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Comparative vibrational study on alkali coadsorption with CO and O on Ni(111) and Cu(111)

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Abstract

High-resolution electron energy loss spectroscopy was used to investigate alkali (Na, K) coadsorption with CO and O on Cu(111) and Ni(111). Measurements provided new insights in these systems. A CO-induced weakening of the alkali–substrate bond was revealed on both substrates. The effect is more pronounced for the Na + CO/Ni(111) system. Submonolayers of alkalis were found to promote the preferential population of the subsurface site for O/Cu(111) but not for O/Ni(111).

1. Introduction

The adsorption of alkali-metal atoms on single-crystal metal surfaces [1–8] and their coadsorption [9–14] with reactive species are a topic of surface science, both of fundamental interest in understanding the mechanisms of heterogeneous catalysis and for technological applications (promotion of catalytic reactions, oxidation rate and enhanced electron emission rates).

In particular, the coadsorption of CO with alkalis on noble-metal and transition-metal surfaces has been widely investigated from both experimentalists [15–22] and theoreticians [23–29]. The main effects of coadsorbed alkali-metal atoms with CO molecules are: a notable increase in the desorption temperature of CO molecules [16, 20–22], changes of work function of the surfaces [30], shifts in CO core- and valence-level binding energies [31] and an enhancement of the CO dissociation rate [32].

Moreover, infrared reflection absorption spectroscopy (IRAS) and high-resolution electron energy loss spectroscopy (HREELS) revealed a significant weakening of the C–O bond in the alkali + CO coadsorbed phase [15, 17]. Several models

have been proposed in order to explain the softening of the C–O stretching frequency. They involve electrostatic interactions [23–25], surface states [26], direct [27] and indirect (substrate-mediated) [28] interactions, and the alkali-induced enhancement of the surface electronic polarizability of the metal surface [29].

Recently, CO molecules have been demonstrated to induce a significant weakening of the alkali–substrate bond [18, 19] on Ni(111). In contrast, all previous research activities were focused on the shift of the C–O stretching vibration, whereas any effect of CO adsorption on the vibrational properties of the coadsorbed alkali atoms was completely disregarded. The shifts of the Na–Ni and C–O stretching frequencies are related to each other. CO molecules locally affect the electronic properties of the Ni(111) surface and ‘activate’ a lengthening of the Na–Ni bond. However, it should be essential to carry out further investigations on another substrate in order to establish the general validity of such an effect.

On the other hand, the electronic, vibrational and bonding properties of alkalis coadsorbed with oxygen have been scarcely investigated [33–35]. However, alkalis play an important role in many oxidation processes, i.e. oxidation of metal and semiconductor substrates [1] and epoxidation chemistry [36–38].

Nickel and copper are suitable substrates for such studies as they have quite different catalytic activities.

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Such a comparative investigation could provide interesting information on surface chemical reactions.

As concerns structural investigations, it has been shown that in K + CO/Ni(111) [39] both K atoms and CO molecules retain the atop site and the threefold hollow site, respectively, as on the clean substrate. However, an increased K–Ni bond length was revealed. In the case of K + O, a complete low-energy electron diffraction (LEED) investigation has been performed by Li and Diehl [40].

Herein we report on HREELS measurements performed for alkalis (Na, K) coadsorbed with CO and O on both Ni(111) and Cu(111). The CO-induced softening of the alkali–substrate bond was revealed on both substrates. Moreover, we found that on alkali-modified copper surfaces the subsurface site for O is energetically favourable with respect to over-surface sites. In contrast, for alkali + O/Ni(111) no subsurface species were revealed.

2. Experimental details

Experiments were carried out in a UHV chamber operating at a base pressure of 5×10^{-9} Pa, equipped with standard facilities for surface characterization. HREEL experiments were performed by using an electron energy loss spectrometer (Delta 0.5, SPECS). The samples were single-crystal surfaces of Ni(111) and Cu(111) with a purity of 99.9999%. The surfaces were cleaned by repeated cycles of ion sputtering and annealing at 900–1000 K. Surface cleanliness and order were checked using Auger electron spectroscopy (AES) and LEED, respectively. Both samples showed an excellent LEED pattern characterized by sharp spots against a very low background. Sodium and potassium were deposited onto the substrate by evaporating from a well-outgassed commercial getter source. The occurrence of the $(3/2 \times 3/2)$ -Na and $p(2 \times 2)$ -K LEED pattern was used as the calibration point of $\theta_{\text{Na}} = 0.44$ ML and $\theta_{\text{K}} = 0.25$ ML, respectively (the coverage of one monolayer, ML, is defined as the ratio between the number of atoms of the adsorbate and that of the topmost layer of the substrate). Very clean alkali adlayers could be obtained at 400 K, as demonstrated elsewhere [8, 18, 19, 33]. Nonetheless, measurements were carried out in a few minutes in order to further reduce the contamination. A constant sticking coefficient was assumed to obtain other desired alkali coverages. A calibration procedure using AES gave similar results. Loss spectra were taken in specular geometry (dipole scattering) with an incident angle of 55° with respect to the surface normal. A primary electron beam energy of 3 eV was used. The energy resolution of our spectrometer ranged from 2 to 3 meV.

