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Surface Science 374 (1997) 1–8

surface science

HREELS study of CO oxidation on Ag(001) by O₂ or O

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Received 12 July 1996; accepted for publication 18 October 1996

Abstract

The interaction of CO with molecularly and atomically bonded oxygen was investigated on Ag(001) by HREELS, dosing the reactants with a supersonic molecular beam. We find that under our best clean working conditions and at a surface temperature of 100 K, CO removes chemisorbed dioxygen with a much lower reaction probability than for Ag(110). For dissociatively chemisorbed oxygen the removal rate was smaller than the experimental sensitivity both at 100 and 300 K. However, impurities strongly affect the reaction probability for CO oxidation by both O and O₂. The reaction mechanism is of the Langmuir–Hinshelwood type as proved by the temperature dependence. CO can be stabilized at the surface under special conditions for which no extra HREELS peaks are observed. CO removed then atomically adsorbed O above 160 K. © 1997 Elsevier Science B.V. All rights reserved.

Keywords: Carbon monoxide; High resolution electron energy loss spectroscopy (HREELS); Oxidation; Oxygen; Silver

1. Introduction

In pure research CO oxidation serves as one of the most important model reactions [1] catalyzed by metal surfaces. Additionally the oxidation reaction is also important for industrial applications [2,3]. In the past CO oxidation has been investigated solely at reaction temperatures well above room temperature, i.e. for conditions corresponding to dissociatively chemisorbed oxygen. In recent years, however, interest has grown within the scientific community for low temperature reactions [4–9] where non-dissociative adsorption occurs.

Such interest was motivated by attempts to discover reactions of the Eley–Rideal (ER) type [10], i.e. with only one reactant adsorbed. One early investigation in this direction (CO oxidation by molecularly bonded oxygen on Pt(111)) [5] failed, however, because of the negligible CO₂ production rate. CO reaction with O₂ chemisorbed on Ag(110) at low temperature (i.e. without a thermally [4] or photon-induced dissociation [11]) was demonstrated to occur by Capote et al. [12]. CO was thereby converted to CO₂ and CO₃. Detailed measurements of the CO₂ production rates by application of the molecular beam titration method demonstrated that a Langmuir–Hinshelwood (LH) [13] mechanism is active for the production of CO₂ [14,15]. To gain further insight into the microscopic reaction mechanism we decided to investigate its dependence on the crystallographic face of Ag. The best candidate is then the (001)

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surface for which chemisorbed dioxygen shows nearly the same vibrational frequencies as for the case of Ag(110) [16]. In spite of this we find that for Ag(001) under clean working conditions the CO oxidation probability by dioxygen is much lower than it was in the case of Ag(110) [14]. Oxygen adatoms on the contrary were not removed by CO under clean conditions within experimental accuracy. Traces of contaminants promote the oxidation reaction. Stabilization of CO adsorption was sometimes observed for conditions corresponding to no additional loss features, so that we are unable to identify the contaminant responsible for the effect. Under such conditions admolecules reacted with coadsorbed oxygen adatoms only for crystal temperatures $T_{\text{rea}} > 160$ K.

2. Experimental

The measurements were conducted in a combined high resolution electron energy loss spectrometer (HREELS), designed following Ref. [17], and supersonic molecular beam system, described in detail elsewhere [18]. The application of a spectroscopic method like HREELS allows one, in principle, to identify directly reaction intermediates, by-products of parallel reaction pathways, and impurities. The HREEL spectra were recorded in-specular, at an angle of incidence of $\theta_e = 63^\circ$, at an impact energy between $1.9 \text{ eV} < E_e < 3.0 \text{ eV}$ with an energy resolution of about 5 meV, and an elastic count rate of about 10^5 cps.

