On the nature of the active state of silver during catalytic oxidation of methanol

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Under the applied high reaction temperatures (~ 900 K) the Ag surface is restructured and a tightly held oxygen species is formed on the surface (O_γ) apart from O atoms dissolved in the bulk (O_β). Methanol oxidation to formaldehyde proceeds through this O_γ species as demonstrated by application of a variety of spectroscopic techniques.

Keywords: Ion-scattering spectroscopy (ISS); methanol oxidation; oxygen; Raman spectroscopy; reflection electron microscopy (REM); silver; X-ray photoelectron spectroscopy (XPS)

1. Introduction

Metallic silver prepared by repetitive electrolytic refining is widely used as an industrial catalyst for the partial oxidation of methanol to formaldehyde. The process is carried out adiabatically at a temperature of about 900 K by using an excess of methanol over $O_2 + H_2O$ with respect to the stoichiometric ratio in order to achieve optimum selectivity [1]. It is believed that the product formaldehyde is formed by interaction of gaseous methanol (presumably through a very short-lived surface intermediate) with dissociatively chemisorbed oxygen [2]. However, previous low-temperature studies on the interaction of oxygen with silver surfaces [3–5] indicated that chemisorbed atomic oxygen is stable on the surface only up to about 600 K beyond which temperature it recombines and desorbs so that at 900 K its coverage would, even at atmospheric partial pressure, be negligibly small. This apparent conflict became resolved in a series of recent studies in which the pressure and temperature ranges of oxygen exposure were considerably extended beyond those usually applied in studies of the "surface science" type [6–9]. When dosing O_2 above 500 K, the oxygen peak in thermal desorption spectroscopy (TDS) was found to shift to higher temperatures and to increase in intensity due to enhanced release of particles originally dissolved in the bulk [6]. It was found that exposure of silver to O_2 at atmospheric pressure and at high temperatures caused pronounced restructuring of the surface region which is associated with the formation of a strongly held oxygen species desorbing only around 900 K. The remarkable thermal stability of this phase together with its pronounced reactivity towards reducing agents signaled that it plays indeed a key role in the technical process of methanol oxidation. The present paper reports on further characterization of silver surfaces in the state catalytically active in methanol oxidation by applying X-ray photoelectron spectroscopy (XPS), reflection electron microscopy (REM), ion-scattering spectroscopy (ISS) and Raman spectroscopy. The high sensitivity of the latter technique for rough silver surfaces enabled even in situ measurements at atmospheric pressure and high-temperature conditions.

2. Experimental

Experiments were carried out on silver (111) and (110) single crystals prepared by standard cleaning and annealing procedures up to 780 K in UHV. The spectroscopic investigations were performed in a modified Leybold LHS 12 MCD system equipped with facilities for UPS, XPS and ISS [7]. Exposure to oxygen at atmospheric pressure and to methanol partial pressures up to 10^{-4} mbar were performed in a preparation chamber. Afterwards the sample could be transferred within 1 min into the UHV analysis chamber. The XPS data were acquired with Mg Kα radiation using a fixed analysator pass energy of 108 eV corresponding to a resolution of 1.0 eV FWHM of the Ag $3d_{5/2}$ line. Binding energies were calibrated using Au $4f_{7/2} = 84.0$ eV.

Raman spectroscopic experiments comprising oxygen exposure and in situ reaction with methanol and oxygen were performed with a home-made reaction cell connected to a Raman setup consisting of a spectrograph (Triplemate of SPEX, model 1828b) and a diode array as a detector (OMA II system of EG & G, model 1420). The details concerning the apparatus and procedures employed have been described in refs. [9,10]. Gaseous methanol as a reactant was introduced into the reactor by saturating a 20% O_2 in N_2 gas stream with methanol, with the partial pressure of methanol being controlled by the temperature of the liquid methanol.

Reflection electron microscopy (REM) investigations were performed with a (111) faceted silver sphere prepared by melting the end of silver wire in UHV by electron beam heating. The electron microscope (Philips 400T) was operated at 100 kV with an incidence angle of about 2°. The images were recorded using the intensity enhanced (666) Bragg reflection near the $[1\bar{1}0]$ zone axis [8].

