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HREELS OF METHANOL OXIDATION ON POLYCRYSTALLINE SILVER: SPECTROSCOPIC EVIDENCE FOR ADSORBED INTERMEDIATES IN THE CONVERSION OF METHOXIDE TO FORMALDEHYDE AND WATER

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The adsorption and the decomposition of methanol on an oxygen precovered polycrystalline silver surface were characterized by high resolution electron energy loss spectroscopy. A stable methoxy species and subsequently two new intermediates related to the decomposition of methoxy have been isolated and identified by temperature profiled ELS.

1. Introduction

The decomposition and selective oxidation of methanol on metal surfaces have been the subject of numerous previous studies [1–12]. This reaction is of interest from two points of view: the low pressure decomposition with various selective pathways, and the high pressure synthesis of methanol from $CO + H_2$. In the former case, the various surface intermediates of methanol adsorbed are of interest because their reactivity with a particular substrate has been found to control the ultimate decomposition products. Recent studies show that on most transition metal surfaces, this reaction proceeds via a methoxy intermediate which decomposes directly to $CO + H_2$. On several transition metal surfaces, e.g. Pt [4], Pd [1,10], Ru [6], this methoxy species has been identified by various techniques including vibration spectroscopy. The mechanism by which the methoxy species decomposes into $CO + H_2$, $CH_4 + O - M$, $H_2 + C - M + O - M$, or recombines with chemisorbed hydrogen to form methanol is reasonably understood. In contrast to this thermal decomposition on transition metal surfaces, methanol

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selectively oxidizes to form formaldehyde on most noble metal surface, e.g. Cu, Ag [11,13,14]. On the silver surface, the oxidation of methanol to formaldehyde is one of the most important commercial processes and has been studied intensively [11,14]. Several recent studies show that this reaction also proceeds via a methoxy surface intermediate. By using various techniques (XPS, UPS and TPRS), surface methoxy species have been identified on well-defined single crystal and polycrystalline silver surfaces [11,14]. A mechanism proceeding via a methoxy surface intermediate has been established by Madix [14], and Benninghoven's [15] work as well as our own previous studies [11].

However, a direct proof of methoxy species on silver surfaces, particularly on the polycrystalline silver surface, has not been obtained. In this paper, we report the first observation of silver methoxide species on a polycrystalline silver surface with high resolution electron energy loss spectroscopy. A new intermediate related to the dehydrogenation of the methoxy species has also been isolated and identified during annealing the surface. This result is agreement with previous studies.

2. Experimental

A complete description of the experimental apparatus and the in situ cleaning methods has been published previously [16]. Briefly, the Leybold Heraeus stainless steel chamber with a base pressure of $1 \cdot 10^{-10}$ mbar equipped with facilities for UPS, AES, LEED, QMS, sputter ion gun and the rotatable Leybold-Heraeus ELS22 spectrometer with 127° cylindrical deflectors. Two effusive molecular beam gas dosers were used to dose oxygen and methanol preferentially onto the surface of the sample while maintaining a low working pressure (10^{-9}–10^{-8} mbar).

All HREELS data shown were obtained in the specular scattering configuration (where dipole scattering dominates) with a primary electron energy of 2.3 eV and resolution of 10–14 meV (10–110 cm^{-1}) full-width-at half-maximum. Selected off-specular scans verified the dipole character of the observed vibrational losses.

Polycrystallline Ag (purity 99.999%) was obtained by means of triple electrolytic refining which was described in detail elsewhere [11]. The sample was prepared by pressing the polycrystalline powder into a disc of about 8 mm in diameter and 0.8 mm in thickness. After polishing both front and back faces mechanically with diamond pastes (final grain size 0.1 μm), the sample was spot welded to a pair of 0.3 mm Ta wires. The Ta wires were bound to a Mo sample holder which was in thermal contact with the liquid nitrogen reservoir of a differentially pumped rotating feedthrough. The sample temperature can be ramped from 180 K to 900 K linearly, and measured by a Pt/Pt–10%Rh thermocouple contacted to the sample.

