig. 2 shows the Raman spectra obtained over the wavenumber range of 200–500 cm^{-1}. A broad band near 436 cm^{-1} is apparent at room temperature (RT). The Raman spectra over the range of 500–1200 cm^{-1} are given in fig. 3. At room temperature, there are three vibrational bands: a shoulder band at 624 cm^{-1}, a symmetric band at 808 cm^{-1} and a broad band around 1078 cm^{-1}. The corresponding states of adsorbed oxygen are denoted as: O_γ (436 cm^{-1}), $O_{\alpha 1}$ (624 cm^{-1}), O_β (808 cm^{-1}) and $O_{\alpha 2}$ (1078 cm^{-1}), respectively.

When the electrolytic silver sample was heated from room temperature to 873 K, the intensities of the bands O_γ and O_β remain unchanged. The intensity of

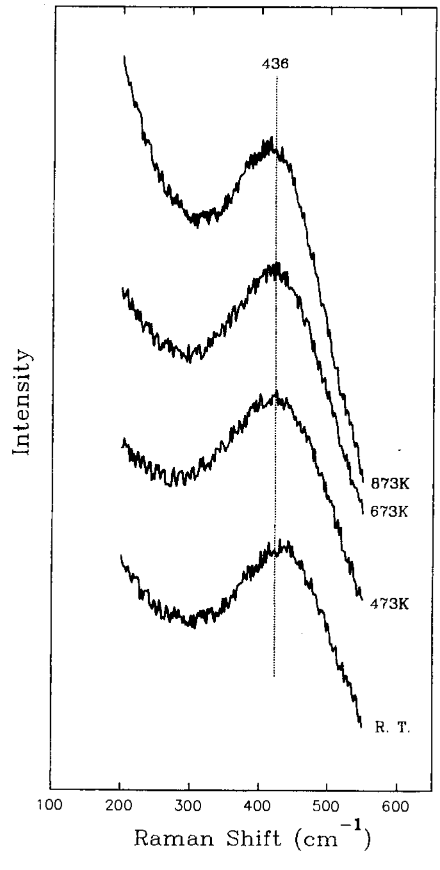

Fig. 2. Raman spectra of adsorbed oxygen on electrolytic silver (wavenumber range from 200 to 500 cm^{-1}) obtained at various temperatures.

the band $O_{\alpha 1}$ became gradually weaker and this band disappeared finally above 873 K. As shown in fig. 3 for the $O_{\alpha 2}$ state (1078 cm^{-1}, RT), a maximum band shift of about 70 cm^{-1} is found at 673 K, and this band disappears above 773 K.

Since the oxidation of methanol to formaldehyde is carried out at about 873 K, one should pay more attention to the Raman spectra at this temperature. From figs. 2 and 3, we see that only two oxygen states, the O_γ and O_β states, remain at 873 K. This spectrum is represented again in fig. 4 (A) and fig. 5 (A). Then we cut off the nitrogen flow and introduced the oxygen flow to the sample at 873 K. The Raman spectrum in oxygen flow is recorded in fig. 4 (B) and fig. 5 (B). Comparing the spectra A and B, we can see that (1) the $O_{\alpha 1}$ state appears again at 624 cm^{-1} in oxygen flow; (2) the O_γ state changes little and (3) the intensity of the O_β state becomes somewhat higher when oxygen is introduced to the sample.

The shoulder band $O_{\alpha 1}$ is assigned to adsorbed dioxygen species, nominally O_2^{2-}, peroxide; and the broad band $O_{\alpha 2}$ is assigned to another kind of adsorbed dioxygen species, nominally O_2^-, superoxide. Similar assignments were reported by

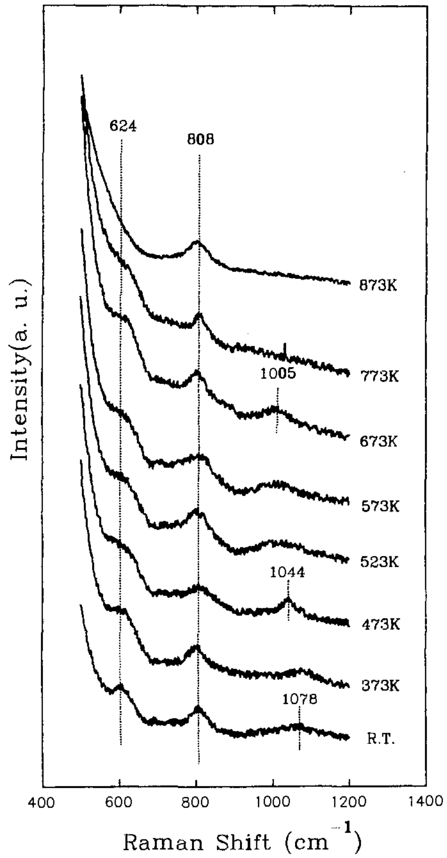

Fig. 3. Raman spectra of adsorbed oxygen on electrolytic silver (wavenumber range from 500 to 1200 cm^{-1}) obtained at various temperatures.