3. Results and discussion

Fig. 1 shows the O 1s XP spectra obtained on Ag(111) after exposure to O_2 at atmospheric pressure. After oxygen exposure at 450 K, a single O 1s peak emerged

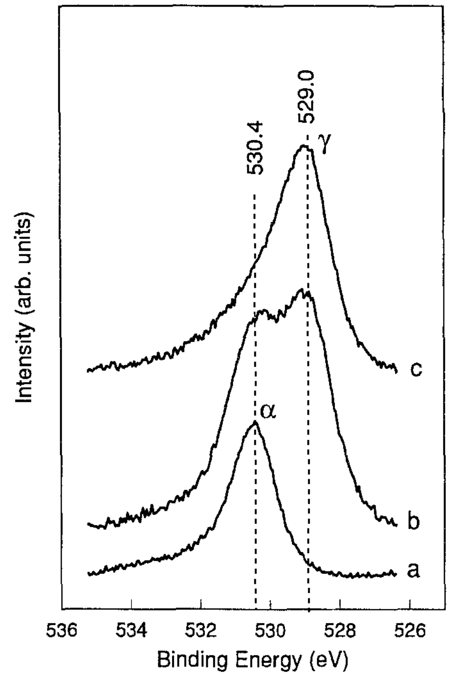

Fig. 1. O 1s XPS data from a Ag(111) surface after exposure to 1 bar O_2: (a) at 450 K for 5 h; (b) at 780 K for 1 h; (c) at 780 K for 7 h.

at 530.4 eV labeled α (curve a). On the basis of the observed binding energy and its desorption temperature of about 620 K, this oxygen species is identified as chemisorbed atomic oxygen [3–5,11]. After raising the exposure temperature to 780 K (spectrum b), a second component labeled γ appeared at a binding energy of about 529.0 eV. Prolonging the duration of treatment caused the O_γ peak to become the dominant feature (spectrum c). The shoulder at higher binding energy is due to dissolved oxygen giving rise to an O 1s peak at 530.3 eV as will be discussed further below.

The corresponding changes of the surface structure after similar oxygen treatment at atmospheric pressure have been described in detail in ref. [8]. Here we report only again on some REM observations. The freshly prepared (111) face was found to be very smooth, exhibiting monatomic steps. After exposure to oxygen at 480 K, the surface remained flat except for the presence of few small particles with diameters of about 10 nm. When the exposure temperature was raised above 780 K, the surface was found to be retextured by forming small islands containing ordered parallel lines with a mutual spacing of about 70 Å (fig. 2a). Based on RHEED measurements the observed long-range restructuring has been identified as a typical moiré pattern with a superlattice in matrix notation as $\left(\begin{smallmatrix}26 & 1\\ -1 & 26\end{smallmatrix}\right)$ [8]. This oxygen-induced restructuring process was found to be enhanced by raising the treatment temperature and prolonging treatment times and, particularly, by add-