3. Results

3.1. Na coadsorption with CO

HREEL spectra of 0.08 ML Na/Ni(111) exposed to CO molecules at room temperature are shown in figure 1. Upon CO exposure, the Na–Ni peak at 20 meV split into two components. Likewise, two different C–O stretching modes were revealed. A local and mutual interaction between coadsorbates should be responsible for the appearance of a

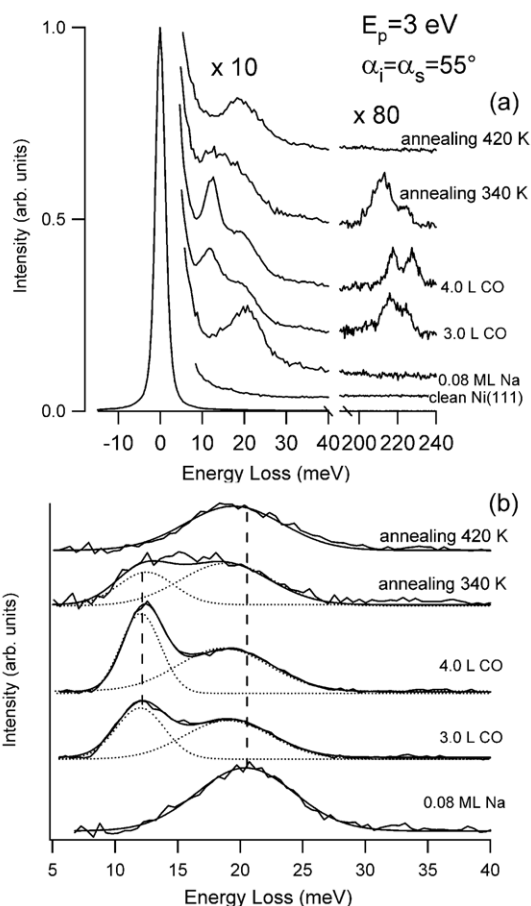


Figure 1. (a) HREEL spectra of 0.08 ML Na/Ni(111) exposed to CO molecules at room temperature and successively annealed. All spectra were normalized to the intensity of the elastic peak and multiplied by the same factor. (b) Each curve was obtained by subtracting an exponential background. The resulting curve was fitted by two Lorentzian lineshapes.

second Na–Ni and C–O mode in the coadsorbed phase. In fact, not all CO molecules can adsorb in the close nearness of pre-adsorbed Na adatoms, and vice versa.

An exponential background was subtracted from each spectrum of figure 1(a) for better analysis of the spectra. The loss features thus obtained were fitted by a Lorentzian curve (figure 1(b)). Carbon monoxide adsorption induced the appearance of a new Na–Ni peak at 12 meV. The intensity of the latter peak increased as a function of the CO coverage, while the intensity of the Na–Ni peak at 19 meV gradually decreased.

The feature at 12 meV was assigned to Na adatoms in close contact with CO molecules. Instead, the Na–Ni vibration at 19 meV was ascribed to Na adatoms far from CO molecules. The absence of an energy shift of the latter peak upon CO exposure is further evidence of a local interaction between Na and CO. The redshift of the Na–Ni peak in the Na + CO coadsorbed phase was ascribed to a CO-induced lengthening of the Na–Ni bond [18, 19]. Studies concerning the structural properties of K + CO on both Ni(111) and Ni(100) [41] reported a significant increase of the alkali–substrate bond length with respect to the case of K/Ni(111) and K/Ni(100).