The advantage of exposure of the reactants by the molecular beam, compared with backfilling the chamber, is the low total pressure in the measuring chamber during exposure and the resulting lower contamination level of the surface, as discussed recently in Ref. [19]; and the possibility of varying the kinetic energy, E_i , of the participating reactants. The energy of the CO molecules was varied in the range 85–700 meV by seeding in He and heating the nozzle of the molecular beam system up to ≈ 650 K. By doing so, a CO flux, $\Phi = 0.40 \text{ ML/s}$, is obtained with the pure CO beam and the nozzle at room temperature; and $\Phi = 0.035 \text{ ML/s}$ with the hot nozzle and 5% of CO

seeded in He ($1 \text{ ML} = 1.198 \times 10^{15} \text{ molecules cm}^{-2}$). Φ was calibrated by a spinning rotor gauge. For the measurements described in this paper the purity of the gas is relevant as impurities strongly affect the results. For our O_2 -He and CO-He mixtures (99.998% purity, 5% O_2 or CO) the following specifications are guaranteed by the company: $< 2 \text{ ppm H}_2\text{O}$, $< 0.05 \text{ ppm CH}_4$ and H_2 , $< 0.02 \text{ ppm CO}$ and CO_2 , $< 0.5 \text{ ppm Ne}$; for pure CO (99.998% purity): $< 3 \text{ ppm H}_2\text{O}$, $< 10 \text{ ppm N}_2$, $< 1 \text{ ppm CO}_2$, $< 10 \text{ ppm Ar}$, $< 3 \text{ ppm O}_2$, $< 1 \text{ ppm H}_2$, $< 2 \text{ ppm C}_n\text{H}_m$. A cold trap in the gas line of the molecular beam system allowed us to reduce surface contamination to below HREELS sensitivity after the exposure time relevant to our experiment. The base pressure in the measuring chamber remained below about $3 \times 10^{-10} \text{ mbar}$ during the HREELS runs.

At 100 K oxygen adsorbs in the molecular state, whereas exposure above about 150 K leads to dissociative adsorption; in both cases the adsorbed phase has no long-range order [16]. During the experiment the surface was pre-dosed by molecularly or atomically bonded oxygen at $T_{\text{ads}} = 100$ or 300 K, respectively. The CO molecules were eventually post-exposed by the supersonic CO beam, at normal incidence, keeping the surface at the reaction temperature of $\text{rm } 100 \text{ K} < T_{\text{rea}} < 300 \text{ K}$. The adsorption of impurities during the exposure of CO was controlled by removal or application of a cold trap in the gas line. The amount of adsorbed impurities was estimated by HREELS. The HREELS spectra were detected as a function of CO exposure (χ_{CO}), oxygen coverage (θ_{O_2}), reaction temperature (T_{rea}), and kinetic energy of the CO molecules (E_i).

The silver surface was cleaned by neon ion sputtering (600 eV, 10 mA for 10 min) and annealing at about 740 K for 1 min. Order and cleanliness of the surface were checked by LEED and HREELS [20]. The crystal temperature was varied by irradiation and electron bombardment of the back of the crystal and by fluxing liquid nitrogen through a cryostat.

3. Results and discussion

For the presentation of the results we will separate the discussion of the spectra obtained under

our best cleanliness conditions and spectra which are affected by impurities.

3.1. Clean working conditions

3.1.1. Dissociatively adsorbed oxygen

Under clean working conditions atomic oxygen removal was at the limit of our experimental sensitivity. A decrease of θ_{O} by less than 5% was observed after $\chi_{\text{CO}}=110$ ML of pure CO at 100 K while no decrease took place after $\chi_{\text{CO}}=480$ ML of pure CO at 300 K. Such results correspond to a reaction probability of:

$$\text{Pr} = \frac{\text{oxygen coverage reduction}}{\text{applied CO flux}} < 1 \times 10^{-5}. \quad (1)$$

Such a value should be compared with $\text{Pr}=0.03$ reported for Ag(110)–O (A-type of oxygen at 100 K in Ref. [15]). We can therefore conclude that Ag(001)–O is, surprisingly, less reactive for CO oxidation than is Ag(110)–O.

