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The effect of water on the formation of strongly bound oxygen on silver surfaces

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Interaction of water with an oxygenated Ag(111) surface leads to an enhancement of the surface restructuring and an activated formation of hydroxyl groups (OH) located stably on the surface and incorporated in the subsurface region, as evidenced by means of reflection electron microscopy (REM) and in situ Raman spectroscopy. Dehydroxylation of OH_{ads} at elevated temperatures releases the strongly bound oxygen species labelled O_γ at the surface, and offers an alternative to the energetically less favorable pathway for the direct formation of the O_γ species from molecular oxygen.

Keywords: oxygen; partial oxidation; reconstruction; reflection electron microscopy; Raman spectroscopy; silver; water

1. Introduction

Silver is widely used as a catalyst for the partial oxidation of methanol to formaldehyde. The process is carried out industrially with an excess of methanol relative to oxygen at temperatures of about 920 K. The selectivity towards formaldehyde can be increased pronouncedly by adding a certain amount of water to the reactant mixture [1,2]. The effect of water inhibiting the non-selective oxidation of methanol was reported first by Trillat already in 1902 [3] and patented subsequently by Uhl and Cooper in 1949 [4]. Afterwards, in order to obtain the better understanding of the role of water in this process, numerous studies with different experimental methods have been performed and several models have been proposed. Valitov and Lakiza [5] supposed that the incorporation of water might reduce the rate of further dehydrogenation of alcohol in the course of oxidative dehydrogenation. Kurina and Morozov [6] assumed that the role of water is to prevent the decomposition of the desired products by blocking the corresponding reaction sites on the catalyst. Based upon data from thermal desorption spectroscopy (TDS) and X-ray photoelectron spectroscopy (XPS) which demonstrated the existence of two different oxygen species on polycrystalline silver surfaces, Lefferts [7] suggested recently that the addition of water blocks the formation of a weakly bound oxygen species which was considered to be responsible for the non-selective reaction of methanol to CO_2. In recent studies from our laboratory [8–12], in which an Ag(111) surface was exposed to O_2 under the conditions usually applied in the commercial process of partial oxidation of methanol to formaldehyde, it was found that the exposure to O_2 at atmospheric pressure at temperatures above 750 K caused a pronounced restructuring on the Ag(111) surface, whereby a tightly held oxygen species, denoted O_γ was identified. This species desorbs only above 900 K and its structural and electronic properties are distinctly different from those of the *normal* adsorbed oxygen species (O_α). Through the application of a variety of spectroscopic techniques, the O_γ species has been identified as one active oxygen species responsible for the exclusively partial oxidation of methanol to formaldehyde, while the more weakly bound O_α species causes to a significant extent the complete oxidation. Formation of the O_γ state is associated with a distortion of the Ag lattice, however distinctly different from bulk silver oxides which decompose below 700 K [13]. This restructuring process is affected by temperature as well as by the composition of the gas phase. In the present report, it will be demonstrated that the presence of water has a promoting effect on the restructuring of an Ag(111) surface and on the formation of the active (O_γ) species, as observed using reflection electron microscopy (REM) and in situ Raman scattering spectroscopy.

2. Experimental

Reflection electron microscopy (REM) observations were carried out with a (111) faceted silver sphere prepared by melting the end of a silver wire in UHV by electron beam heating [10]. Experiments on exposures of O_2 gas and mixture of $O_2 + H_2O$ were performed in a quartz tube heated by a cylindrical electric furnace, through which the gases passed with defined flow rates. The electron microscope (Philips EM 400T) was operated at 100 keV 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. Raman spectroscopy experiments 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 detector (OMA II system of EG&G, model 1420), as described in detail in refs. [14,11]. In both cases, water vapour was introduced to the reactor by saturating an O_2 gas stream with H_2O. The partial pressure of water vapour in the mixture, being controlled by the temperature of liquid water, was about 20% of that of O_2, which ratio is fairly close to that applied in the industrial processes for the catalytic oxidation of methanol to formaldehyde over silver catalysts [1].

