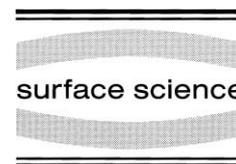




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Surface Science 429 (1999) 1–13



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Coverage grating template for the study of surface diffusion: K coadsorbed with CO on Re(001)

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Received 10 October 1998; accepted for publication 26 January 1999

Abstract

The coverage grating method as a template for coadsorbates is introduced for the study of surface diffusion. The effect of coadsorbed CO inside coverage troughs formed by laser induced thermal desorption (LITD) on potassium surface diffusion on Re(001) has been investigated using the coverage grating optical second harmonic diffraction method. Enhancement of the first-order diffraction peak at a certain CO coadsorption coverage, observed for the first time, demonstrates the very strong electronic interaction between these coadsorbates. The activation energy for K surface diffusion and the pre-exponential factor significantly increase with CO coverage. At initial potassium coverage of 1.0 ML, the activation energy for potassium diffusion increases from 5.0 kcal/mol on the clean rhenium surface to 15.0 kcal/mol in the presence of 0.065 ML CO, and the pre-exponential factor increases from 5.6×10^{-3} to 2.0×10^2 cm²/s. The activation energy doubles for potassium coverages of 0.9 ML and 0.8 ML as a result of the same CO coverage. TPD measurements indicate that strong attractive interactions exist between CO and K on Re(001). Coadsorbed CO and K stabilize each other while forming K_x-CO surface complexes which slow down the potassium surface diffusion predominantly by site-blocking effect. This site-blocking effect increases as the number of potassium atoms (*x*) interacting with a single CO coadsorbate increases at higher initial K coverages. The nature of this site-blocking is discussed. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Coverage grating; Diffusion; Laser induced thermal desorption; Potassium

1. Introduction

Surface diffusion is among the basic processes in gas–solid heterogeneous catalysis, and is often affected by complex adsorbate–surface and adsorbate–adsorbate interactions [1,2]. Significant progress has been made over the last decade with the introduction of laser induced thermal desorption (LITD) techniques for macroscopic diffusion and STM for microscopic hopping measurements. Yet only a few systems have been studied so far due

to experimental difficulties. LITD can be used to create a periodic coverage modulation on a surface, from which diffusion can be measured using optical diffraction, either second harmonic or linear [3–10]. Most recently, a new development of this method has demonstrated the use of template grating procedure. In this technique, a weakly bound inert gas forms the first grating and then the desired atom or molecule forms its own periodic pattern in the open troughs [11]. This method can be further developed for study of surface diffusion of a coadsorbed system, as will be presented here. In all these studies, the decay of the

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first-order diffraction peak is used as a direct monitor of the diffusion process at a certain surface temperature.

LITD hole-refilling surface diffusion studies of hydrogen in the presence of copper or carbon atoms adsorbed on Ru(001) have indicated that the coverage dependence of hydrogen diffusivity can be ascribed to hydrogen trapping by surface carbidic species [12] or copper islands [13]. Similar LITD measurements of hydrogen surface diffusion on Ru(001) in the presence of sulfur have shown that sulfur acts to block hydrogen diffusion paths [14]. The investigation of hydrogen and CO coadsorbed on Ru(001) reveals that hydrogen diffusion occurs by percolation around $\sqrt{3} \times \sqrt{3}$ islands [15]. In addition, most recently the coadsorbed surface diffusion of carbon monoxide and potassium on Ru(001) has been studied using the hole-refilling method where it was shown that the CO–K interaction is mutually stabilizing and that a CO–K surface complex has been formed in 1:1 stoichiometry [16].

LITD coverage grating linear diffraction was used to study the effect of surface impurities such as sulfur, oxygen, and potassium on the surface diffusion of CO on Ni(110) [17,18]. It was found that all three are acting to drastically impede CO diffusion, no matter whether repulsive or attractive interactions occur between the CO and the coadsorbate atoms. With sulfur and oxygen, impurity-covered step-controlled diffusion appears to be the dominant mechanism. With K, the nearest-neighbor attractive interaction between CO and K seems to be most important.