Removal of the impurities (C, Cl, S) was accomplished by Ar^+ sputtering followed by 300–900 K cyclic heat treatment at oxygen pressures of $5 \cdot 10^{-7}$ mbar. The cleanliness of the sample was monitored by AES and EELS.

The CH_3OD was obtained from the equilibrium vapor pressure of reagent-grade liquid from MERCK Co. after freeze-thaw cycling and introduced into the chamber through beam doser. The doser can make an effective pressure at the surface, which is twelve times greater than that measured in the background during exposures of the gases.

3. Results and discussion

3.1. ADSORPTION OF OXYGEN: EVIDENCE FOR DIOXYGEN AND ATOMIC OXYGEN

The interaction of oxygen with a silver surface has been investigated very intensively [11,14,17,18], and three types of oxygen species on silver surfaces have been identified. These are dioxygen species, activated atomic oxygen species and sub-surface atomic oxygen. Recent studies show that the characteristics of oxygen adsorption, particularly dioxygen adsorption, are governed by the surface structure and surface morphology [18]. On the well-defined surface [e.g. Ag(110)], only at temperatures below 150 K or at oxygen pressures above 10^{-2} Torr, are both dioxygen and atomic oxygen species observed. Upon annealing these surface to about 180 K, dioxygen dissociates and only the dissociated atomic oxygen remains.

In our recent investigation [17,18], oxygen adsorption on a polycrystalline electrolytic silver surface was characterized by XPS, TDS and Work Function measurements. At room temperature and under UHV conditions both weakly chemisorbed oxygen species and the strongly bonded oxygen species were detected. The behavior of the stronger state is consistent with associative desorption of atomic oxygen. Isotope scrambling experiments showed adsorption and desorption of this "weak-state" without any exchange, indicating that the O–O bond remains intact throughout the adsorption-desorption process. The observation that this species is unreactive towards CO is also consistent with the property of a dioxygen species. It has been concluded that except for an atomically adsorbed state, a dioxygen species can stably exist on electrolytic silver even at room temperature and low oxygen pressure.

The thermal desorption spectra of oxygen on electrolytic silver for various adsorption temperatures are showed in fig. 1. At oxygen adsorption temperatures below 180 K only a weakly adsorbed oxygen species exists on the surface, and at elevated adsorption temperature both weakly or strongly adsorbed oxygen adsorbed oxygen species can be monitored. The adsorption species seem to be controlled by changing the oxygen adsorption temperature. Comparing with our previous results, the "weak" and the "strong" oxygen species corresponded to

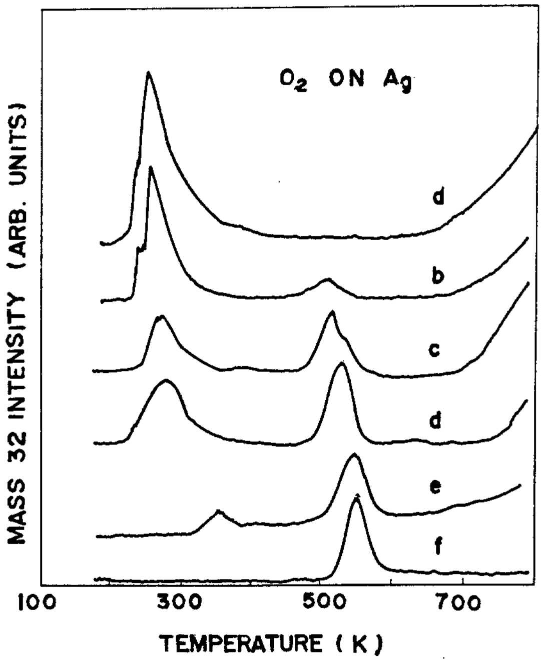


Fig. 1. Thermal desorption spectra after oxygen exposure of 30 L with the surface temperature during oxygen adsorption controlled at: a, 180 K; b, 195 K; c, 210 K; d, first 400 K and subsequent to 180 K; e, 300 K and f, 400 K. The temperature was recooled to 180 K before each flash.