The main difference between the two systems is that no substrate reconstruction takes place for Ag(001)–O. For Ag(110)–O, above 200 K Ag–O–Ag–O–Ag adrows form and $(n \times 1)$ superstructures with $2 < n < 7$ are reported, while at lower temperatures a local reconstruction is present [15,21]. Such local rearrangement of the substrate atoms could thus be associated with the enhanced reactivity of Ag(110)–O to CO oxidation.

3.1.2. Molecularly adsorbed oxygen

The removal reaction was more evident with chemisorbed dioxygen as is shown in Fig. 1. The crystal temperature in that case is 100 K and the starting θ_{O_2} is 0.06 ML. Such low coverage was chosen as under such condition the intensity of the loss peak associated with the O_2 –substrate vibration at 30 meV is very weak [22]. The 33 meV peak, corresponding to the vibration of dissociated oxygen adatoms, should thus be clearly visible if dissociation takes place. The intensity of the O–O stretch vibration (at 80 meV) is on the other hand, already large and for this coverage range proportional to θ_{O_2} . Finally, the small shoulder at 65 meV was previously assigned to oxygen admolecules

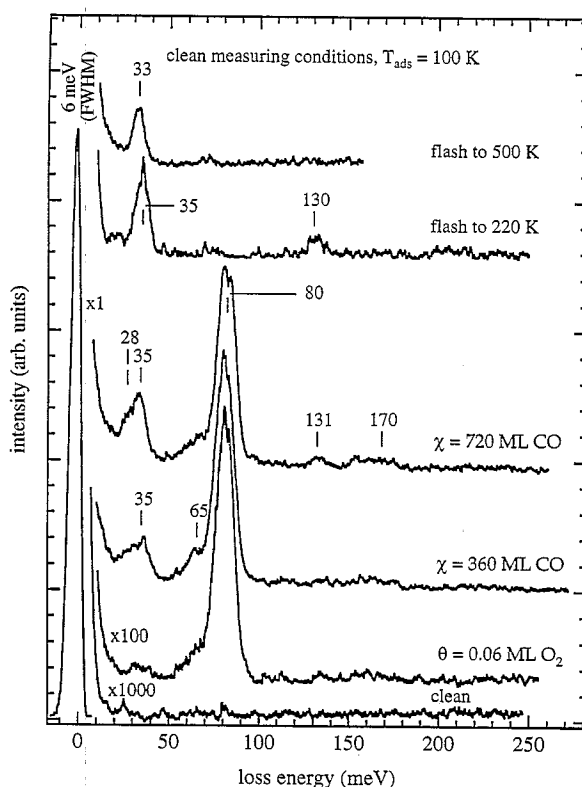
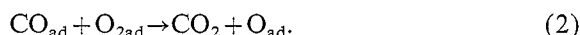


Fig. 1. HREEL spectra recorded in-specular under clean measuring conditions at $E_e=2.97$ eV and $\theta_e=63^\circ$. Oxygen molecules with $E_{\text{O}_2}=390$ meV are dosed by the molecular beam along the surface normal at 100 K. CO molecules with $E_{\text{CO}}=85$ meV are then dosed at the same temperature and incidence angle. In the upper part, the spectra recorded after flashing to 220 and 500 K are also shown. The spectra are normalized to the elastic intensity.

adsorbed at defect sites [22]. As one can see, the intensity of the loss at 80 meV decreases with χ_{CO} and is 30% smaller after $\chi_{\text{CO}}=720$ ML (dosed with the pure CO beam, $E_i=85$ meV). The reaction probability is thus $\text{Pr}=2.6 \times 10^{-5}$.