3. Results and discussion

3.1. REFLECTION ELECTRON MICROSCOPY (REM)

The structural and electronic characteristics of the overlayer on Ag(111) restructured by formation of the O_γ state have been described in detail elsewhere [10–12]. Here we present only some REM observations to illustrate the influence of the addition of water vapour to the gas phase on the restructuring process. As shown in fig. 1a, after exposure of an Ag(111) face to 1 bar O_2 at 900 K for 3 h, the REM image shows clearly the surface restructuring with the appearance of the small islands on the surface, upon which ordered parallel lines with a mutual spacing of about 70 Å along the [112] direction are visible. By combining with the corresponding RHEED measurements, the observed long-range reconstruction has been identified as a typical moiré pattern with a superlattice in matrix notation as $\begin{pmatrix} 26 & 1 \\ -1 & 26 \end{pmatrix}$ [10], in which the lattice of the overlayer is expanded by about 3% with respect to bulk silver. Fig. 1c displays the REM image obtained after exposure of an Ag(111) face to a gas mixture consisting of 200 mbar H_2O and 800 mbar O_2 at 900 K for 1 h. As can be seen, now a more complete restructuring of the surface in short times has been achieved by introducing a small amount of water vapour during O_2 exposure. This effect becomes even more pronounced upon inspection of the curved regions of the silver sphere. As shown in fig. 1b, after exposure to pure O_2 for 3 h only small portions of the surface in these regions were etched, exhibiting few (111) facets as evidenced by RHEED. If, however, the sample was exposed to a mixture of O_2 and H_2O for only one hour, the corresponding region became pronouncedly faceted. In addition, the identical superstructure could be identified very clearly on the facets (fig. 1d). Careful comparison of the REM images shown in figs. 1a and 1c reveals a distinct difference in the dimension of the superlattices according to the presence of water vapour; after addition of water vapour, the reconstruction exhibits a larger fringe spacing (about 90 Å) as in the dry case (70 Å), indicating a slighter mismatch of the lattice constants between the overlayers and the bulk of silver.

3.2. IN SITU RAMAN SPECTROSCOPY

The structural effects of oxygen interaction with Ag(111) cause pronounced modifications of the Raman scattering process [10,12]. A cooperation of both the delocalized "electromagnetic" (EM) enhancement and the localized "charge transfer" (CT) enhancement effects leads to very high Raman cross sections enabling spectroscopy with well-defined species [15]. In the present experiment, by means of in situ Raman spectroscopy, the influence of water vapour on the formation of oxygen species on an Ag(111) surface is investigated. Prior to the measurement, the sample was exposed to 1 bar O_2 at 750 K for several hours. Two distinct enhanced Raman bands at about 800 and 640 cm^{-1}, representing the tightly bound O_γ on surface and O_β in subsurface sites respectively, emerged on such surface [15,12]. The