dioxygen and atomic oxygen species respectively. From fig. 1 we can see that the desorption temperature of the dioxygen species shifts to lower temperature with decreasing oxygen adsorption temperature. This phenomenon can be reasonably explained by the lateral interactions between oxygen adsorbates on the surface. For dioxygen species the interaction between molecular oxygen and the silver is not very strong, and the bonding energy is about 23 kcal. With the decreasing adsorption temperature, the coverage of dioxygen on the surface will increase (see fig. 1), and the repulsive between the adsorbates on the surface will become considerable while inevitably weakening the interaction between oxygen and the silver. This consideration is consistent with Rovida's explanation for molecular oxygen on an Ag(110) surface [19].

Figure 2 shows the EELS spectra of the clean electrolytic silver and the oxygen-covered surface. In fig. 2 an obvious background of electron loss below 1000 cm^{-1} was present on the clean surface, which has been monitored on the clean Ag(110) face by Backx [20]. Comparing our recent results from clean Ag(110) with various surface treatment procedures this loss can be reasonably ascribed to surface defects.

TDS measurements have shown that below 180 K or above 400 K, oxygen adsorption only results in one state. However, if the adsorption condition is selected to expose the surface first to 30 L of oxygen at 400 K and subsequently

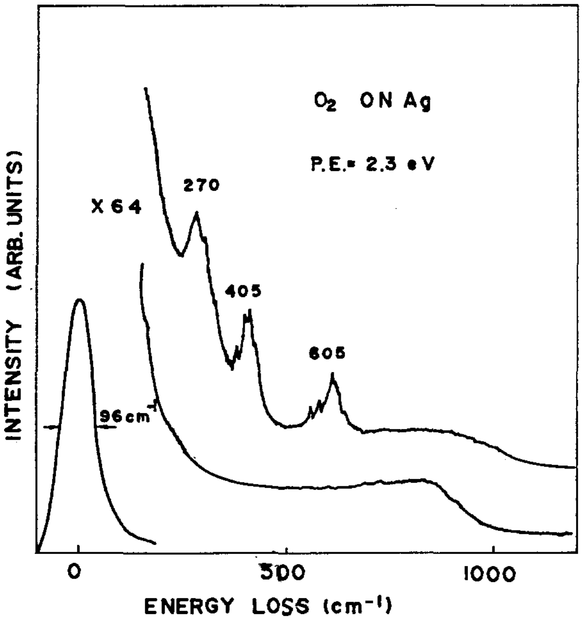


Fig. 2. Energy loss spectra of molecular and atomic oxygen adsorbed on electrolytic silver at 180 K. The beam energy was 2.3 eV.

to 30 L at 180 K, both oxygen species can be clearly detected (fig. 1d). Figure 2b shows the EELS spectrum under this oxygen exposure condition. Three losses were detected, at 270, 405 and 605 cm^{-1}. Heating the sample to above room temperature, the temperature at which dioxygen is desorbed, the two loss peaks at 270 cm^{-1} and 605 cm^{-1} disappear and the 415 cm^{-1} loss remains accompanied by the slight increase of the loss peak intensity. Further heating of the sample to 550 K causes the loss peak at 405 cm^{-1} to completely disappear and a clean surface was obtained. An assignment of the vibrational losses for adsorbed oxygen on a well-defined silver surface in EELS experiments was performed by Sexton et al. [21] and Backx et al. [20]. Comparison of the available sets of data with the vibrational frequencies here (table 1) allows us to assign the vibration at 405 cm^{-1} to v(Ag–O) and those at 270 cm^{-1}, 605 cm^{-1} to v($Ag-O_2$) and v(O=O) respectively.

In our previous studies, the electron transfer and the orientation of dioxygen on silver surface have been discussed [17,18]. By comparing the Extended Hückel Molecular Orbital (EHMO) calculation [23] we have concluded that dioxygen is adsorbed in a side-on configuration with the O–O axis parallel to the surface and forms a triangular $Ag-O_2$ complex on the surface.