While the removal reaction proceeds, loss peaks grow at 28, 35, 131 and 170 meV. The peak at 131 meV is always associated to the presence of dissociated oxygen and was tentatively assigned to a subsurface species [23]. Although such frequency is relatively high compared with the other O–Ag(001) modes, similar high frequency losses were assigned to Ag–oxide in the literature [24,25]. An alternative mode at 130 meV was observed

upon coadsorption of H_2O and O_2 on $\text{Cu}(111)$ [26] and assigned to the bending mode of OH. Such assignment does not seem to be appropriate in the present case as no high-frequency OH stretch is observed. The feature at 35 meV is due to oxygen adatoms left over by the reaction:



The reaction rate is too low to produce an increase of the CO_2 partial pressure with our residual gas analyzer. The loss at 170 meV, is on the other hand, known to be associated with CO_2^- [27], a bent species bonded to the metal via the O atoms. Its presence thus demonstrates that CO oxidation does indeed take place. Our data are, however, not quantitative enough to determine whether CO_2^- is the only reaction product or whether $\text{CO}_{2\text{ gas}}$ is also produced. When heating the crystal the mode at 170 meV disappears together with the dioxygen modes at 80 and 28 meV (see Fig. 1). This indicates that CO_2^- cannot exist on $\text{Ag}(001)$ unless stabilized by oxygen coadsorption. The peak at 28 meV is assigned to the $\text{O}_2\text{-Ag}(001)$ vibration. The peak is shifted by 2 meV from the 30 meV value observed for a pure dioxygen layer [22]. Such a shift is associated with the presence of coadsorbed dissociated oxygen and is present also when dissociation is induced by hyperthermal Xe-atom bombardment [28].

As one can see in Fig. 1, the oxygen-substrate stretch frequency occurs at 35 meV after flashing the crystal to 220 K instead of at 33 meV, as observed after thermal dissociation [16]. The latter frequency is eventually recovered when flashing to 500 K. The final state of the oxygen adatoms is thus not the same for CO and thermally induced dissociation. Fang [29] observed the oxygen surface vibration at 37 meV for dissociative adsorption of O_2 on $\text{Ag}(001)$ at 180 K and remarked that it was associated with a weak $c(2 \times 2)$ LEED structure. As we could not reproduce his result for oxygen exposure on the clean surface we suggest that his frequency shift was also induced by the presence of C compounds.

Similar results for CO oxidation were obtained with a 5% CO-He seeded beam at an impact energy of the CO molecules of 700 meV, as shown in Fig. 2. The reaction probability in this case is

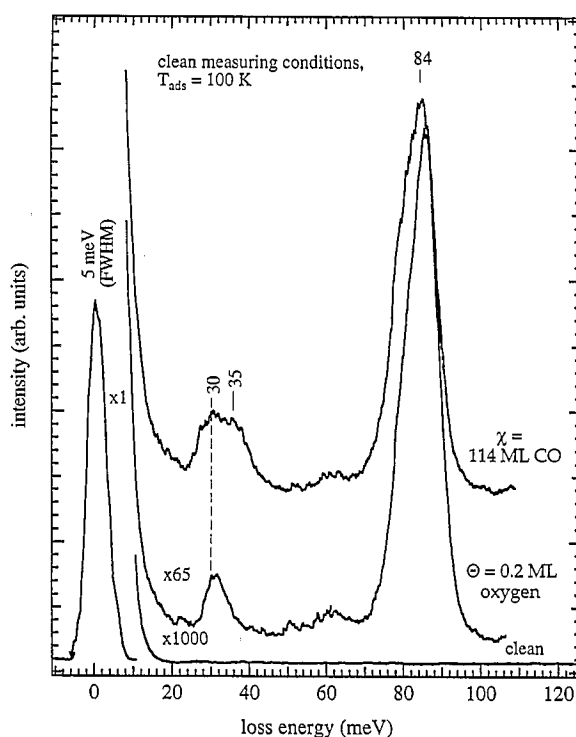


Fig. 2. HREEL spectra under clean measuring conditions as in Fig. 1 but with $E_{\text{CO}}=700$ meV and for a higher initial oxygen coverage (0.2 ML instead of 0.06 ML) ($E_e=2.97$ eV and $\Theta_e=63^\circ$).

$\text{Pr}=7 \times 10^{-4}$. The effect is not due to an energy dependence of the process but to the larger initial coverage, $\Theta_{\text{O}_2}=0.2$ ML. This result reflects either the lowering of the adsorption energy of O_2 molecules with coverage [30] or a kinetic effect of the higher coverage.