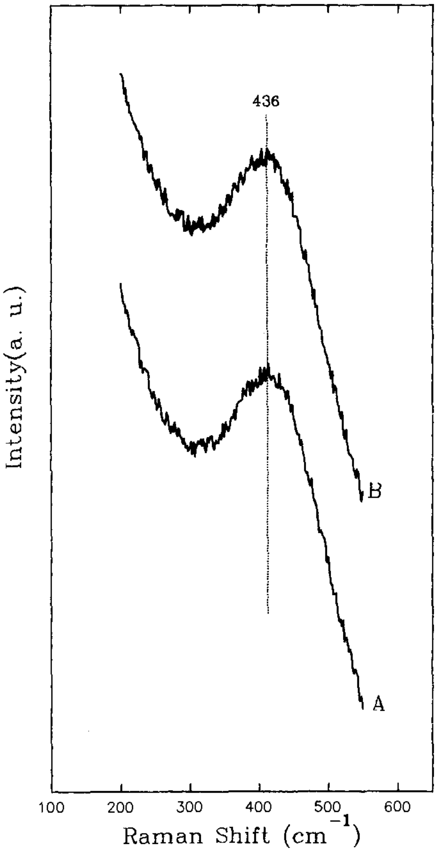

Fig. 4. Raman spectra of adsorbed oxygen on electrolytic silver obtained at 873 K (wavenumber range from 200 to 500 cm^{-1}). (A) after exposure to oxygen at RT, the sample was heated to 873 K in pure nitrogen flow; (B) obtained in oxygen flow at 873 K.

other researchers. Pettenkofer et al. [7] employed surface-enhanced Raman spectroscopy (SERS) studies on silver film and observed vibrational bands at 697 and 1053 cm^{-1} at 120 K, which were assigned to peroxide and superoxide species, respectively. EELS studies on Ag(110) below 150 K gave O–O stretch vibrations at 640 cm^{-1} [8] and 628 cm^{-1} [9], which were ascribed to a reduction of the O–O bond. In a HREELS study of polycrystalline silver film [10], vibrational bands at 645 and 1320 cm^{-1} were observed and assigned to dioxygen species. McBreen and Moskovits [11] studied the interaction of oxygen and ethylene on supported silver catalysts by means of SERS and they observed two spectral features at 995 and 676 cm^{-1}, which were ascribed to O_2^- and O_2^{2-} moieties, respectively. A reflection–absorption infrared spectroscopy (RAIRS) study of silver surface at 90 K gave the results that bands at 622 and 983 cm^{-1} were due to molecularly adsorbed oxygen [12]. In addition to this, matrix isolation experiments of silver atoms and molecular oxygen revealed that vibrations around 1080 cm^{-1} by infrared spectroscopy

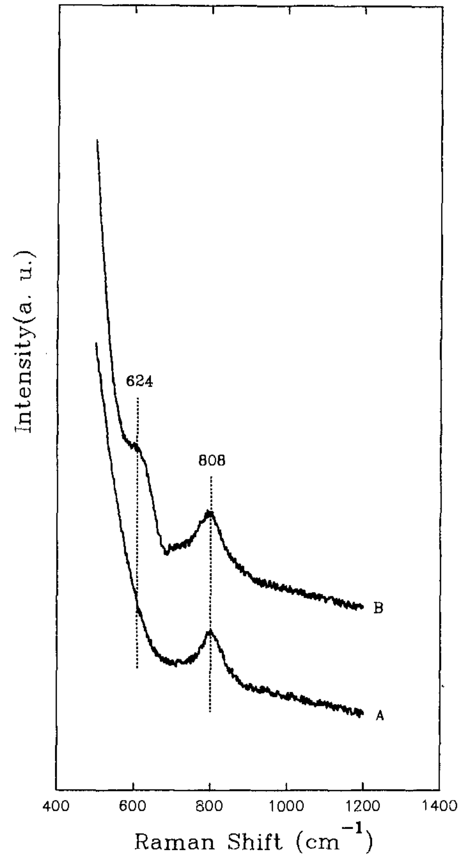

Fig. 5. Raman spectra of adsorbed oxygen on electrolytic silver obtained at 873 K (wavenumber range from 500 to 1200 cm^{-1}). (A) after exposure to oxygen at RT, the sample was heated to 873 K in pure nitrogen flow; (B) obtained in oxygen flow at 873 K.

were assigned to the O–O stretch vibration of $Ag^+O_2^-$ [13,14]. According to the works mentioned above, our assignments are reasonable.