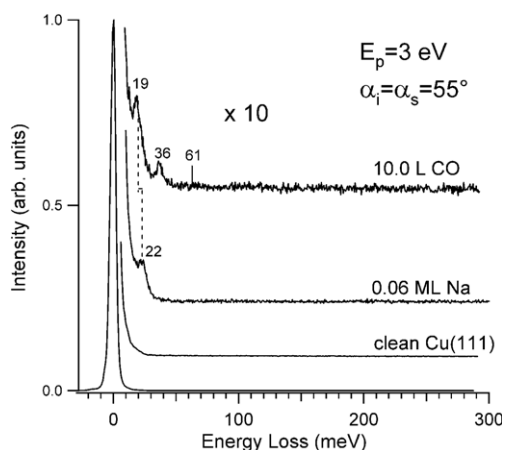


Figure 2. HREEL spectra for 0.06 ML Na/Cu(111) exposed to CO molecules at room temperature. The surface phonon of Cu(111) at 21 meV [49] was not excited under these scattering conditions in present HREELS experiments.

Such a finding is in excellent agreement with the weakening of the Na–Ni bond in the Na + CO coadsorbed phase.

As concerns the C–O vibration, a peak at 216 meV with a shoulder at 225 meV arose after an exposure of 3.0 L (1 L = 1.33×10^{-6} mbar·s) of CO. Further CO exposure allows a better separation of such features. Two well-distinct losses were recorded at 217 and 227 meV. The presence of two C–O features is ascribed to different environments for CO molecules and it is indicative of different local [Na]:[CO] stoichiometries.

Present results are in good agreement with those reported in a recent theoretical investigation [42] for K + CO/Ni(111). Such calculations indicated that the K-induced effect is short-ranged. The alkali-induced energy shift of molecular levels causes the $2\pi^*$ states of CO to be partially occupied.

The CO molecules less bonded to the surface desorbed upon annealing at 340 K (figure 1(a)). As a consequence, the C–O stretching peak at higher energy disappeared. After a further annealing up to 420 K, CO molecules completely desorbed from the surface. Instead, only a part of the Na adatoms desorbed, as indicated by the slight overall decrease of the integral of the Na–Ni peaks⁵. However, the Na–Ni vibration was still present in the HREEL spectrum even with the sample kept at 600 K. Upon annealing the component at 12 meV decreased in intensity (figure 1(b)) and finally disappeared. As expected, a single Na–Ni peak at 19 meV was recorded after CO desorption.

These findings disagree with previous results. In fact, it was generally assumed that a coincident desorption of both alkalis and CO occurs [21, 43–45]. However, the presence of the Na–Ni stretching in the absence of any CO-derived mode ensures that Na and CO desorption are not at all coincident.

With the aim of verifying if similar effects occur also on a noble-metal substrate, we carried out measurements

⁵ It is worth noticing that, in principle, HREELS intensities can be affected by several external factors. Besides depolarization effects caused by coadsorbates, further problems can originate, for example, from the changes in reflectivity due to the different surface conditions (temperature, adsorbate coverage and consequent work function changes, angle of incidence of the electron beam, etc).

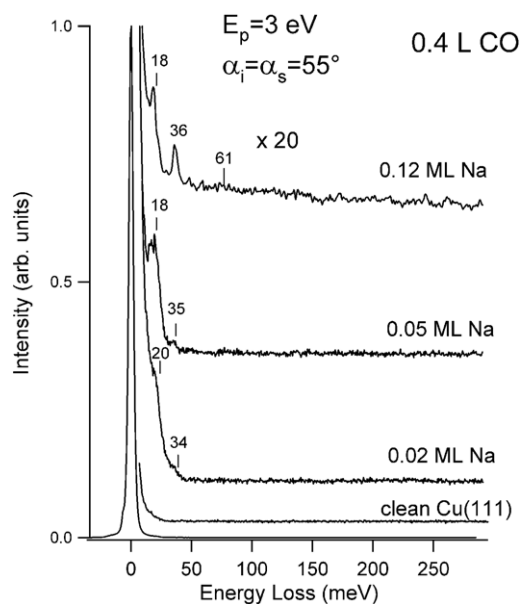


Figure 3. HREEL spectra for different amounts of Na deposited onto the Cu(111) surface and successively exposed to 0.4 L of CO. No critical precoverage for CO dissociation exists.

on Na + CO/Cu(111). A submonolayer of Na (0.06 ML) was deposited on Cu(111) and the surface was successively exposed to 10.0 L of CO (figure 2).