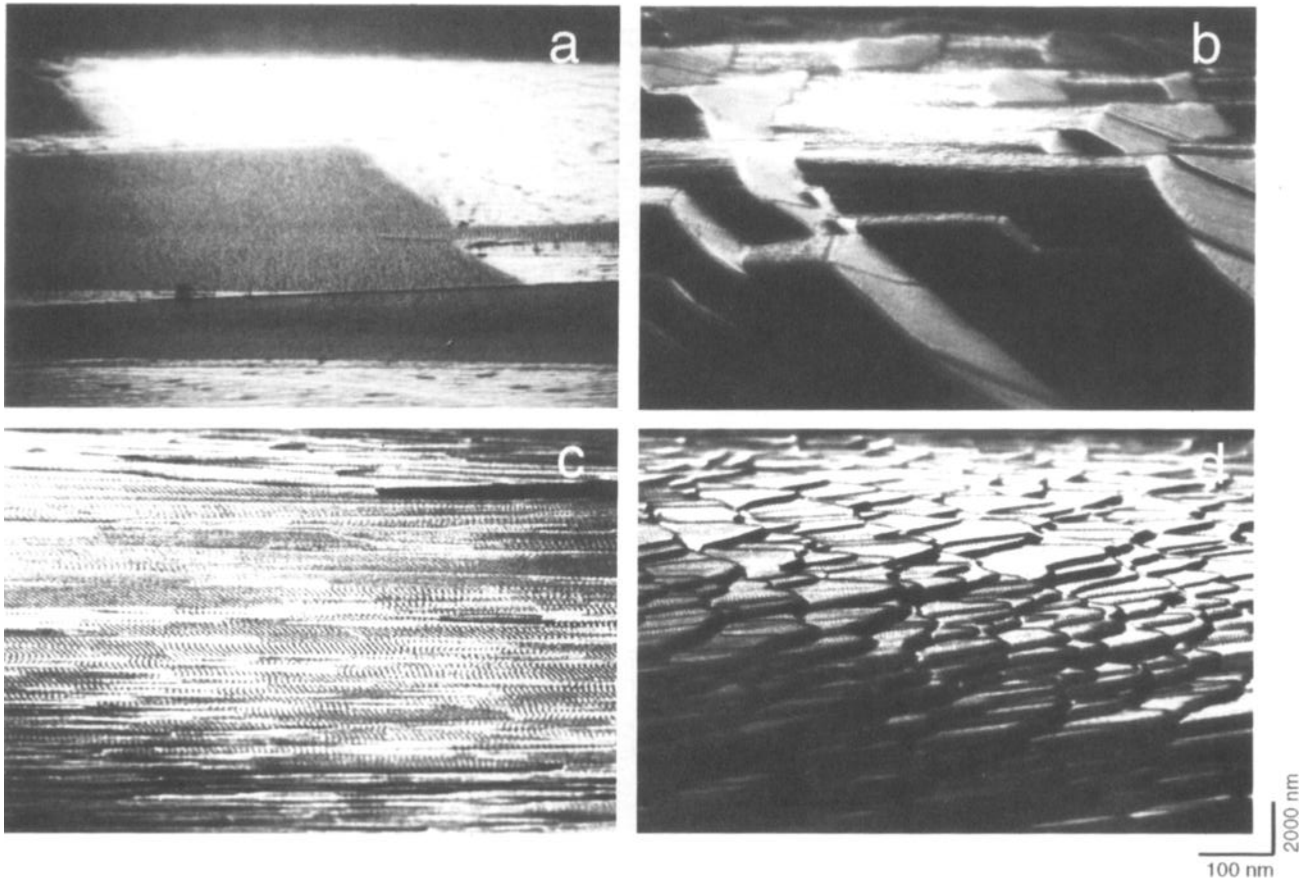


Fig. 1. Reflection electron microscopy (REM) images after exposure of a faceted Ag sphere to 1 bar O_2 for 3 h (a) from a (111) face; (b) from a curved region of the sphere. After exposure to a gas mixture consisting of 200 mbar H_2O and 800 mbar O_2 for 1 h (c) from a (111) face; (d) from a curved region of the sphere. The images were recorded with the (666) Bragg reflection near the $[1\bar{1}0]$ azimuth.

oxygenated sample was subsequently exposed to the different gas mixtures and the corresponding Raman spectra were recorded in situ while varying the sample temperature. Fig. 2 presents the spectral data obtained by exposing the sample to a pure O_2 atmosphere. Initially, the intensity of the O_γ peak grew with the increase of the sample temperature and reached a maximum value at about 600 K. With further increase of the exposure temperature, the intensity of the O_γ-relating Raman line decreased progressively and became very weak at 900 K. Obviously, the variation of the observed intensity of the O_γ Raman line reflects a dynamic competition among four different surface reaction processes: (1) formation by dissociative chemisorption of O_2; (2) decrease through the migration of the surface O_γ to O_β sites; (3) increase through segregation of the subsurface O_β to the O_γ positions; and (4) removal by the thermal decomposition. The appearance of the maximum value of the O_γ intensity at about 600 K implies an apparently high rate of O_γ formation and low rate of O_γ migration and desorption. When the oxygen-treated sample was exposed to a pure N_2 atmosphere, the spectrum shows an increase in