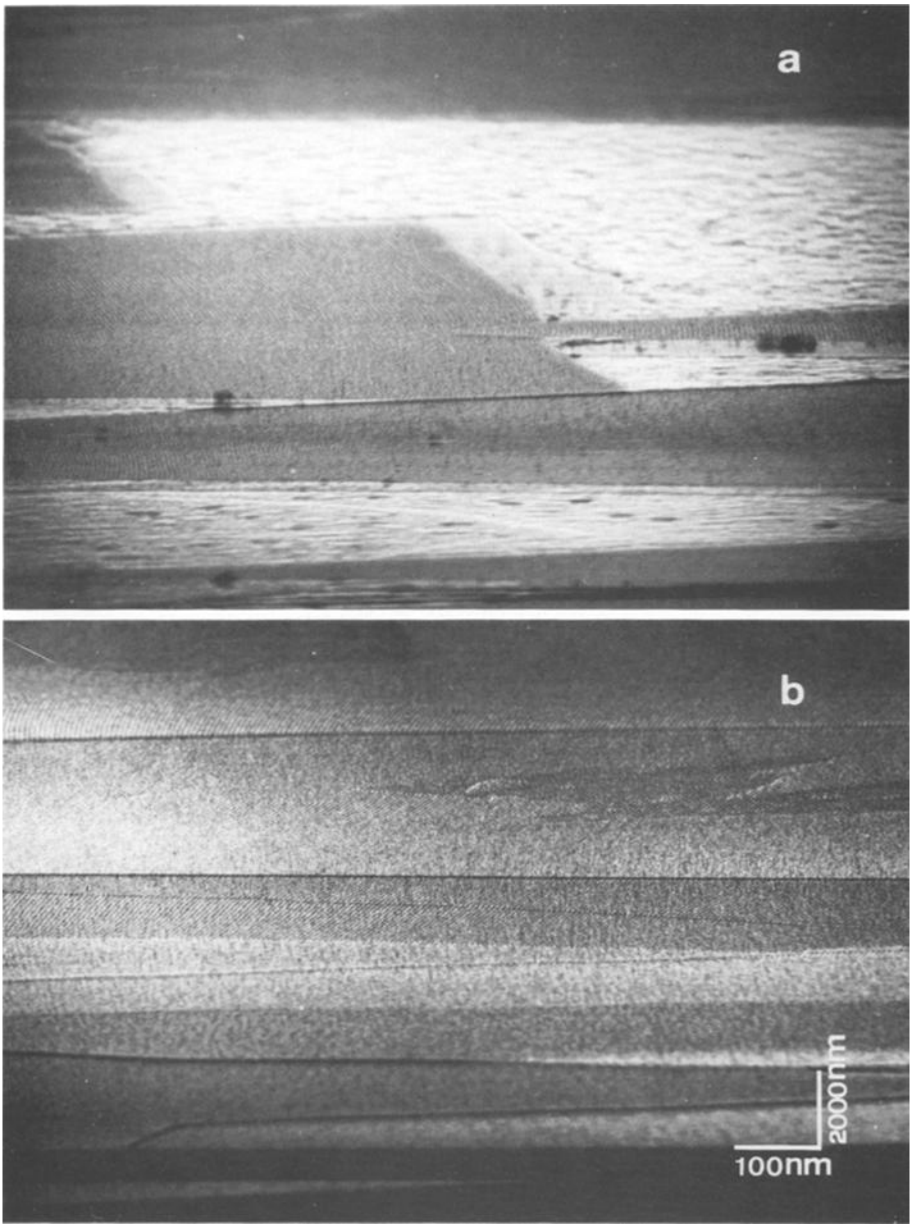

Fig. 2. Reflection electron microscopy (REM) images from a Ag(111) surface after exposure to 1 bar O_2 at 900 K: (a) after 3 h; (b) after 36 h. The images were recorded with the (666) Bragg reflection near the [$1\bar{1}0$] azimuth. The fringes arise from the formation of the O_γ phase associated with distortion of the Ag lattice and long-range order periodicities of about 70 Å in [112] direction and 40 Å in [$1\bar{1}0$] direction [8].

ing a small amount of water vapor to O_2. When prolonging the O_2 exposure at 900 K, the surface was found to be completely reconstructed (fig. 2b). In agreement with the REM findings, the same type of reconstruction has also been observed on a massive Ag(111) single crystal surface by scanning tunneling microscopy (STM) after O_2 exposure at 800 K for several hours [8].

Combining the results from the XPS and REM investigations leads to the following model for the interaction of Ag(111) surfaces with O_2 at atmospheric pressure: At low temperature, exposure to O_2 results in the formation of dissociatively chemisorbed oxygen (O_α) as identified commonly in previous studies [11–13]. The O_2 exposure at higher temperatures restructures the Ag(111) surface, and the tightly held O_γ species appears. Initially, this process may be restricted to very small areas if the temperature is not high enough. In these cases, both the O_α species adsorbed on non-reconstructed parts of the surface and O_γ species on the reconstructed islands coexist on the surface. As can be seen from fig. 1, the O 1s binding energies of the two species differ by 1.4 eV, indicating different types of Ag–O interactions. When the surface is completely reconstructed, it is no longer possible to populate the O_α species by O_2 exposure at low temperatures. Hence, the relative amounts of O_α and O_γ on the surface depend on the history of the sample treatments. The tightly held O_γ species is presumably the dominant one at high temperature under the industrial conditions of partial oxidation of methanol.