The Na–Cu feature shifted from 22 (Na on the clean substrate) down to 19 meV. Interestingly, HREEL spectra recorded on the Na-modified Cu(111) suggested a fully dissociative CO adsorption at room temperature, as indicated by the existence of a peak at 36 meV assigned to the O–Na vibration [33]. The weakening of the Na–substrate bond is more effective in the presence of molecular CO, as in the case of Na + CO/Ni(111).

It is worth mentioning that the sticking coefficient for CO molecules on copper surfaces at 300 K is extremely reduced compared with on transition-metal substrates (Ni, Pt, Ru). The saturation coverage for CO molecules on clean copper was found to be about zero for temperatures higher than 200 K [46], while for Ni(111) the surface was fully covered by CO molecules at 300 K even for small CO exposures [47, 48]. Accordingly, it is quite expected that CO adsorption on alkali-modified copper substrates might occur only in the close vicinity of alkali adatoms. HREEL spectra acquired for several Na coverages on Cu(111) exposed to 0.4 L of CO (figure 3) indicated that no critical precoverage for CO dissociation exists.

In contrast, on alkali-precovered Ni(111) surfaces CO adsorption at room temperature was molecular up to a critical precoverage, i.e. the saturation of the first layer (figure 4(a)). The Na–Ni stretching peak shifted from 10 to 24 meV as a function of the Na coverage while the C–O stretching continuously shifted down to 186 meV as a consequence of the increasing Na/CO ratio.

However, at the highest Na coverage (0.40 ML) loss spectra revealed the occurrence of a partial CO dissociation. In fact, a close inspection of the corresponding loss spectrum

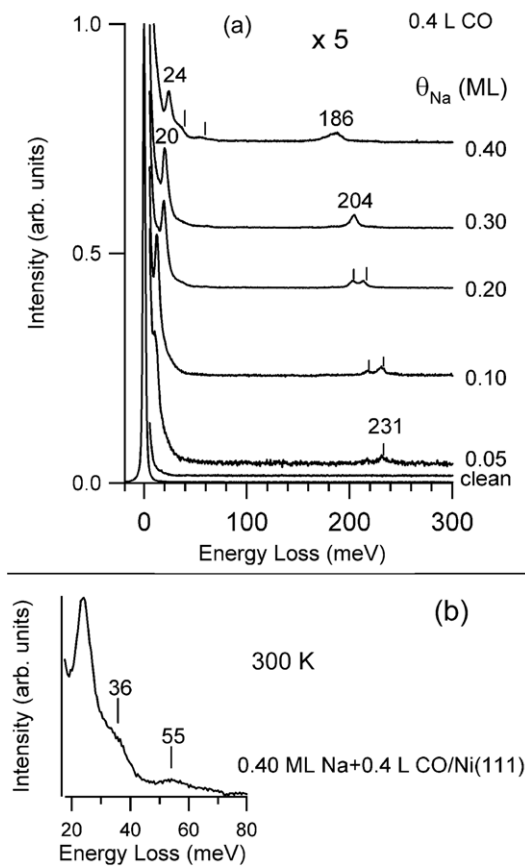


Figure 4. (a) HREEL spectra of various coverages of Na deposited onto the Ni(111) surface and exposed to 0.4 L of CO at 300 K; (b) magnification of the spectrum of 0.40 ML Na/Ni(111). Two loss features at 36 meV (O–Na) and 55 meV (C–Na) were recorded.

(figure 4(b)) revealed two new loss features at 36 (Na–O vibration) and 55 meV. The peak at 55 meV is assigned to a C-derived vibration [50].

A possible explanation for the different behaviour of the Cu(111) and Ni(111) surfaces towards alkali-promoted CO dissociation could be the existence of a different average alkali–CO distance. The reduced reactivity of copper towards CO adsorption should imply that CO adsorb only in the close vicinities of alkali adatoms, so as to enhance the short-range character of the alkali–CO interaction, which play the main role in CO dissociation [51].

3.2. K coadsorption with CO

Substituting Na with K we obtained similar findings. Carbon monoxide adsorption was molecular for K + CO/Ni(111) up to saturation of the first K layer (0.33 ML, figure 5) and partially dissociative in the case of K + CO/Cu(111).