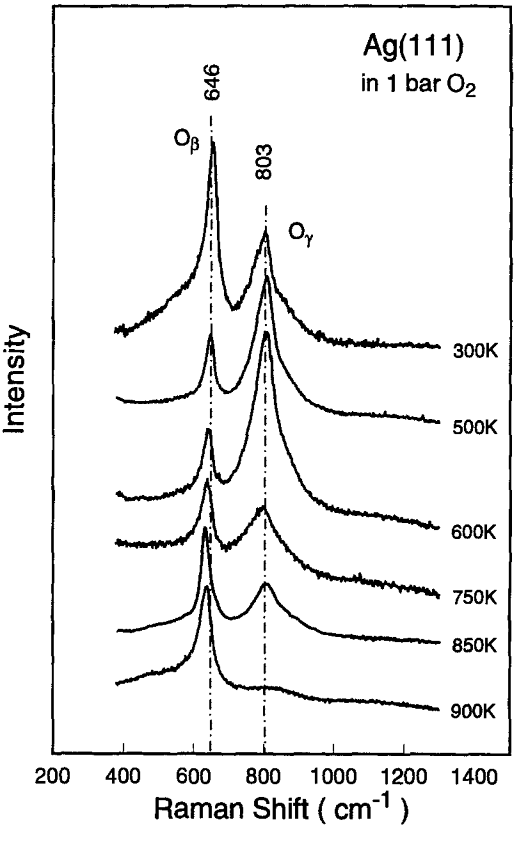


Fig. 2. Raman spectra from an oxygenated Ag(111) surface during the exposure in 1 bar O_2 at different temperatures. Prior to the experiment, the sample was treated in 1 bar O_2 at 750 K for several hours.

the intensity of the O_γ peak with raising the sample temperature which has to be attributed to the segregation process $O_\beta \rightarrow O_\gamma$ (3).

The spectral features around the O_γ peak were markedly changed if water vapour was added to the oxygen stream. As shown in fig. 3, in addition to the Raman bands representing surface O_γ and subsurface O_β, the exposure of the sample to a mixture consisting of 20% H_2O and 80% O_2 at a temperature below 400 K leads to two new Raman peaks centered at about 550 and 985 cm^{-1}. At higher temperatures, the H_2O-induced peaks faded out and a new band emerged at about 860 cm^{-1}. Simultaneously, the intensity of the Raman peak relating to O_γ increased. Moreover, in the presence of water vapour, the concentration of the O_γ species on the surface is still fairly high even at 900 K, while in a pure O_2 atmosphere this species has practically disappeared at this temperature (fig. 2). Fig. 4 presents the variation of Raman intensities as function of temperature in various atmospheres. The data are expressed in term of I_{O_γ}/I_{O_β}, as evaluated by integrating the peaks using a curve fitting procedure. As can be seen in fig. 4, over the whole temperature range, the pres-

