

# Transformation of Various Oxygen Species on the Surface of Electrolytic Silver Characterized by in Situ Raman Spectroscopy

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**Abstract:** Transformation of various oxygen species adsorbed on the electrolytic silver surface pretreated by pure oxygen at 423–973 K under ambient pressure was observed for the first time by in situ confocal microprobe Raman spectroscopy. Ag–O<sub>2</sub> species can transform into Ag[O–O]<sup>–</sup> species slowly at temperatures below 423 K. Once the temperature rises to 423 K, the transformation of Ag[O–O]<sup>–</sup> to Ag–O( $\alpha$ ) species takes place. With further increase in temperature, the Ag–O( $\alpha$ ) species first transforms to Ag–O–O–Ag and then to Ag–O( $\gamma$ ) species, which is the most stable oxygen species on the silver surface and can be maintained even above 973 K. As for the practical reaction system, the adsorbed molecular oxygen was found to be present on the silver surface at low temperature. It transforms to Ag–O( $\alpha$ ) species under similar conditions to those for the partial epoxidation of ethylene, and then transforms to Ag–O( $\gamma$ ) oxygen species under conditions similar to those for selective oxidation of methanol to formaldehyde. A possible mechanism for the detailed transformation of oxygen species was also proposed.

**Key Words:** electrolytic silver; oxygen species; in situ Raman spectroscopy

The well-known peculiar activity and selectivity of electrolytic silver as catalyst for the heterogeneous partial oxidation of methanol to formaldehyde and ethylene to ethylene epoxide have been extensively investigated [1]. A great number of studies were devoted to the surface properties of electrolytic silver and the interaction of oxygen with silver surfaces, which has been widely considered to play a key role in the above-mentioned reactions [2,3]. To understand the nature and properties of the adsorbed oxygen species is one of the central problems for the investigation of the reaction mechanism. Based on previous studies, all kinds of oxygen species are usually classified into four main groups: physisorbed molecular oxygen, chemisorbed molecular oxygen, dissociative adsorbed atomic oxygen, and the one incorporated into the sub-surface layers or dissolved in the bulk [4,5].

Most of the previous research was carried out in an ultra-high vacuum (UHV) system, in which the low exposure of molecular oxygen restricted the reasonable explanation for the

practical system under atmospheric pressure. Due to the very different conditions between the UHV system and the practical industrial process, the chemical states of adsorbed oxygen on electrolytic silver under the practical reaction conditions must be different from those under UHV conditions. We have reported some preliminary results about the oxygen species under practical conditions [6]. Recently, Waterhouse et al. [7] reported a silver-oxygen system, in which different oxygen species were detected and a possible transformation process was proposed. However, the relationship among these oxygen species has not been clearly revealed, and it has never been reported for the transformation of various oxygen species under ambient pressure and relatively low temperature (373 K).

In this work, with the help of in situ Raman spectroscopy, the detailed adsorption behavior of oxygen on electrolytic silver and the transformation of various oxygen species were investigated, and the relationship among these species under practical conditions was also studied.

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## 1 Experimental

### 1.1 Samples and instruments

The polycrystalline silver catalyst was first calcined in pure oxygen at 873 K for at least 10 h and then pressed under the pressure of 22 MPa for 30 min. The as-obtained thin-sheet sample shows much high stability and reproducibility during the in situ Raman experiment.

In situ Raman spectra were obtained on a Jobin Yvon Horiba LabRam Infinity confocal microprobe Raman spectrometer equipped with a holographic notch filter, a CCD detector, and a specially designed Raman sample cell for in situ studies. The silver sample was put in a stainless steel cup covered and sealed with a thin quartz window. With a heater under the cup, the sample can be heated up to 973 K. Temperature of the sample is controlled by a temperature programmer and measured through a Pt-Rh thermocouple attached to the bottom of the sample. The laser source was chosen as  $\text{Ar}^+$  ( $\lambda_0 = 514.5 \text{ nm}$ ), and the power was set as 9.6 mW to avoid any influence of the heat effect from the laser. For most of the Raman spectra, the 100–2000  $\text{cm}^{-1}$  region was focused on in the present work where almost all of the important stretching vibrations were generally located. The Raman spectra were then recorded based on an Olympus BX40 system and by using a 50-fold long working-length objective (8 mm). In situ X-ray photoelectron spectra were obtained on a PHI 5000C ESCA system.