The side-on adsorption mode of dioxygen on a silver surface is not in conflict with the normal dipole selection rule, significant intensity for bonds oriented parallel to a metal surface have also been observed [8]. Their arguments are related to considerable change oscillation perpendicular to the bond direction.

Table 1
Comparison of free oxygen with the observed losses for dioxygen and atomic oxygen on Ag(110) and electrolytic silver surfaces (band positions are in cm^{-1})

mode	free	on Ag(110) [b]	on Ag(110) [c]	On electrolytic Ag
$\nu(Ag-O)$	490	325	314	405
$\nu(Ag-O_2)$		240	240	270
$\nu(O_2)$ [a]	1555			
$\nu(O_2^-)$ [a]	1145	640	628	605
$\nu(O_2^{-2})$ [a]	842			

[a] ref. [22]; [b] ref. [23]; [c] ref. [20].

Our triangular model for dioxygen side-on adsorption is in agreement with their discussions. In this model the parallel stretch vibration of O–O bond induces a changing flow from the silver to the dioxygen species, which results in a dipole moment change perpendicular to the surface.

3.2. DECOMPOSITION OF METHOXY SPECIES

By heating an initial methanol multilayer to various temperatures, the desorption and decomposition of condensed methanol and the subsequent dehydrogenation of methoxy species were characterized by EELS (see fig. 3). In each case the sample was held at the required temperature for 2 min. All spectra were taken after recooling to 180 K and were normalized to constant intensity of the elastic peak.

Exposing the oxygen precovered surface to 0.7 L of CH_3OD will cause condensation of methanol at 180 K (fig. 3a). The vibrational frequencies absorbed from the condensed methanol can be identified as follows: $\nu(OD)$, 2460 cm^{-1}, $\nu(CH_3)$, 2980 cm^{-1}, $\delta(CH_3)$, 1450 cm^{-1}, $\nu(CO)$, 1010 cm^{-1}, $\delta(OD)$ out-of-plane bend, 530 cm^{-1}. This assignment relies upon the good agreement of the vibrational losses with those of liquid CH_3OD [24]. While warming the sample to 195 K, multilayer methanol desorbs leaving an adsorbed monolayer. Heating from 200 K to 220 K, an adsorbed methoxy species (CH_3O) is formed as evidenced by the disappearance of the characteristic $\nu(OD)$ and $\delta(OD)$ bands of methanol and by the appearance of an Ag–O stretching mode at 320 cm^{-1}. The vibrational band at 610 cm^{-1} indicates the revelation of adsorbed dioxygen species, which will desorb at 250 K. The remaining bands for adsorbed methoxy can be identified as the methoxy CH_3 asymmetry and symmetry stretches (2952 cm^{-1} and 2823 cm^{-1}) respectively, CH_3 band (1452 cm^{-1}) and CO stretch (990 cm^{-1}). The higher intensity of the CO stretching band with respect to other loss peaks suggests that CO bond lies perpendicular to the surface plane [28]. A comparison of our observed vibrational frequencies with those of gaseous CH_3OD and methoxy species on other metals, is given in table 2.