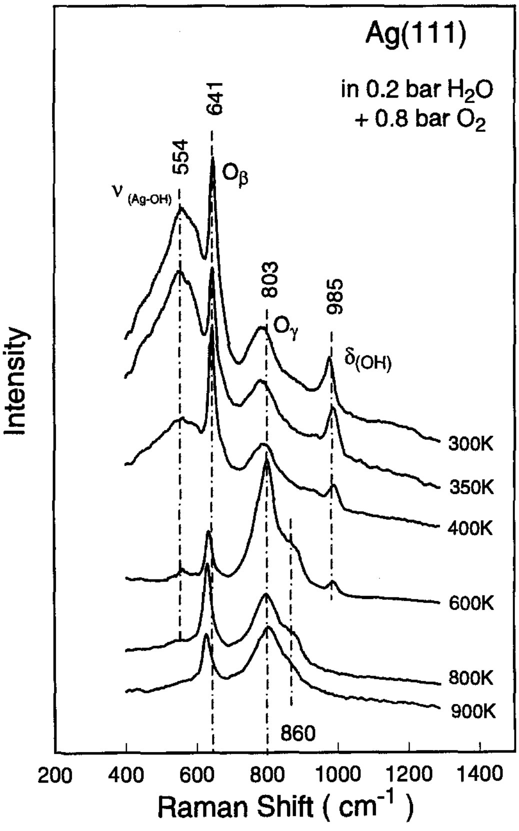


Fig. 3. Raman spectra from an oxygenated Ag(111) surface during the exposure in a gas mixture consisting of 200 mbar H_2O and 800 mbar O_2 at different temperatures. Prior to the experiment, the sample was treated in 1 bar O_2 at 750 K for several hours.

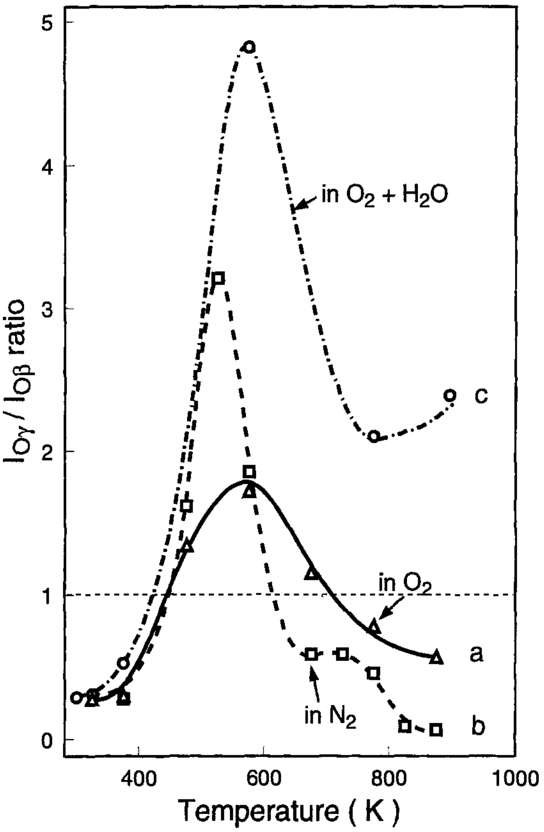


Fig. 4. Variations of the I_{O_γ}/I_{O_β} ratio as the function of the sample temperature during the exposure (a) in 1 bar O_2; (b) in 1 bar N_2 and (c) in a gas mixture of 200 mbar H_2O and 800 mbar bar O_2.

ence of water vapour in the oxygen stream causes a pronounced enhancement of the O_γ species on the surface. This finding, together with the observed enhancement of the surface restructuring, clearly demonstrates that water vapour promotes the formation of surface O_γ, which species is in turn decisive for the selective oxidation of methanol [12].

The interaction of silver with water was already subject of numerous studies with, however, still conflicting conclusions. Kurina and coworkers [16], using TPD and adsorption kinetic measurements, demonstrated that water could dissociatively adsorb on both oxidized and bare polycrystalline silver surface at temperatures between 300 and 600 K to form a surface hydroxyl species, which was found to be stable on the surface up to 900 K. Furthermore, direct evidence for the existence of such OH species during the exposure of polycrystalline silver to water vapour at around 450 K has been reported by Bazilio et al. based on in situ IR spectroscopy [17]. In contrast, based upon the experimental results obtained using TPD aided by isotopic exchange and photoelectron spectroscopy, Bowker et al. [18] and Au et al. [19] concluded that the surface OH groups formed after the adsorption of water on oxidized Ag(110) are stable only up to temperatures of 320 K. In addition, a SIMS measurement [20] showed that no hydrogen-containing species were present at an oxidized polycrystalline silver surface even after exposure to water vapour at room temperature.