Compared to the O_α species [14], the O_γ species shows a different reactivity towards methanol. Fig. 3a displays the O 1s XPS data recorded from the completely reconstructed surface. The spectrum consists of the dominant O_γ peak at 529.0 eV and a shoulder centered at 530.3 eV. Obviously, the latter has an O 1s binding energy similar to that of the O_α species. However, after He^+ sputtering with high dosage which removed O_γ completely, a broad peak at 530.3 eV is still observed (curve e). Hence, it is assigned to oxygen dissolved in the bulk (O_β) in agreement with ref. [7]. If the completely reconstructed surface is exposed to methanol at temperatures below about 625 K, the intensity and the shape of the O 1s peak remained essentially constant indicating a very low reactivity towards methanol at low temperature. However, when the reaction temperature was increased above 625 K, the O_γ peak decreased substantially (curves b and c) and completely disappeared by methanol dosing up to 3×10^4 L (curve d). In this case, only the O_β peak was left. The gradual removal of O_γ can be seen even more clearly in the difference spectra displayed in the lower part of fig. 3. Due to the segregation of O_β to the surface, the O_β peak was also found to decrease progressively after prolonged exposure to methanol.

The distortion of the Ag lattice associated with the formation of the O_γ state had originally led to the speculation that the oxygen atoms are incorporated into subsurface sites [8]. However, the high reactivity of this species towards methanol from the gas phase strongly suggests that it is indeed located *on* the reconstructed Ag surface. This was verified by applying ISS which is an exclusively surface-sensitive technique. The experiment was carried out on the completely reconstructed

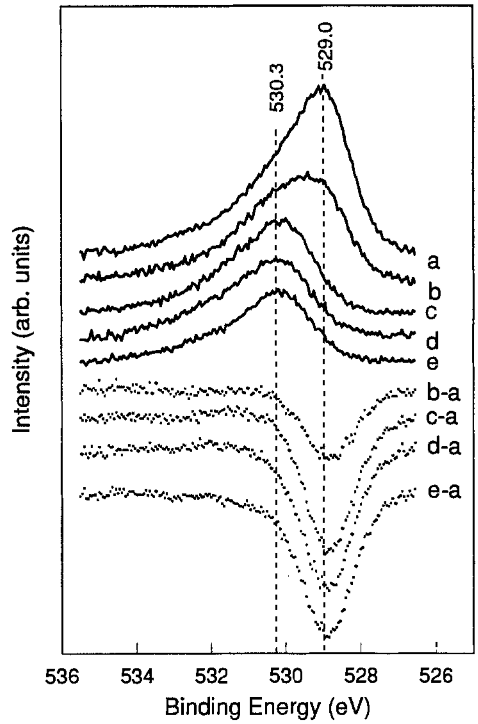

Fig. 3. O 1s XPS data from a Ag(111) surface after different treatments: (a) after complete restructuring by high-temperature oxygen treatment; (b)–(d) after exposure to increasing doses of CH_3OH at 780 K: 1, 2, and 3 × 10^4 L, respectively (1 L = 10^{-6} mbar s); (e) after sputtering of the initial state (a) by He^+ ions (1000 eV, 10 mA) for 8 min at 300 K. The dotted traces represent the respective difference spectra.

Ag(111) surface which had been prepared by exposing the sample to 1 bar oxygen at 780 K for several hours. Prior to the ISS measurement, the sample was sputtered at room temperature with a high current He^+ ion beam until O_γ was removed completely as evidenced by subsequent XPS and ISS inspections. The "clean" surface was heated rapidly within about 1 min to 680 K in UHV, and a series of ISS spectra was acquired continuously monitoring the changes in intensity of the oxygen peak around 400 eV and of the silver peak around 840 eV. In order to minimize the sputtering damage, the ISS data were generated using a scanning defocused 1000 eV He^+ primary beam and a short acquisition time of 60 s for every spectrum. The heat treatment restores the reconstruction as evidenced by REM and XPS together with the O_γ species by diffusion of bulk O_β to the surface. As shown in fig. 4a, the relative ISS intensity ratio of oxygen to silver increased rapidly, and the increase of the oxygen peak was found to be linearly correlated with the decrease of the corresponding Ag peak which demonstrates clearly that the O_γ species is located *on* the surface. Fig. 4b demonstrates that admission of a very low CH_3OH partial pressure leads to a substantial reduction of the O signal intensity due to continuous con-