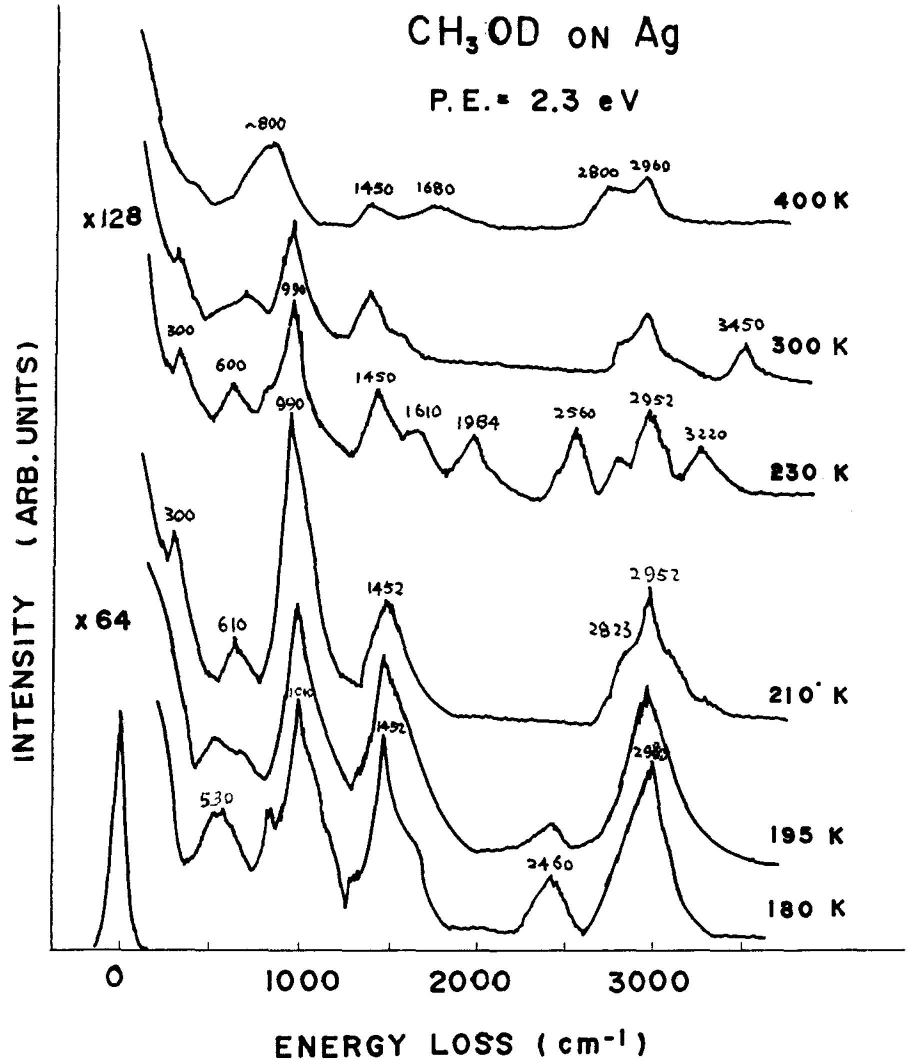


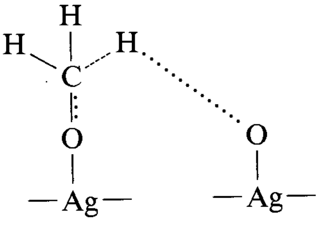
Fig. 3. Vibrational spectra of methanol decomposition on oxygen precovered electrolytic silver. The CH_3OD multilayer (0.7 L) was sequentially annealed to the indicated temperature for 2 min, and then recooled to 180 K for ELS measurement. (The procedure for oxygen adsorption is the same as fig. 1d.)

Further heating results in the decomposition of methoxy species. The spectrum after annealing to 230 K is shown in fig. 3d, which is of a completely different form. Although the characteristic vibrations of methoxy species still remain on the surface, their intensities have shown an obvious decrease, and the appearance of several new vibration bands indicates that partial decomposition of methoxy species has occurred. Additional experiments (not shown here) prove that the percentage of methoxy that decomposes is governed by the coverage of preadsorbed atomic oxygen. Higher oxygen coverage will lead to more decomposition of methoxy species.