A possible explanation for these seemingly conflicting facts might be based on the dynamic aspects of the adsorption process. According to a calculation [21] on the thermodynamics of water adsorption and dissociation on metal surfaces, water molecules are expected to be dissociatively adsorbed as hydroxyl at an oxidized silver surface. From the point of view of dynamics, however, the apparent behaviour of such interaction would depend critically on the experimental parameters used, such as the partial pressure of water and the sample temperature. Therefore, an adsorbed OH species being detectable in an atmosphere containing mbar partial pressures of water vapour may be absent in UHV, due to insufficient interaction with the surface. In the present investigation, a gas flow consisting of 200 mbar of water vapour in O_2 was employed. At room temperature, two Raman peaks centered at 554 and 985 cm^{-1} were observed, as shown in fig. 3. By comparison with the HREELS and IR results relating to the formation of OH groups on other metal surfaces [21], the additional Raman lines can be clearly assigned to the vibration of μ(Ag–OH) and δ(OH) respectively. In the present study, the characteristic stretch vibration of O–H with frequencies usually in the range of 3200 and 3500 cm^{-1} was not detected due to the decrease of the Raman scattering cross section at high frequency shifts. The adsorbed OH group revealed to be stable up to 600 K and disappeared at higher temperatures. Simultaneously, the intensity of the O_γ Raman peak (800 cm^{-1}) increased pronouncedly, suggesting a transformation $OH_{ad} \rightarrow O_\gamma$. In addition, however, a new Raman line at 860 cm^{-1} emerged, indicating the development of a new component under these conditions. The same spectral feature appeared after exposure of an Ag(111) surface to methanol-containing atmospheres at the same elevated temperatures. In fig. 5, curve (a) shows the typical spectrum after O_2 treatment with two peaks assigned to the O_β and O_γ species respectively. Addition of methanol (200 mbar) to the O_2 stream caused apart from the expected decrease in the intensities of both oxygen-related Raman peaks, the appearance of two additional bands at about 560 and 870 cm^{-1} (fig. 5b). Moreover, when the reaction gas was changed to an O_2-free mixture consisting of 200 mbar methanol and 800 mbar N_2, the oxygen-related peaks were removed by the reaction with methanol, but the 560 and 870 cm^{-1} peaks remained still present (fig. 5c). Similar Raman bands were observed on a silver electrode and were assigned to the Ag–O stretching vibration and to the bending vibration of AgOH formed by the reaction of water with bulk Ag_2O [22].

Analogous experiments were carried out using X-ray photoelectron spectroscopy (XPS). After exposing an oxygenated Ag(111) surface to 10 mbar methanol, an additional spectral feature of the O 1s signal with a binding energy of 531.5 eV was observed. If compared with the corresponding XPS results obtained after exposing metallic Ni [23] and Zn [24] to water as well as with recent studies on the