There are almost no data reported concerning the bands at 436 and 808 cm^{-1}. From figs. 2 and 3, we observe that the O_γ state (436 cm^{-1}) remains unchanged in a wide temperature range from room temperature up to 873 K. From TDS of oxygen on electrolytic silver [3], we obtained that the starting desorption temperature of the subsurface oxygen species is above 800 K, so we assigned the band near 436 cm^{-1} to the subsurface oxygen species. This assignment was supported by the following facts: a vibration at 499.2 cm^{-1} was attributed to matrix isolated AgO [15], and a Raman band at 430 cm^{-1} was reported for solid AgO [16]. As for the band at 808 cm^{-1}, Pettenkofer et al. [7] observed bands at 815/838 cm^{-1} and they assigned these bands to an ozonide species, O_3^-. Since, under the conditions in our experiment, little possibility would be available for the transformation of O_2 to ozonized species, this assignment should be excluded. Recently, Pettingerm et al.

[17] studied the surface and subsurface oxygen species at silver surfaces by SERS and assigned a band at 803 cm^{-1} to species strongly chemisorbed on the surface. Compared with the XPS results of the O_{1s} spectrum, they indicated that the 803 cm^{-1} band was due to atomic oxygen on silver surface. With consideration of the roughness of electrolytic silver surface and the reconstruction of the sample under pretreatment, we support the assignment in ref. [17] and prefer the band O_β to be an atomic adsorbed state of oxygen. Of course, some works contradict this kind of assignment, such as a recent report of the 803 cm^{-1} line to molecular oxygen [18]. Since the O_β state exists above 873 K and molecularly adsorbed oxygen seems impossible to keep stable on silver surface at such a high temperature, assignment of the O_β state to atomic oxygen on silver surface is more believable.

Therefore, there are four adsorption states of oxygen on the surface of electrolytic silver: the $O_{\alpha1}$ state, peroxide species; the $O_{\alpha2}$ state, superoxide species; the O_β state, atomic adsorbed oxygen; the O_γ state, subsurface species. The O_β and O_γ states are stable over the temperature range of 298–873 K. The $O_{\alpha1}$ state is stable below 773 K and the $O_{\alpha2}$ below 673 K. The characteristics of these four adsorption states are listed in table 1. At the reaction temperature, only atomic adsorbed oxygen and subsurface species remain on the surface. The peroxide species appears again when oxygen is introduced to the sample at 873 K. This result proves that the oxygen flow causes the formation of peroxide species on the surface. At reaction temperature, no superoxide species is found on the surface even in the oxygen flow.

4. Discussion

4.1. STABILITY OF OXYGEN ADSORBED ON THE SURFACE OF ELECTROLYTIC SILVER

Both atomic adsorbed oxygen and molecularly adsorbed oxygen were detected on the Ag(110) and Ag(111) surfaces and the electrolytic silver surface under UHV conditions. The desorption temperatures (T_p) in the literature are listed in table 2 for comparison with our results.

In this work, the desorption temperatures of the adsorbed oxygen are much

Table 1
The characteristics of adsorbed oxygen on electrolytic silver

Frequency (cm^{-1})	State label	Assignment	Temperature behavior
436	γ	subsurface O	persists up to 600°C
624	α_1	peroxide	weakens, disappears above 600°C
808	β	adsorbed O	persists up to 600°C
1078	α_2	superoxide	shifts, disappears above 500°C

higher than those listed in table 2. The atomic adsorbed oxygen remains stable above 873 K and the peroxide and superoxide species exist up to 773 and 673 K, respectively. We ascribed this high stability of surface oxygen species at ambient pressure to the following cases:

(a) *More defects on the surface of electrolytic silver stabilize the adsorbed oxygen.*

Our previous works showed that electrolytic silver had special surface structure and surface morphology [4,5]. It was estimated that the defect concentration on electrolytic silver surface was more than 20%, with comparison of single crystal silver surface. It is generally agreed that oxygen, particularly dioxygen, favorably sticks on surface defect sites [21–23]. This is one of the reasons why the adsorbed oxygen species can exist on electrolytic silver even at higher temperature.