Table 2
Comparison of vibrational losses for methoxy species adsorbed on a variety of metal surface (band positions are in cm^{-1})

	Methoxides[27]	Ni(111)[8]	Pd(110)[1]	Cu(100)[7]	Ag(poly)
$v_a(CH_3)$		2955	2975	2910	2952
$v_s(CH_3)$		2814	2800	2830	2823
$\delta(CH_3)$		1440	1460	1450	1450
Rock(CH_3)			1130		1150
v(CO)	1000–1100	1040	1010	1010	992
v($MOCH_3$)	< 600	500	710	290	300

In fig. 3d, the vibrational frequencies at 990 cm^{-1}, 1450 cm^{-1} and 2952 cm^{-1} can be attributed to methoxy species as discussed above. From separate studies of the adsorption of CO on metal surfaces, the strong 1984 cm^{-1} loss can be assigned to the v(CO) vibration of adsorbed CO species. In separate studies on the adsorption of H_2O on a polycrystalline silver surface, the adsorbed hydroxide was monitored and its vibration loss was found to present at 3450 cm^{-1}. Based on this, the loss at 3220 cm^{-1} can be interpreted as the stretching of a "softened" OH bond. Besides these peaks, the losses at 1610 cm^{-1} and 2565 cm^{-1} are of particular interests, and we tentatively assign them to the v(C–H) and v(C=O) modes of a v($H_nC{=}O$)Ag surface species. The "softening" of bonds can account for the shifts of the loss peaks to lower energy, which implies a strong interaction of hydrogen in the methoxy species with the preadsorbed atomic oxygen (O_{ads}^{-2}) on the surface. These results, together with the TPRS observations, suggest that a new intermediate related to the decomposition of methoxy species has been formed, as shown schematically below:



(II)

In this feature the common concept of electron resonance can be used to explain the "softening" of interrelated bonds i.e. C–H, O–H, and $H_nC{=}O$, where n is 2 or 3. This behavior appears not to have been previously observed from the interaction of methanol on either transition-metal or noble-metal surfaces.

Further annealing the surface, on which methoxy species and intermediate (II) coexist results in the breaking of a C–H bond in intermediate (II), and leads to the further decomposition followed by the evolution of gaseous formaldehyde, carbon monoxide and a small amount of water. The results can be summarized in the scheme shown below:

$$\text{intermediate (II)} \longrightarrow H_2CO_{(a)} + OH_{(a)} \qquad (1)$$

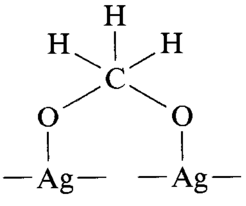
$$\begin{array}{lll} & \nearrow CH2O_{(g)} & (2) \\ H_2CO_{(a)} & & \\ & \searrow CO_{(g)} + 2OH_{(a)} & (3) \end{array}$$

$$2OH_{(a)} \longrightarrow H_2O_{(g)} + O_{(a)}$$

Reaction step (1) is believed to be the rate-determining step with first order kinetics. In this process, not all of the hydroxyl recombines to gaseous water, a considerable amount of adsorbed hydroxyl species has been monitored by EELS at the employed temperature. The losses at 3450 cm^{-1} and in the range from 600 to 800 cm^{-1} are assigned to the $\nu(OH)$ and $\delta(OH)$ modes.

Figure 3e shows that at 300 K, the methoxy species is stable on the silver surface, as identified unambiguously by the appearance of the characteristic vibration $\nu(Ag-OCH_3)$, $\nu(CO)$, $\delta(CH_3)$ and $\nu(CH_3)$. This behavior is contrasted with that of transition metal surfaces, e.g. Ru, W, Pd, Ni, [1,3,6,8], on which methoxy species are relatively unstable and rapidly decomposed to adsorbed CO and H_2 even at lower temperature. The stability of methoxy on noble metal surface, e.g. Ag, Cu, has been explained by the extremely low heats of chemisorption of CO and H_2 on these metals [32]. Above the temperatures, which are required to activate the OH bond breaking process and consequent methoxy formation, CO and H_2 are not adsorbed strongly, and the major reaction channel will be methoxy decomposition, which gives rise primarily to formaldehyde. The EELS observations, with respect to our previous results obtained from CO, H_2O and H_2 adsorption on the electrolytic silver strongly support this explanation.