The reaction probability for clean $\text{Ag}(001)\text{-O}_2$ is thus $2.6 \times 10^{-5} < \text{Pr} < 7 \times 10^{-4}$ and should be compared with 0.12 on $\text{Ag}(110)$ [14].

3.2. Effect of trace impurities on the reaction rates

The level of impurities deposited by the supersonic molecular beam can be increased by eliminating the cold trap in the gas line. Inspection of HREELS intensities associated with impurities indicates that the contamination level at a given exposure time increases roughly by a factor of 15. Such a series of measurements is reported in Fig. 3

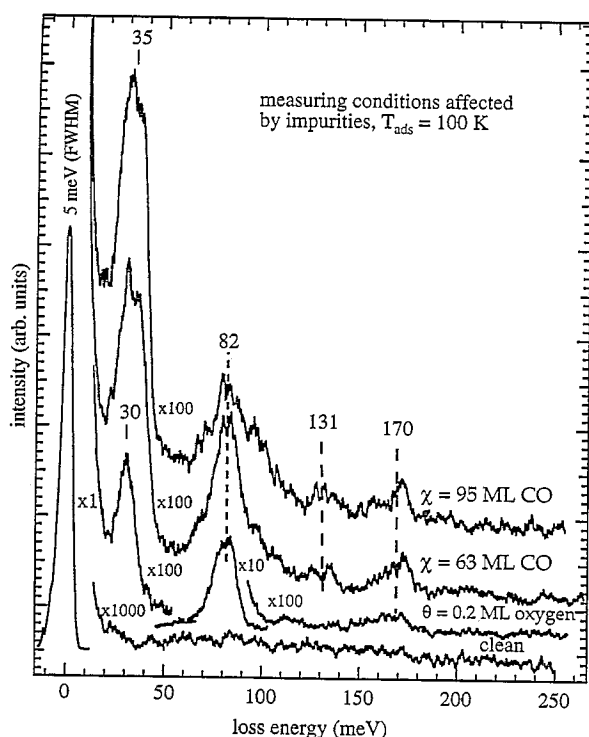


Fig. 3. HREEL spectra recorded for the same initial oxygen coverage as in Fig. 2 and with $E_{CO}=700$ meV, but under conditions affected by impurities ($E_c=2.97$ eV and $\theta_c=63^\circ$).

and should be compared with the "clean" spectra in Fig. 2. As one can see, upon CO exposure the peak at 80 meV decreases strongly in intensity and broadens considerably. The intensity of the 35 meV peak indicates that substantial O₂ dissociation has occurred. The large intensity of the 170 meV peak, with respect to Fig. 1, is indicative that a larger amount of CO₂⁻ has been formed. A comparison of the loss intensity (normalized to the specular intensity) of the two experiments is shown in Fig. 4. As one can see, under "dirty" conditions (open symbols) dioxygen removal took place at a much higher rate. Pr reads then 1×10^{-2} .

A large bump forms under these conditions at about 90 meV (see uppermost spectrum in Fig. 3). The most likely contaminant is H₂O. However, Stuve et al. found the following frequencies for H₂O on Ag(110) [31] which only partially coincide with our findings: 28 meV (H₂O–metal vibration), 80–100 meV (strong librational modes), 208 meV

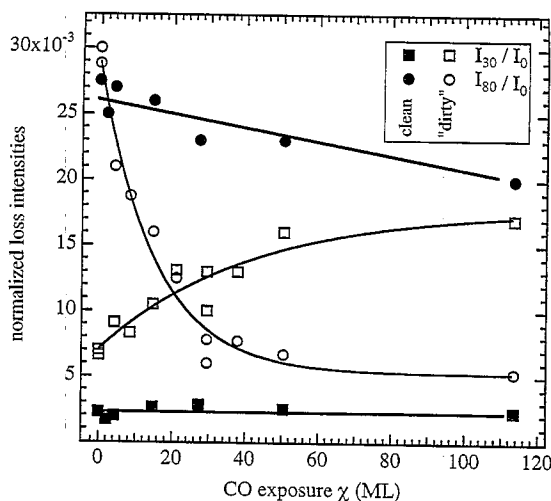


Fig. 4. Normalized loss intensities corresponding to Fig. 2 and Fig. 3 versus χ_{co} .