### 1.2 Experiment

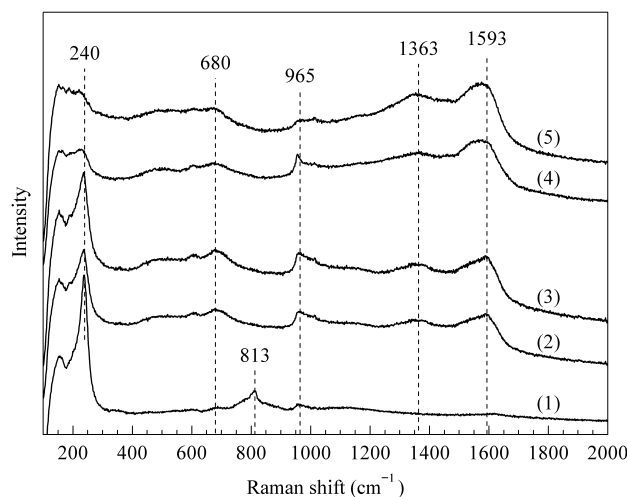
The pretreated silver sheet was carefully placed in the in situ Raman cell and heated to 773 K in pure oxygen (>99.999%) flow for 1 h to remove any contaminant carbon species adsorbed on the silver surface when exposed to air. The sample was then cooled down to room temperature (ca. 298 K) in oxygen flow and remained for at least 30 min until the adsorption of oxygen was complete. An argon flow with high purity (> 99.999%) was then introduced to the in situ cell instead of the oxygen flow.

## 2 Results and discussion

### 2.1 Raman spectra for the sample from RT to 413 K

Fig. 1 shows the Raman spectra of the adsorbed oxygen species on the pretreated electrolytic silver surface at different temperatures from room temperature to 413 K. There are only one strong and narrow band at 240  $\text{cm}^{-1}$  and a relatively weak band at 813  $\text{cm}^{-1}$  at room temperature. Weak bands located at 680  $\text{cm}^{-1}$  and 965  $\text{cm}^{-1}$  are also observed. With temperature increasing to 323 K, the weak band at 813  $\text{cm}^{-1}$  disappears, and the intensity of the one at 240  $\text{cm}^{-1}$  becomes much

weaker than that at room temperature. In addition, except for the intensity enhancement of the ones at 680  $\text{cm}^{-1}$  and 965  $\text{cm}^{-1}$ , two new bands at 1363 and 1593  $\text{cm}^{-1}$  appear at 323 K, which can be commonly assigned to surface-contaminant carbon species [8]. However, in the present work, the silver surface is cleaned with pure oxygen flow at high temperature in advance, and there is not any carbon species detected under either high temperature or room temperature by Raman spectroscopy.



**Fig. 1** In situ Raman spectra of the adsorbed oxygen species on electrolytic silver at different temperatures  
(1) 298 K, (2) 323 K, (3) 333 K, (4) 373 K, (5) 413 K

In order to confirm this conclusion, in situ X-ray photoelectron spectroscopy (XPS) was used to detect the surface carbon species, and no carbon was observed on the surface after the pretreatment. In the in situ XPS experiment, the silver sheet was treated following the same procedure as in the Raman test in the pretreatment chamber. After that, it was transferred in situ to the analysis chamber without contacting with air. There are only peaks for Ag and oxygen in the XPS spectra. The XPS analysis was carried out at a much higher pass energy (197 eV) and high X-ray power (350 W) in order to obtain a much high sensitivity. Moreover, no chloride contaminant could be found on the surface of the silver sample used in our experiment although it appears in Waterhouse's report [7]. Therefore, the two bands at 1363  $\text{cm}^{-1}$  and 1593  $\text{cm}^{-1}$  may be associated with certain other kinds of oxygen species, but must be irrelevant with carbon on the surface.