In a higher temperature, the preadsorbed atomic oxygen was activated, and acts as a surface lewis base to attack the carbon atom in the methoxy species to form another stable intermediate as shown in the scheme below:



(III)

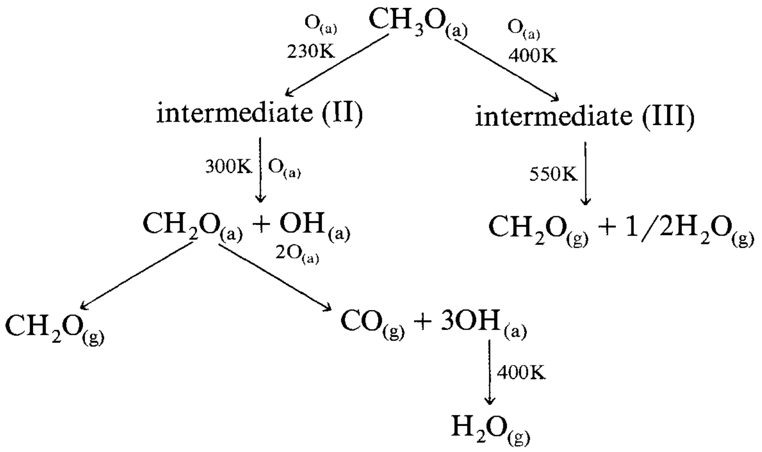
Our previous TPRS experiments with the isotope scrambling technique indicated that by forming the intermediate (III) the preadsorbed oxygen would stabilize the methoxy species [11]. The decomposition of this species only occurs after oxygen desorbs from the vicinity of intermediate (III), which would show pseudo-second-order kinetics which mimic those of O_2 desorption. The mechanism is formulated as follows:

$$\begin{tikzcd}
\text{intermediate (III)} \arrow[r] & H_2CO_{(g)} + OH_{(a)} \arrow[d] & & (4) \\
 & 1/2H_2O + O_{(a)} & & (5)
\end{tikzcd}$$

The EELS results from annealing the sample to 400 K can support this speculation related to the new intermediate. In fig. 3f, a new species can be isolated and identified by the disappearance of CO stretch of methoxy species at 995 cm^{-1} and by the appearance of new vibrational bands at 1680 cm^{-1} and in the range from 600 to 900 cm^{-1}. Toby, Sexton, White and their coworkers [4,33,34] have observed the same vibrational bands in the investigation of the decomposition of formic acid on Ru(001) and formaldehyde on Pt(111) and Ag(110) respectively. They interpreted the loss features in terms of the stretch and band of OCO species. These considerations lead us to assign our loss peaks as follows: δ(OCO), at the range 600–900 cm^{-1}, δ(CH) at 1450 cm^{-1}, v(OCO) at 1680 cm^{-1}, and v_s(CH), v_a(CH) at 2800 and 2960 cm^{-1}, respectively, which provides spectroscopic evidence for the existence of intermediate (III).

Further annealing the sample to above 550 K results in the decomposition of intermediate (III) and the evolution of gaseous formaldehyde. The ratio of H_2CO and H_2O was found to be 2 : 1. EELS shows no losses that can be detected after annealing at this temperature, which means that the sample has to return to a clean surface.

To summarize, on the oxygen preadsorbed silver surface, at coverages of methanol below a monolayer the interaction of methanol with the active atomic oxygen species leads to the breaking of an O–H bond and the forming of an adsorbed methoxy species at 180 K. Higher exposures (> 0.7 L) result in the formation of a multilayer. Increasing the sample temperature to above 210 K removes the methanol multilayer and forms methoxy species. Subsequent annealing leads to decomposition of methoxy species with different reaction channels, which can be summarized schematically as follows:



Although the mechanisms above have been supported by TPRS and catalytic kinetics, it is not unambiguous to conclude the configurations of the intermediate and the reaction pathway of methoxy decomposition, based on this evidence. In order to settle these speculations directly it would be particularly valuable to carry out a RAIRS study of the methoxy species under catalytic conditions on a silver surface.

Acknowledgement

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