Figure 6 shows HREEL spectra acquired for several coverages of K deposited on Cu(111) and successively exposed to 0.4 L of CO. The K–Cu vibration was measured at 15 meV for K/Cu(111) (not shown), in agreement with previous measurements of K adsorbed on copper surfaces [52, 53]. Upon CO exposure, a partial CO dissociation was revealed, as indicated by the appearance of a well-distinct O–K peak

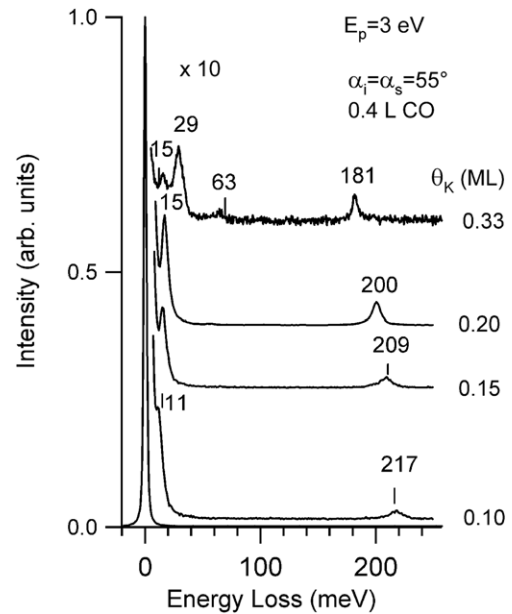


Figure 5. HREEL spectra for different amounts of K deposited on Ni(111) and exposed to 0.4 L CO at 300 K. The CO-induced shift is only 4 meV, so as not to allow the separation of the two K–Ni features due to the insufficient experimental resolution. The peak at 29 meV (O–K vibration) indicates the dissociation of CO molecules for 0.33 ML of K.

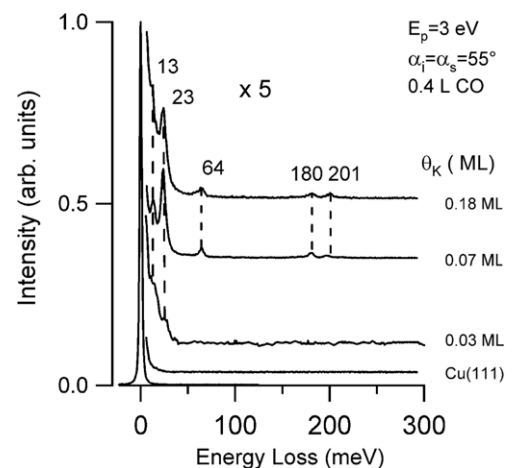


Figure 6. HREEL spectra for various coverages of K deposited at 400 K on Cu(111) and exposed to CO at 300 K. Measurements were carried out at 300 K. A partial CO dissociation was argued by the presence of O-related modes.

at 23 meV. The observation of the C–O stretching at 180 and 201 meV suggests that only a part of the CO molecules dissociates. The presence of two C–O features is ascribed to different local [K]:[CO] stoichiometries. As a consequence, different environments for CO molecules exist, thus implying different shifts of the C–O vibration compared with the value of the C–O stretching on clean copper surfaces, i.e. 255–258 meV [54, 55]. The K–Cu vibration redshifted to 13 meV in the K + CO coadsorbed phase, as a consequence of the CO-induced lengthening of the alkali–substrate bond [41]. The increased intensity of the K–Cu vibration in the K + CO coadsorbed phase is due to the CO-promoted depolarization

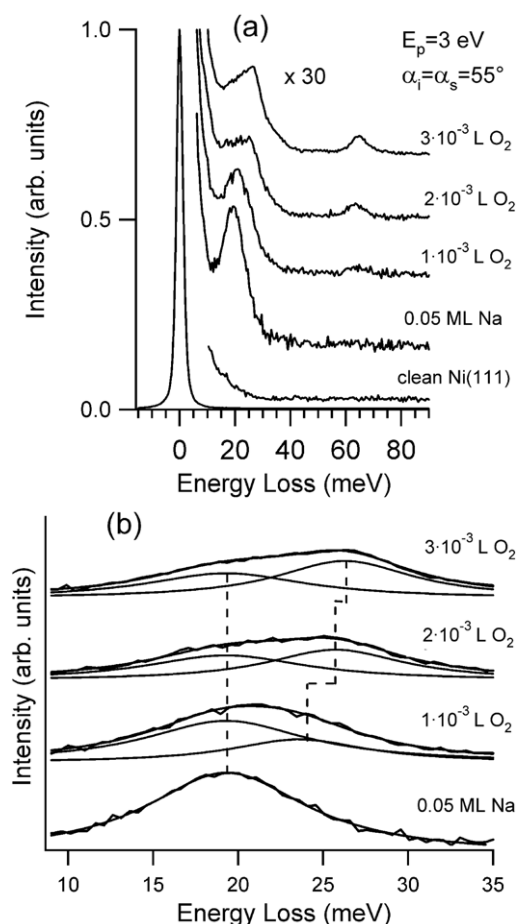


Figure 7. HREEL spectra of 0.05 ML Na/Ni(111) exposed to O_2 molecules at 400 K. (b) Each curve was obtained following the same procedure of figure 1(b).