(b) *High pressure and temperature of oxygen make the adsorbed oxygen more stable.*

The previous works listed in table 2 were accomplished at lower oxygen pressures, usually 10^{-2}–10^{-8} Torr. In this paper, the adsorption of oxygen is carried out at an oxygen pressure of 0.2 atm (about 150 Torr) or in oxygen flow. Much higher partial pressure of oxygen caused quite different adsorption behavior.

We considered the molecularly adsorbed oxygen species: $O_{\alpha 1}$ and $O_{\alpha 2}$ states, first. Lambert et al. [21] pointed out that the dioxygen species was much more strongly adsorbed on Ag(111) at higher oxygen pressures (10^{-2} Torr) (see table 2, e), while Campbell et al. [20] observed the weakly adsorbed molecular oxygen at lower oxygen pressures (10^{-4} Torr) on Ag(111). It seemed that higher oxygen pressures caused stronger adsorption of dioxygen species. Therefore, we can expect that the desorption temperature of adsorbed molecular oxygen which adsorbed at ambient pressure would be even more higher than that under UHV conditions (462 K [3]).

Our previous works showed that the states of atomic adsorbed oxygen species changed while the coverage of oxygen increased [3]. The O_{1s} XPS spectrum gave a peak at 528.3 eV which was due to adsorbed atomic oxygen over the range of exposure between 10^2 and 10^3 L. But this peak diminished when the exposure of oxygen rose to 10^5 L. Meanwhile a new peak at 529.7 eV appeared. This phenomenon indi-

Table 2
The desorption temperature (K) of oxygen from silver surface [a]

	Surface of silver		
	Ag(110)	Ag(111)	electrolytic silver
molecularly adsorbed oxygen	150 [b,c]	217 [d] 380 [e]	462 [f]
atomic adsorbed oxygen	597 [d]	617 [d]	620 [f]

[a] The desorption temperature was measured by TDS in UHV chamber.

[b] Ref. [19]. [c] Ref. [9]. [d] Ref. [20]. [e] Ref. [21]. [f] Ref. [3].

cated that the adsorbed atomic oxygen did not tend to recombine to form molecular oxygen but rather formed another phase of atomic oxygen as the coverage increased. Recently, Bao et al. [24] studied the active state of silver during catalytic oxidation of methanol and pointed out that under ambient pressures and high temperature, the Ag(111) surface was reconstructed and the atomic oxygen adsorbed more strongly on this distorted silver lattice, which was quite different from the results obtained in UHV systems. Therefore, we suggest that the O_β state in this paper is a similar atomic oxygen species with high stability under the high pressure of oxygen and temperature.

4.2. OXYGEN SPECIES PARTICIPATING IN THE OXIDATION OF METHANOL

The molecular mechanism of methanol oxidation to formaldehyde on silver surface has been studied by many researchers. Wachs and Madix [25] studied Ag(110) and gave a mechanism containing the reaction of atomic adsorbed oxygen with molecular methanol in the gas phase. We studied the process of methanol oxidation on electrolytic silver surface in detail by using TPRS [4] and HREELS [6], and suggested that atomic adsorbed oxygen reacted with a gaseous methanol molecule to form a methoxide intermediate, then the methoxide reacted further with atomic oxygen to form formaldehyde at the appropriate temperature. The mechanism is shown schematically below:

$$CH_3OH + O(a) \rightarrow CH_3O(a) + OH(a)$$

$$CH_3O(a) + O(a) \rightarrow H_2CO(a) + OH(a)$$

$$H_2CO(a) \rightarrow H_2CO(g)$$

$$HO(a) + OH(a) \rightarrow H_2O(a) + O(a)$$

$$H_2O(a) \rightarrow H_2O(g)$$

The TPRS and HREELS experiments were accomplished in the UHV system, and, as shown in table 2, the desorption temperature of atomic adsorbed oxygen on silver was just 620 K. It is well known that the oxidation of methanol to formaldehyde was carried out at the range of 870–970 K. Thus, according to the TDS experiment [3], no atomic oxygen existed on the surface of electrolytic silver at the temperature of the industrial process. Therefore, there are still some doubts about this molecular mechanism when it is used to understand the industrial process.

In situ Raman spectroscopy proved the existence of atomic adsorbed oxygen species on electrolytic silver surface even above 873 K (fig. 3). This atomic oxygen could react with methanol at 873 K (the results will be published elsewhere). This result gives a direct evidence that under the industrial conditions, the adsorbed atomic oxygen actually exists on the silver surface and participates in the reaction.

Thus, the molecular mechanism mentioned above seems to be effective not only in UHV systems but also in the practical process.