(HOH scissor mode) and 350 meV (O–H stretch). In the upper spectrum of Fig. 3 the loss at 28 meV might not be resolved from the 35 meV loss, corresponding to the vibration of oxygen adatoms; the peak at 208 meV and the O–H stretch at 350 meV are however missing in our data. Similarly the contaminant is unlikely to be CO₃ as Backx et al. [32] and Sexton and Madix [33] observed losses at 39, 105, 131 and 168 meV in the presence of CO₃ on Ag(110). The 168 meV coincides with our loss at 170 meV but the prominent mode at 105 meV (assigned to the π (CO₃) vibration) is missing. Moreover, CO₃ decomposition is expected to occur at 450 K, in analogy to the case of Ag(110) [33] while our extra losses disappear at $T < 200$ K and the disappearance of the modes at 130 and 170 meV are not correlated. The nature of the contaminant therefore remains open, but our work proves that CO oxidation on Ag(001) can be strongly promoted under non ideal conditions.

The reaction probability under these conditions depends on crystal temperature, an increase in the reaction rate by a factor of 2.5 being observed between $T=100$ and $T=135$ K. The relevance of the Langmuir-Hinshelwood mechanism is thus demonstrated.

Trace impurities also affect atomic oxygen

removal. Indeed, as shown in Fig. 5, a strong uptake was observed at 300 K when the CO was dosed by backfilling the chamber to 1×10^{-6} mbar. Pr was then $\approx 2 \times 10^{-5}$. Again we suggest that the effect is due to the contamination level of the vacuum. Notably, no extra EEL peak is formed, indicating that the contaminant has desorbed within the time of our measurements (taking an EEL spectrum takes ≈ 20 min). The importance of contamination is demonstrated by the fact that the effect was poorly reproducible. The role of the contaminant would then be to stabilize CO adsorption for long enough to allow the reaction to take place but for a short time compared to the acquisition time.

3.3. Stabilization of CO_{ad}

No CO adsorption was observed under reproducible measuring conditions at 100 K even after a CO exposure as large as 360 ML. By assuming

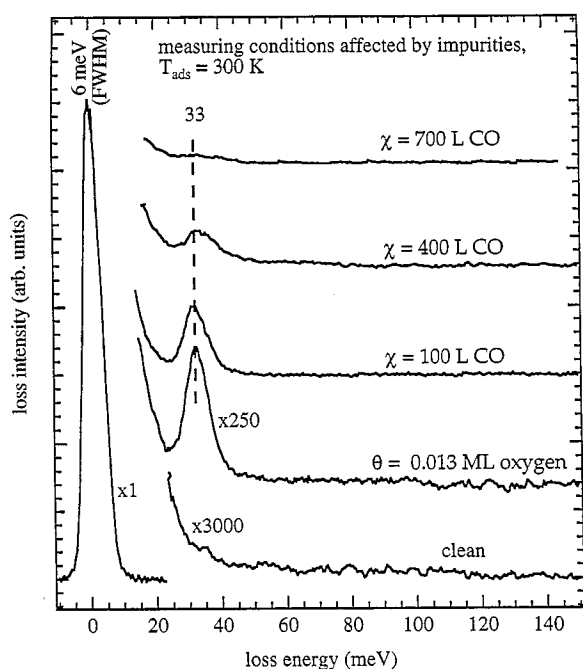


Fig. 5. HREEL spectra after dissociative oxygen adsorption ($E_{O_2} = 390$ meV) at 300 K and CO exposure, also at 300 K, by backfilling the chamber. Same electron scattering conditions as in the previous figures.