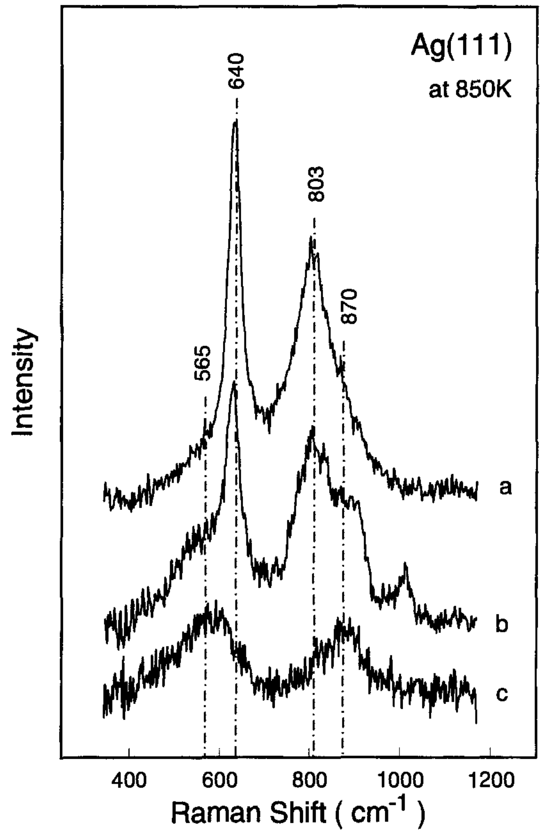


Fig. 5. Raman spectra from an Ag(111) surface at 850 K during the exposure (a) in 1 bar O_2, (b) in a gas mixture consisting of 200 mbar CH_3OH and 800 mbar O_2 and (c) in a gas mixture of 200 mbar CH_3OH and 800 mbar N_2.

oxydehydrogenation of ammonia at Cu [25], this signal has to be attributed to the formation of species incorporated below the silver surface.

The existence of OH groups dissolved in silver was first proposed by Kluch et al. [26] in a study of the diffusion of hydrogen and oxygen. They suggested that recombination of diffusing hydrogen with dissolved oxygen atoms leads to formation of such species. At elevated temperature the OH groups recombine further to produce water molecules. Their accumulation at defect sites results in local explosions near the silver surface and, consequently, to severe distortions of the morphology. Similar findings were reported by Lefferts [7], in which an additional TPR peak appearing after exposing polycrystalline silver to O_2 and subsequently to H_2 has been attributed to the intermediate formation of subsurface OH species. In our recent studies on the morphology of silver surface in the course of thermal and catalytic etching [27], it was found that the diffusing hydrogen can react with dissolved oxygen in near-surface regions of silver. This reaction creates hydrostatic pressure by the water vapour formed and significant excess energy localized near defect sites which are likely to be the nuclei of the reaction. The resulting mechanical stress is released by an eruption of silver forming the pin-holes on the surface.

The suggested formation of subsurface OH by exposure of an oxygenated Ag(111) surface to water at high temperatures is further supported by Raman observations on the interaction of H_2 with an oxidized silver surface. Fig. 6 presents the Raman data obtained from an oxygenated Ag(111) surface, prepared in 1 bar O_2 at 750 K for several hours, after exposure to 200 mbar H_2 at different temperatures. Before the introduction of H_2, the oxygenated silver surface showed the presence of O_β and O_γ species with the two typical Raman bands. As can be seen in fig. 6, the reaction of hydrogen with both oxygen species takes place immediately after the introduction of H_2. The produced OH groups recombine to H_2O at the surface and rapidly desorb. (Note there is no appreciable H_2O partial pressure for readsorption.) Hydrogen atoms adsorbed at surface may also readily diffuse into the bulk where they react with subsurface oxygen atoms, as indicated by the decrease in the Raman intensity of O_β. The OH groups formed in this way are located at subsurface sites as reflected by the appearance of two Raman bands at