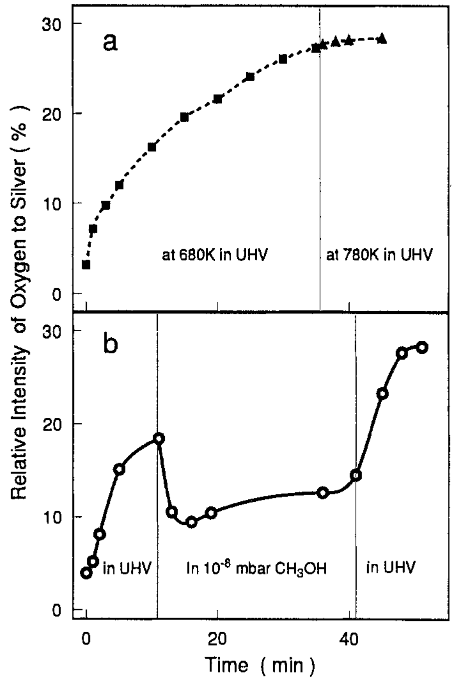

Fig. 4. Ion scattering spectroscopy (ISS) experiments: Intensity ratio of the O to Ag signals: (a) restoration of O on the surface by annealing of a previously sputtered sample at 680 and 780 K in UHV; (b) similarly at 780 K with intermediate admission of 10^{-8} mbar CH_3OH.

sumption of the O_γ species by reaction. If the methanol flow is switched off, the oxygen concentration on the surface increases again up to saturation by supply from the bulk.

Further characterization of the γ (surface) and β (bulk) species of atomic oxygen, being associated with the reconstructed silver surface, was achieved by applying Raman spectroscopy. Under normal conditions the sensitivity of this technique would be far too low to record rapidly spectra with low surface area single crystal samples under in situ conditions. However, the restructuring of the surface associated with the high-temperature oxygen treatment causes roughness on length scales favorable for strong surface enhancement (SERS) by a factor $> 10^3$ [9]. The experiments to be described next were performed with a sample originally exposing a (110) single crystal surface which after prolonged O_2 treatment was, however, strongly faceted. SEM and RHEED demonstrated the predominant formation of (111) planes with diameters typically in the range of 0.5–1 µm. The microtopography of the surface still exhibits crystallinity of good quality and essentially well-defined adsorption sites at high temperatures, quite in contrast to usual SERS conditions.

Characteristic spectral data obtained with this sample are displayed in fig. 5: After annealing at 900 K in N_2 atmosphere for a few minutes the spectrum exhibits

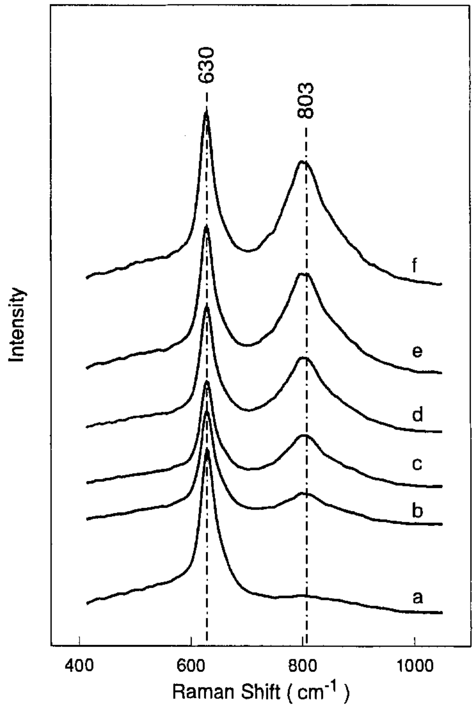

Fig. 5. Raman spectra monitoring the formation of O species on and near a faceted Ag(110) surface previously treated with oxygen at high temperature: (a) after heating in N_2 at 900 K for 30 min; (b)–(f) after exposure to 0.2 bar O_2 at 780 K for 2, 8, 15, 20 and 30 min, respectively.

a single line at 640 cm^{-1} (curve a). From previous studies [6,8] we know that such a treatment causes desorption of the γ state and destruction of the reconstructed surface phase. Hence, the spectral feature is identified with the Ag–O vibration of the O_β species dissolved in the bulk. Subsequent exposure to 1 atm O_2 at 780 K causes the emergence and continuous growth in intensity of a second feature centered at 803 cm^{-1} (curves b–f). On the basis of the previous experience this peak can clearly be identified with the O_γ species. Its somewhat larger width indicates some spread in its local geometry on the surface while the O_β species, on the other hand, is presumably located in well-defined sites inside the bulk crystal giving rise to a narrower peak at 630 cm^{-1}.