effect [56] enhancing the ionic character of the alkali–substrate bond upon coadsorption with CO [8].

The peak which appears at 64 meV upon CO exposure was assigned to oxygen atoms in subsurface sites [57–59] and this will be discussed later (sections 3.3 and 3.4).

3.3. Na coadsorption with O

Figure 7 shows HREEL spectra of 0.05 ML Na/Ni(111) exposed to O_2 . A splitting of the Na–Ni vibration was revealed upon small O_2 exposures. Further oxygen exposures did not cause remarkable changes in the HREEL spectrum. The appearance of a higher-energy component for Na–Ni stretching could be ascribed to an O-induced shortening of the Na–Ni bond. As the technique does not allow direct evidence of changes in bond distances, accurate structural studies are needed to further support this suggestion. An explanation in the framework of the electrostatic model has to be excluded. In fact, the O–Ni bond is largely covalent and, thus, the O-induced electrostatic field should be relatively small and it would have only a little effect on the Na–Ni bond.

A small blueshift of the alkali–substrate vibration energy upon oxygen exposure was also revealed for Cs/Ru(0001) [56].

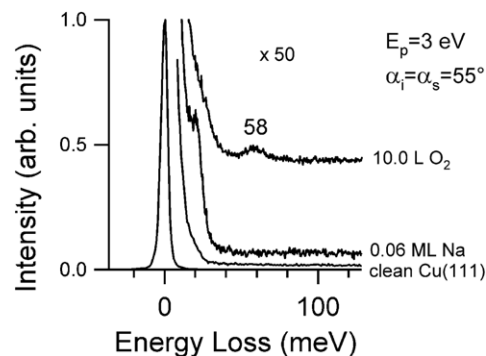


Figure 8. HREEL spectra for 0.06 ML Na/Cu(111) exposed to oxygen at 400 K.

The Cs–Ru vibration shifted from 8 to 10 meV. However, the authors did not discuss such findings.

The O–Ni vibration shifted from 70 meV, recorded for $p(2 \times 2)$ -O/Ni(111) [19, 33, 60], down to 63 meV. The softening of the O–Ni bond is in agreement with theoretical findings suggesting a short-range alkali-induced population of O $2p_z$ anti-bonding orbitals [51].

A similar experiment was performed on Cu(111). Loss spectra for 0.06 ML of Na on Cu(111) and for (Na + O) are reported in figure 8. The loss peak observed at 22 meV was assigned to the Na–Cu vibration, as also for Na adsorbed on other metal substrates [8]. For small O_2 exposures a loss feature at 58 meV arose in the spectrum.

Previous HREELS studies on O/Cu(111) [61] found the O–Cu vibration at 46 meV. As concerns the adsorption of molecular oxygen [61], it is allowed on Cu(111) only up to 230 K and it is characterized by vibrational peaks at 77 and 108 meV.

As regards the peak at 58 meV, its vibration energy suggests the occurrence of atomic oxygen adsorption on subsurface sites. As expected, the presence of O in a higher coordination site leads to the appearance of a feature with higher vibration energy in the loss spectrum. On silver surfaces, O adsorption in the octahedral subsurface sites was argued from the presence of a loss peak at 53–59 meV [57–59]. However, on Ag the subsurface site for O is metastable [57–59], i.e. it is accessible only after the complete occupation of available on-surface sites. Similar conclusions were reached by theoretical results for O adsorption on clean Cu(100) [62, 63]. In contrast, for Na-doped Cu(111) the energetic conditions are completely reversed, as shown in figure 8. In the first stage of O adsorption, only subsurface sites are occupied. Such a finding deserves particular attention as subsurface oxygen has been widely demonstrated to play an important role in activating chemical reactions [37, 38, 64–68].