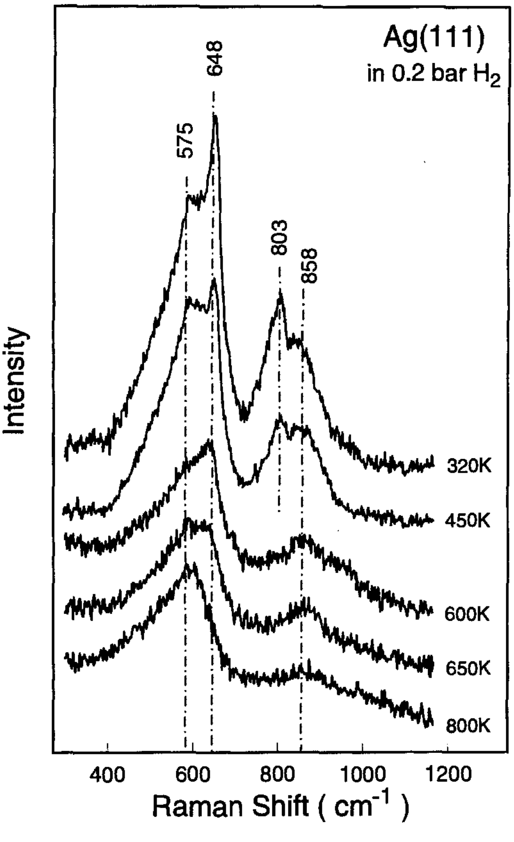
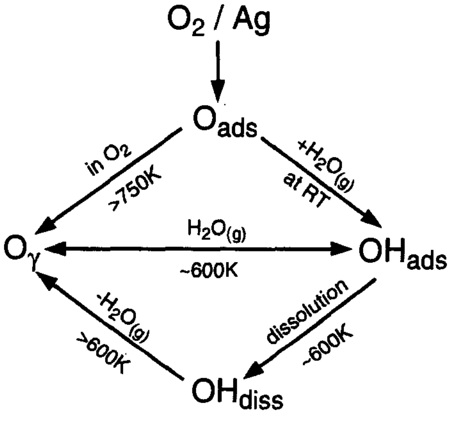


Fig. 6. Raman spectra from an oxygenated Ag(111) surface during the exposure in 200 mbar H_2 at different temperatures.

about 575 and 858 cm^{-1} (in fig. 6). Earlier XPS data [9] showed that after exposure of an oxidized silver surface to 1 mbar H_2 at 890 K for 15 min, the O 1s binding energy shifted from 530 to 531.2 eV, indicating the transformation of atomic oxygen to hydroxyl species.

In summary, the present findings lead to two important functions of water in its interaction with the oxygen-covered silver surface. The first is hydrogen abstraction induced by adsorbed oxygen ($H_2O + O_{ads} \rightarrow 2OH_{ads}$) at low temperatures. The oxygen species (O_{ads}) involved corresponds to the previously identified "normal" chemisorbed oxygen species (O_α) [28,29]. Hence, the water in the reaction feed of methanol oxidation acts as a reduction agent which removes the non-selective oxygen species (O_α) from the silver surface. This is consistent with the early assumption that the role of water in the course of catalytic oxidation of methanol over silver catalyst is to prevent the total oxidation of methanol or formaldehyde by blocking the corresponding reaction sites on the catalyst [6]. The second function is that OH_{ads} will recombine at elevated temperatures to form water and leave the strongly bound oxygen species O_γ on the surface, as described in scheme 1. As illustrated, the participation of water opens a new reaction channel for the formation of the O_γ species: it forms not only through the direct dissociation of molecular oxygen but also through the dehydrogenation of the surface OH intermediate. In the latter pathway, the energetically less favourable route for the activation of dioxygen by pumping of electrons from the metal surface to the adsorbed species [30] is bypassed.

The analogous effect of water vapour as a promoter for the oxidation and corrosion of metals was reported frequently [31,32,30]. It is commonly recognized that the change of the potential across the surface oxide by the adsorption of water molecule with hydrogen pointing outwards and the change of the average bond strength of the surface layers by the incorporation of OH will increase the rate of metal oxidation. Recently, it was reported that the activity of oxide catalysts could



Scheme 1.

be improved by a pretreatment in hydrogen and water, which has been attributed to an effective formation of the coordinatively unsaturated site (CUS) through the dehydroxylation of the formed OH^- groups [33,34].

4. Conclusion

(1) Interaction of H_2O with oxygenated silver leads to the formation of the stable surface OH species on the oxygenated silver surface.

(2) The migration of surface OH into subsurface sites of silver occurs at elevated temperature, as evidenced by the shift of the δ(OH) Raman peak from 985 to 860 cm^{-1}.

(3) The subsequent dehydroxylation of the OH groups at high temperature promotes the restructuring of silver surface and, in turn, the formation of the tightly bound oxygen (O_γ) species, which is relevant for selective oxidation of methanol to formaldehyde.

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