The bands at 240  $\text{cm}^{-1}$  and 965  $\text{cm}^{-1}$  can be naturally assigned to the molecularly chemisorbed oxygen species, named as Ag–O<sub>2</sub> vibration according to that previously reported by Waterhouse et al. [7] — in their work three bands ascribed to Ag–O<sub>2</sub> species can be observed at 225, 970, and 1180  $\text{cm}^{-1}$ , respectively. The band at 813  $\text{cm}^{-1}$  can also be ascribed to Ag–O( $\gamma$ ) according to that reported by Waterhouse et al [7]. However, this Ag–O( $\gamma$ ) seems very unstable and shows similar

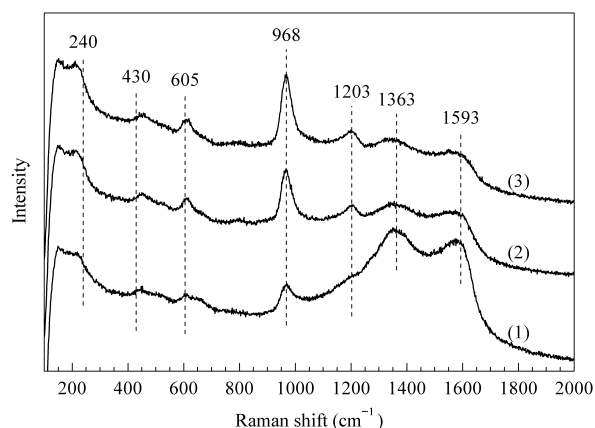
action as  $\text{Ag-O}_2$  with the change of temperature. Therefore, we can consider this species as another kind of  $\text{Ag-O}(\gamma)$  that appeared at different sites on the silver surface. The band at  $1363\text{ cm}^{-1}$  can be assigned to super-oxide species ( $\text{Ag}[\text{O-O}]^-$ ) according to that reported by Prabhakaran et al [9]. Since the bands at  $1363\text{ cm}^{-1}$  and  $1593\text{ cm}^{-1}$  appear and change with the temperature simultaneously, the band at  $1593\text{ cm}^{-1}$  should also be naturally assigned to another Raman mode of  $\text{Ag}[\text{O-O}]^-$  species. The band located at  $680\text{ cm}^{-1}$  cannot be easily assigned, not only for its weak intensity but also for its disappearance at relatively high temperature of  $333\text{ K}$ . Therefore, it can be concluded that the  $\text{Ag-O}_2$  species can transform to  $\text{Ag}[\text{O-O}]^-$  species with temperature increasing from room temperature to  $323\text{ K}$ . With further increase in temperature, the intensity of the Raman band for  $\text{Ag-O}_2$  becomes much weaker while that for the  $\text{Ag}[\text{O-O}]^-$  species increases remarkably, which further confirms the transformation of  $\text{Ag-O}_2$  to  $\text{Ag}[\text{O-O}]^-$  species. Table 1 lists the vibrational frequency and assignment for various chemisorbed oxygen species.

**Table 1** Vibrational frequency and assignment of various chemisorbed oxygen species

Species	Assignment	Raman shift ( $\text{cm}^{-1}$ )	
		Present study	References
$\text{Ag-O}_2$	$\nu(\text{Ag-O}_2)$	240	225 <sup>[7]</sup>
	$\nu(\text{O-O})$	886, 965	970 <sup>[7, 10, 11]</sup>
	$\nu(\text{Ag-O}_2) + \nu(\text{O-O})$	–	1180 <sup>[7]</sup>
$\text{Ag}[\text{O-O}]^-$	$\nu(\text{O-O})^-$	1363, 1593	1320 <sup>[10]</sup>
$\text{Ag-O}(\alpha)$	$\nu(\text{Ag-O})$	968, 1203	956, 985 <sup>[11]</sup>
$\text{Ag-O}(\beta)$	$\nu(\text{Ag-O})$	430, 605, 630	640 <sup>[7, 11]</sup>
$\text{Ag-O}(\gamma)$	$\delta(\text{Ag-O})$	345	350 <sup>[7]</sup>
	$\nu(\text{Ag-O})$	805, 813	810 <sup>[7]</sup>
	$2\nu(\text{Ag-O})$	1610	–