a detection limit of about 10^{-3} ML for CO by HREELS we estimate an upper limit of the sticking minus desorption coefficient of about 3×10^{-6} . This negative result is not surprising because of the low heat of adsorption for CO on clean silver surfaces (determined for example by the vibrating capacitor method [34] or by the molecular beam relaxation spectroscopy method [35]). If we assume a heat of adsorption of 23 kJ/mol and a pre-exponential frequency factor of $5 \times 10^{13} \text{ s}^{-1}$, as determined for the clean Ag(110) surface [35], a steady state value of θ_{CO} well above the detection limit of the HREELS method could be attained ($\theta_{CO} = 8.6 \times 10^{-3}$ ML, for $\Phi_{CO} = 0.4$ ML/s, $S_{CO} = 1$). However, under non-steady state conditions ($\Phi_{CO} = 0$) a 50% drop of θ_{CO} is expected at 100 K within 15 ms. As the typical acquisition time with HREELS is of the order of 10–20 min, it is impossible to detect adsorbed CO on a clean, defect free silver surface at 100 K.

Literature on this point is on the other hand quite contradictory. Canepa et al. [36] reported CO adsorption on Ag(110) at 100 K by metastable deexcitation spectroscopy, the thermal desorption temperature being as high as 170 K. Additionally, the heat of adsorption (27 kJ/mol) measured for the flat Ag(111) surface [34] is reported to be larger than for the Ag(110) surface [35] contrary to expectation. The bonding configuration of CO on Ag is still debated, too: Krause et al. [37] conclude from UPS measurements that physisorption of CO takes place on Ag(110); in contrast, Sandell et al. [38] conclude from UPS and XPS that a weak chemisorption of CO on Ag(110) occurs at adsorption temperatures of about 50 K.

As demonstrated in Figs. 1–5, no CO adsorption was usually observed in our EELS experiment. However, under particular conditions intense losses were present at 51 and 256 meV. Such frequencies are a clear fingerprint for the presence of CO ad molecules, as: (a) 256 meV is very near to the gas-phase value of the CO stretch vibration; (b) CO on Cu(001) presents very similar vibrational frequencies (42 and 259 meV [39]); (c) no further higher frequency losses were observed, thus ruling out e.g. accidental oil contamination; (d) the assignment of the loss peaks to carbonates is ruled out as more loss peaks would be expected

[31]; (e) it cannot be CO_2 as its heat of adsorption is even lower than that of CO and a higher stretch frequency would be expected (≈ 280 meV [40]). The loss frequency indicates that the ad molecules stand upright on the surface in analogy to the case of Cu. The sticking coefficient could be estimated to be 6.4×10^{-4} . CO desorbed at about 140 K and was stable at even higher temperatures in the presence of O coadsorption. CO_{ad} must therefore be stabilized by some other factor. Any reasonable impurity (in particular CO_{ad} is known to be stabilised by alkali metals [41]) is however expected to give rise to observable peaks in the EEL spectra (see Ref. [42] for alkali metals). The possibility that CO is attached at defect sites looks improbable in view of the large attainable coverage [43]. Also, subsurface oxygen is not expected to stabilize CO_{ad} , so that the origin of the effects is not clear.

In the light of the above quoted publications the positive result of CO adsorption on Ag(100) at rather high surface temperatures (100 K and higher), could contribute to the controversial discussion. The observation of an Ag–CO loss vibration points to weak chemisorption rather than to physisorption. CO however is not stable under clean conditions at 100 K unless stabilized by an impurity which unfortunately was not evidenced by our HREELS study.

4. Summary

In summary we have reported on CO oxidation by O_2 and O adsorbed on Ag(001). We find that the reaction probabilities are much smaller than in the case of Ag(110). Such rates depend, however, in our case strongly on the presence of contaminants. No $\text{CO}_{3\text{ad}}$ formation was observed at low temperature, contrary to the finding on Ag(110) [12].

Acknowledgements

Financial support from the Human Capital and Mobility Program under contract number CHRX-CT93-0104 and discussion with Flora Boccuzzi are greatly acknowledged.

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