The surface diffusion of clean potassium on Re(001) has recently been studied as well [10]. It was found that the potassium surface diffusivity was particularly sensitive to the background pressure. CO has been chosen as a coadsorbate due to its relevance together with potassium in the Fischer–Tropsch catalysis. This choice enables us to compare the role of attractive lateral interactions on the surface diffusion in contrast to the repulsive interactions which characterize the pure K atoms, as shown in our previous K/Re(001) diffusion studies [10]. The CO–K system has been the subject of various experimental and theoretical

investigations on several metal substrates in the past [19–21].

In this article we present results of the effect of coadsorbed CO prepared by the unique template method on the potassium surface diffusion on Re(001). In addition, TPD spectra of coadsorbed CO and K, quenching of the optical second harmonic generation (SHG) signal by CO are also discussed in order to obtain the necessary calibration of coverages, which is required to understand the potassium diffusion process and the overall interaction between CO and K.

2. Experimental

Details of the experimental apparatus for surface diffusion were given elsewhere [8–10]. Briefly, the experiments were performed in a UHV chamber, equipped with a quadrupole mass spectrometer (QMS) for residual gas analysis and TPD. A Kelvin probe (Besocke S-type) was used for work function measurement. The system base pressure was less than 2×10^{-10} Torr. The procedure used to clean the Re(001) sample is the same as in Ref. [22]; namely, Ne⁺ sputtering at 0.6 keV with a sample current of 6–10 μ A, followed by annealing at 1300 K for 8–10 min. The rhenium crystal was spot-welded between two 0.02" diameter rhenium wires, which were spot-welded to two molybdenum rods. Sample temperature is monitored by a W–5%Re W–26%Re thermocouple spot-welded to the sample edge, computer controlled by an a.c. resistive heating procedure.

The dosing procedure and calibration of the potassium coverage were described in detail previously [22]. Briefly, potassium was dosed onto the Re(001) surface by passing current (4.5–6.5 A) through a commercial potassium source (SAES Getters) located approximately 15 mm from the sample. This was sufficient to produce a monolayer of potassium on the surface in 2–3 min. The crystal temperature was kept at 250 K during potassium adsorption to minimize the adsorption of more weakly bound background gases, e.g. water, CO₂. Reproducible coverages were obtained by dosing potassium to coverage more than a monolayer, in situ monitored by SHG, and then heating

the surface to a given temperature at a heating rate of 3 K/s to produce the desired coverage. TPD results have shown that this coverage determination procedure results in much more reproducible values than by simply controlling potassium dosing time and current. A full monolayer (ML) potassium is defined as that just before the appearance of the multilayer TPD peak at 335 K, where potassium surface SHG intensity is just over the maximum [22]. This coverage was assumed to correspond to a ratio $K/Re=0.33$, as it does on most hexagonal surfaces, e.g. potassium on Ru(001) [23], where it forms an ordered $(\sqrt{3} \times \sqrt{3})R30^\circ$ at 1 ML.

CO was then dosed onto each of the potassium precovered surfaces. CO sticking on K/Re(001) has been determined by TPD analysis and its coverage was measured by integrating the CO TPD spectra and has been normalized to the TPD area corresponding to a saturation coverage of CO on clean Re(001). Based on the above TPD analysis, one can calculate the coverage profile of CO on the modulated potassium coverage prepared by the LITD grating formation.

The optical set-up used here utilizes one Nd:YAG laser (Quantel YG585) at a fundamental wavelength of $\lambda=1.064 \mu\text{m}$, repetition rate of 10 Hz, and pulse duration of 10 ns [full width at half maximum (FWHM)]. The laser is used for both grating formation and SHG diffraction. In these experiments, a beam-splitter forms two beams with equal intensity, which strike the potassium covered Re(001) surface at incident angles of $\phi = \pm 6^\circ$ from the normal to the surface. The resulting grating period, given by $d = \lambda/2 \sin \phi$, is therefore $5.1 \mu\text{m}$. These beams spatially overlapped at the center of the sample having a spot size of 0.34 cm^2 . The maximum effective laser intensity from the desorption laser actually absorbed by the surface per pulse (both beams) was 10 MW/cm^2 (155 mJ/pulse). A spatial intensity modulation is formed under these conditions due to interference between the two beams. The 2.5 mJ/pulse of the fundamental laser intensity has been separated out by using a reflecting glass. This fraction is used as the SHG probe laser with incident angle 43° from the normal to the surface having a spot size of

0.05 cm^2 . The absorbed fundamental laser intensity of the probe beam was at most 1 MW/cm^2 , which corresponds to a maximum change in the surface temperature of 30 degrees while the laser pulse strikes the surface during its 10 ns pulse width. This ensures that there is no potassium diffusion originated by the SHG probe laser heating. The first-order SH diffraction appeared at an angle of 8.2° away from the zero-order diffraction. Following the first-order decay provides a direct probe of the potassium surface diffusion, by fitting it to the appropriate solution of Fick's second law of diffusion to determine the diffusion coefficient [3–10].