4.3. PEROXIDE ACTS AS PRECURSOR TO ADSORBED ATOMIC OXYGEN

In the above, we discussed the facts that atomic adsorbed oxygen on electrolytic silver remained stable at the reaction temperatures and reacted with gaseous methanol to produce formaldehyde. Since oxygen can adsorb in dissociated form under industrial conditions, the adsorption behaviors of oxygen on silver surface should be studied and compared with the previous works. The adsorption behavior of oxygen on silver surface has some interesting features, one of which is the transformation of molecularly adsorbed oxygen to atomic adsorbed oxygen species. The precursor state was observed by Campbell on Ag(111) [20]. According to the results based on the sticking probability experiment and TDS of oxygen adsorbed on electrolytic silver, we also suggested the following adsorption mechanism with the precursor [5]:

$$O_2(\text{gas}) = O_2(\text{ads. as precursor}) \rightarrow 2O^-(\text{ads.})$$

When this mechanism is used to explain the industrial process, it meets a difficulty that the precursor state (molecularly adsorbed oxygen) cannot exist above 460 K. This contradiction is solved by the Raman spectra in this paper. From fig. 5 it is seen that without oxygen flow through the electrolytic silver sample at 873 K, there is only the adsorbed atomic oxygen species (O_β state), which would be exhausted by methanol. But when oxygen passes through the sample at 873 K, the peroxide species ($O_{\alpha 1}$ state) appears again on the surface of silver and the intensity of the O_β state becomes somewhat higher. This result suggests directly that the continuous oxygen flow supplies the peroxide species as a precursor, and makes the adsorption process in equilibrium. This is also the evidence that under the industrial conditions, molecularly adsorbed oxygen acts as a precursor to the atomic adsorbed oxygen.

Since the TDS method could not give a clear distinction between peroxide and superoxide species, the previous works did not recognize which one was the precursor to atomic adsorbed oxygen. An interesting result from Raman spectra in this paper is that peroxide species is detected to be on the silver surface above 873 K in O_2 flow. Therefore, we can at least suggest that the configuration of the precursor is related with the peroxide species. From fig. 5 we can also see that superoxide species cannot exist on electrolytic silver at 873 K even in oxygen flow. So we can exclude the possibility of superoxide acting as a precursor.

This result is consistent with our recent theoretical calculations in quantum chemistry [26]. In this ab initio study, a six Ag atom cluster was chosen to model the long bridge site on the Ag(110) surface and adsorbed geometry, species and energies were investigated with conventional cluster model (CM) and dipped adcluster model (DAM) methods. The two most stable states are:

(1) peroxide ${}^1A_1, O_2^{2-}$, adsorbed energy $E_b \approx 12.50$ kcal/mol, $R_\perp = 83$ pm, $R_{O-O} = 148$ pm;

(2) superoxide ${}^3A_2, O_2^-$, adsorbed energy $E_b \approx 6.51$ kcal/mol, $R_\perp = 189$ pm, $R_{O-O} = 127$ pm

(here $R_\perp$ represents the distance between O–O bond and Ag surface).

The calculation results show that the peroxide species is closer to the silver surface and the O–O bond length is longer. So it tends to form the precursor of dissociation–adsorption at high temperature. But for the superoxide species, it is far away from the silver surface ($R_\perp = 189$ pm) and the O–O bond length is shorter. So desorption of this species in a molecular form at high temperature would be expected. From the data of adsorbed energy E_b of these two species, one can also conclude that peroxide species is more stable than superoxide species. This is also confirmed by the Raman spectra in this paper.

5. Conclusion

(1) In situ Raman spectroscopy has been employed to investigate the oxygen adsorbed on the electrolytic silver catalyst and four Raman bands are found at room temperature. These bands are assigned to four different surface oxygen species: two molecularly adsorbed oxygen species (peroxide oxygen species and superoxide oxygen species), chemisorbed atomic oxygen species and subsurface oxygen species. The desorption temperatures of these species are much higher under ambient pressures than under UHV conditions. This means the ambient pressures stabilize the adsorbed oxygen species.

(2) The vibration band of atomic adsorbed oxygen can be found at temperatures up to 873 K. This species can react with the methanol molecule to form methoxide intermediate, and finally form formaldehyde.

(3) The molecularly adsorbed oxygen formed on the surface of electrolytic silver when oxygen was passed through the surface at reaction temperature (above 873 K). In the process of methanol oxidation, the molecularly adsorbed oxygen acts as a precursor and transforms to atomic oxygen. It supplies the consumption of atomic adsorbed oxygen in the reaction. The molecularly adsorbed species is proved to be peroxide species at reaction temperature.

(4) The molecular mechanism of methanol oxidation to formaldehyde and the adsorption mechanism of oxygen with a precursor are proved to be effective under industrial conditions.

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