Spectral changes accompanying the interaction with methanol are displayed in fig. 6. Under steady-state reaction conditions all methanol derived surface intermediates are present only in such low concentrations that they are not discernible in the spectra. Spectrum a represents the initial situation with an oxygen saturated, fully restructured surface. Exposure to a $CH_3OH + O_2$ gas mixture under flow conditions causes at first reduction of the intensity of the O_γ peak at 802 cm^{-1} due to continuous consumption of the surface species by the reaction. Later also the peak at 630 cm^{-1} decreases in intensity due to depletion of the bulk until a steady-state

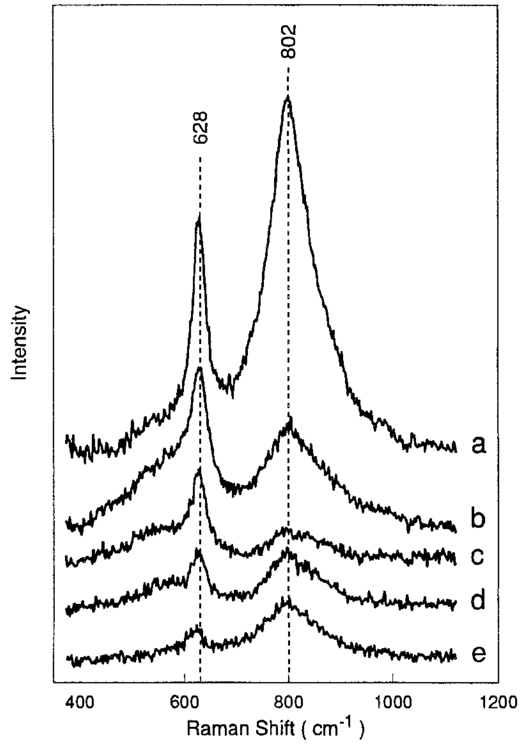

Fig. 6. Raman spectra from the faceted Ag(110) surface during catalytic reaction: (a) fully oxygen-saturated sample; (b)–(d) after exposure to a gas mixture consisting of 80 mbar CH_3OH, 180 mbar O_2 and 740 mbar N_2 at 850 K under flow conditions for 5, 15 and 42 min, respectively; (e) after 10 min at 900 K.

situation is reached (curve e) which represents the state of the working catalyst under the applied conditions. O_γ is continuously consumed by reaction with CH_3OH, and supplied by chemisorption of O_2 from the gas phase and by segregation from the bulk. The coupling $O_\beta \rightleftharpoons O_\gamma$ also causes partial depletion of the bulk by dissolved oxygen atoms, and the steady-state concentrations of both species reflect the interplay of the kinetics for oxygen chemisorption, surface reaction, bulk dissolution and surface segregation which will be studied in more detail in future work in order to further elucidate the mechanism of this important catalytic process.

4. Conclusions

The characteristic data of the atomic oxygen species which may be present at Ag surfaces are summarized in table 1. Exposure of silver to O_2 at temperatures below 600 K leads to the formation of chemisorbed O atoms (O_α state) on the undistorted surface as characterized by an O 1s binding energy of 530.4 eV and a vibra-

Table 1
Characteristic data of the three atomic oxygen species on silver

	Species		
	α	β	γ
O 1s b.e. (XPS)	530.4 eV	530.3 eV	529.0 eV
localization (ISS)	surface	bulk	surface
thermal stability	$\leqslant$600 K	–	$\leqslant$900 K
reconstruction	–	–	$\begin{pmatrix}26 & 1\\ -1 & 26\end{pmatrix}$
reactivity towards methanol	$\leqslant$300 K [14]	–	$\leqslant$625 K
Raman shift	954 cm^{-1}	630 cm^{-1}	803 cm^{-1}

tional frequency of 954 cm^{-1} (determined by Raman spectroscopy [9]). These recombine and desorb around 600 K and can, hence, not be the dominant surface species involved in partial oxidation of methanol taking place around 900 K. Under these conditions, however, the surface is reconstructed and a strongly held surface species (O_γ state) is present, apart from atoms dissolved in the bulk (O_β species). The O_γ state is identified with oxygen atoms on the surface of the distorted Ag lattice and it is this species which enters the catalytic reaction with methanol to formaldehyde. Its unusually low O 1s binding energy of 529.0 eV agrees with data reported for bulk Ag_2O [15] and indicates a high degree of basicity which might assist the dehydrogenation of methanol. The restructuring of the surface associated with the formation of the O_γ species is facilitated by the presence of H_2O which probably explains the promoting effect of water vapor in industrial catalysis.

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