## 2.2 Raman spectra for the sample at 423 K

When the temperature reached  $423\text{ K}$ , the adsorbed oxygen species change obviously with time. As shown in Fig. 2, the intensity of the two bands located at  $1363$  and  $1593\text{ cm}^{-1}$  decrease, and two new bands at  $1203$  and  $968\text{ cm}^{-1}$  appear, which may be named as  $\text{Ag-O}(\alpha)$  [10], and the intensity of which obviously increases with time. Thus, a transformation of the oxygen species from  $\text{Ag}[\text{O-O}]^-$  to  $\text{Ag-O}(\alpha)$  at  $423\text{ K}$  may occur. The  $240\text{ cm}^{-1}$  band does not change obviously, while two new bands at  $430$  and  $605\text{ cm}^{-1}$  appear and continue to gain intensity with time, similar to those at  $1203$  and  $968\text{ cm}^{-1}$ . According to the literature results, these two bands can be ascribed to subsurface  $\text{Ag-O}(\beta)$  species shifted by neighboring subsurface hydroxyl groups [7]. Considering their weak intensity, the two bands are not discussed in detail in the present work.

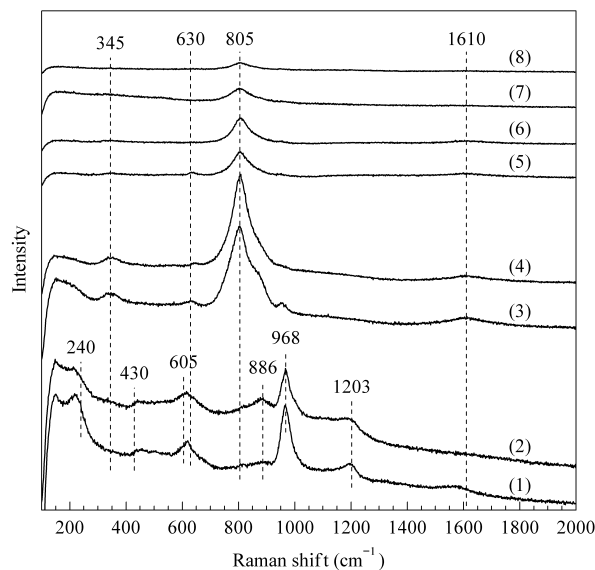


**Fig. 2** Time resolved in situ Raman spectra of adsorbed oxygen species on electrolytic silver treated at  $423\text{ K}$  for different times

(1) 10 min, (2) 20 min, (3) 30 min

## 2.3 Raman spectra for the sample from 433 K to 973 K

Fig. 3 shows the change of Raman spectra with temperature further increasing from  $433\text{ K}$  to  $973\text{ K}$ . There are great changes of the spectra in the temperature range of  $433$ – $473\text{ K}$ , suggesting the presence of further transformation of the adsorbed oxygen species on the electrolytic silver surface. With the intensity decrease of the bands at  $968$  and  $1203\text{ cm}^{-1}$ , a new Raman band at  $886\text{ cm}^{-1}$  appears, which can be assigned to a low stable chemisorbed molecular  $\text{Ag-O-O-Ag}$  species [11], that is to say, the transformation of atomic adsorbed oxygen species from  $\text{Ag-O}(\alpha)$  to  $\text{Ag-O-O-Ag}$  occurs. In addition, a new band at  $240\text{ cm}^{-1}$  appears, which is observed