It is worthwhile noticing that the formation of Cu_2O (promoted by Na) has to be excluded for the lack in the loss spectrum of the infrared-active mode at 79 meV [69], which is indicative of oxidation of the copper surface.

3.4. K coadsorption with O

For O + K/Cu(111), besides subsurface oxygen (peak at 57–61 meV), also over-surface O vibration against Cu(111) [61]

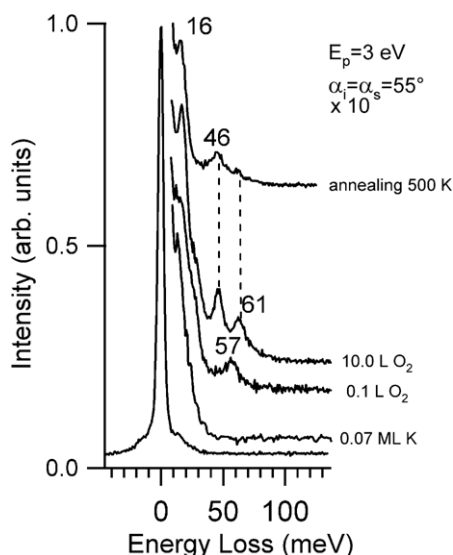


Figure 9. HREEL spectra for 0.07 ML K/Cu(111) as a function of O₂ exposure. In the first stage of O adsorption, only the subsurface site was populated by O adatoms.

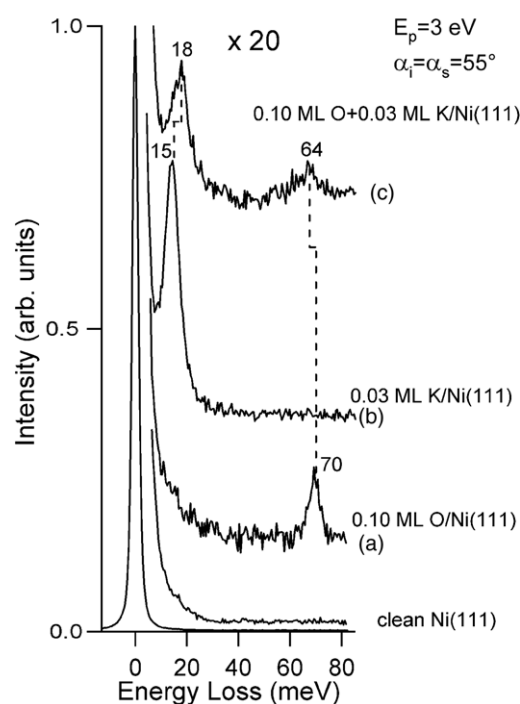


Figure 10. HREEL spectra of: (a) 0.10 ML O/Ni(111) at 400 K; (b) 0.03 ML of K deposited at the same temperature onto the Ni(111) surface; (c) 0.03 ML K coadsorbed at 400 K with 0.10 ML of O on the Ni(111) surface.

was observed at 46 meV (figure 9). Annealing caused the disappearance of subsurface species, as also found for silver [57–59]. Moreover, spectra in figure 9 show that the effect of alkali adatoms on the stability of subsurface oxygen is reduced once oxygen atoms adsorb also in over-surface sites. Probably this is a consequence of the formation of a direct O–K interaction. In fact, upon annealing at 500 K

the amplitude of the feature assigned to subsurface oxygen drastically decreased. In contrast, only a slight variation in the intensity of the O–Cu vibration at 46 meV was recorded.

As regards K + O/Ni(111), no significant differences with respect to Na + O/Ni(111) were observed (figure 10). No subsurface oxygen was revealed on Ni(111), as also predicted for Rh(110) [70]. These findings demonstrate that noble-metal and transition-metal catalysts behave very differently towards the migration of oxygen atoms in subsurface sites.

4. Conclusions

HREELS measurements reported here provided direct evidence of a substrate-independent weakening of the alkali–substrate bond in the alkali + CO coadsorbed phase. Short-range effects dominate the alkali interaction with coadsorbates (CO, O). No critical alkali precoverage for CO dissociation was found on Cu(111), in contrast with results obtained for Ni(111). Alkalis induced a softening of the O–Ni bond, which is well described within the framework of the electrostatic model. In contrast, such a mechanism is not efficient for the Cu(111) substrate, where alkali doping renders negative the adsorption energy of the subsurface site for O. Present results should open new pathways in understanding heterogeneous catalysis at metal surfaces.

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