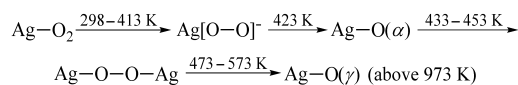
**Fig. 3** In situ Raman spectra of the adsorbed oxygen species on electrolytic silver at different temperatures

(1)  $433\text{ K}$ , (2)  $453\text{ K}$ , (3)  $473\text{ K}$ , (4)  $573\text{ K}$ , (5)  $673\text{ K}$ , (6)  $773\text{ K}$ , (7)  $873\text{ K}$ , (8)  $973\text{ K}$

for the first time and the transformation mechanism is not clear as yet. In order to distinguish this band from that appears at low temperature, this species is denoted as Ag–O–O–Ag, but not Ag–O<sub>2</sub> in the following discussions. Once the temperature is further increased to 473 K, two other new Raman bands at 345 and 805 cm<sup>-1</sup> appear, and the one at 886 cm<sup>-1</sup> is weakened and disappeared finally.

It is very interesting to note that with increasing temperature from 473 K to 573 K (Fig. 3 (b)), the Raman band at 805 cm<sup>-1</sup> becomes very strong and symmetrical, suggesting the thorough disappearance of the band at 886 cm<sup>-1</sup> and the transformation of the corresponding species at this position to that at 805 cm<sup>-1</sup>. Also, a new band at 1610 cm<sup>-1</sup> appears and is easily ascribed to the octave frequency band of that at 805 cm<sup>-1</sup>. The band at 630 cm<sup>-1</sup> may be somewhat related to Ag–O(β), and reasons are as that raised in 2.2 section. As the temperature was further increased from 573 K to 973 K, no Raman bands disappear and no new bands appear except for the intensity change of the two bands at 630 and 805 cm<sup>-1</sup>, implying that the surface oxygen species was stable in the temperature range from 573 K to 973 K. The intensity change of the Raman bands is resulted from the minor change of the surface structure with the increase in temperature. For the excellent stability of the species at 345 and 805 cm<sup>-1</sup>, they can be naturally assigned to the most stable subsurface Ag–O(γ) oxygen species [1].

Scheme 1 shows the transformation pathways of various oxygen species. As the temperature is lower than 423 K, Ag–O<sub>2</sub> species can transform to Ag[O–O]<sup>-</sup> slowly. Once the temperature is raised to 423 K, a time-resolved transformation will take place, that is, Ag[O–O]<sup>-</sup> to Ag–O(α) species. When the temperature further increases, the Ag–O(α) species will transform to Ag–O–O–Ag and then to Ag–O(γ), which is the most stable oxygen species on the silver surface and can be maintained in this form even above 973 K.



**Scheme 1** Transformation pathways of the adsorbed oxygen species on the pretreated electrolytic silver surface

### 3 Conclusions

In situ Raman spectroscopy was used to investigate the ad-

sorbed oxygen species on the pretreated electrolytic silver surface, and the transformation of various oxygen species was observed under ambient pressure for the first time. This is very important for the reaction mechanism speculation of a practical reaction system with silver as the catalyst. Previous experimental and theoretical studies have shown that only a specific adsorbed oxygen species Ag–O(γ) plays the key role in the dehydrogenation of methanol [12]. Our present work provides the reasonable transformation pathways of the associated oxygen species and also much reasonable evidence. The in situ Raman spectroscopy results clearly demonstrate that the adsorbed molecular oxygen is actually present on the silver surface at low temperature, and will transform to Ag–O(α) species under similar conditions as that of the partial oxidation of ethylene, and will then transform to Ag–O(γ) oxygen species undoubtedly under conditions similar to that employed for selective oxidation of methanol. In other words, the present in situ Raman studies clearly reveal the active sites of silver for the two kinds of famous industrial manufactures using silver-based catalysts. Further research on the reaction properties of these different species and the mechanism at the molecular level is under way.

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