3. Results

3.1. CO coadsorption on K precovered Re(001)

CO adsorption on different uniform coverages of potassium preadsorbed on Re(001) at 250 K is shown in Fig. 1. CO surface coverage, normalized to its saturation coverage on the clean rhenium surface, is indicated at the various potassium initial coverages as a function of CO exposure, as obtained from TPD area under the CO peak. It shows that CO adsorption on K/Re(001) strongly depends on the potassium surface coverage. The solid lines through the data points are standard

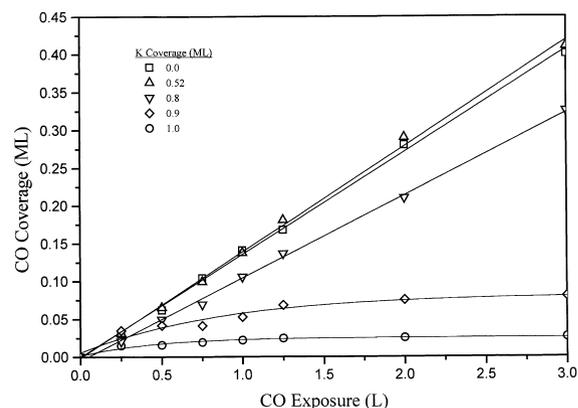


Fig. 1. CO surface coverage vs. CO exposure on potassium precovered Re(001). Potassium coverages are indicated in the figure. Surface temperature is 250 K.

non-linear least-squares fits which are later used to obtain the continuous CO coverage profile.

Fig. 2a depicts CO TPD spectra from clean Re(001) surface at a heating rate of 6 K/s. There are two peaks at 475 K and 800 K. When CO exposure is small, the high temperature peak dominates the TPD spectra. When more CO is dosed onto the rhenium surface the 800 K peak saturates, while the 475 K peak increases further. Fig. 2b displays CO TPD spectra from 0.52 ML potassium precovered Re(001). The CO low temperature desorption peak totally disappears, while the high temperature peak near 800 K moves up by several degrees. A new CO TPD peak emerges as a

shoulder near 750 K for CO exposures above 0.5 L. Potassium TPD spectra are also affected by the CO postadsorption, as shown in Fig. 2c. The potassium TPD peak at 590 K decreases, while the peak at 800 K grows. CO and K TPD spectra clearly show coincident desorption near 750–800 K.

3.2. K coverage grating and CO surface coverage profile

The preparation of well-calibrated potassium surface coverages and the grating formation which follows have been described in detail in Refs. [10,22]. Briefly, a detailed knowledge of the coverage dependence desorption kinetics should be at hand before the modulated potassium coverage can be calculated. An electrostatic model was used to describe the activation energy for the desorption of K from Re(001) as a function of its coverage [22]. For the sake of simplicity the pre-exponential factor for desorption was kept constant at 10^{13} /s. Then the absorbed laser power density should be measured in order to calculate the modulated surface temperature profile caused by the two interfering laser beams [8–10]. Once the time dependent surface temperature is established, the potassium desorption during the laser pulse can be calculated, leading to the modulated surface coverage profile. A verification of the correlation between the actual and calculated potassium coverage profiles is obtained by comparison between the observed diffraction peak intensities and the calculated Fourier components of the calculated profiles, as discussed in Ref. [10].

After the potassium modulated coverage profile has been established, the surface was exposed to CO at a given dose. The corresponding and complementary CO coverage profiles were then determined from the non-linear least-squares fitting curves in Fig. 1. Shown in Fig. 3 are both the K and CO modulated surface coverages, where the initial potassium coverage has been 0.9 ML. The LITD laser power density was 7.6 MW/cm^2 , the average potassium coverage after desorbing a small fraction of the potassium coverage was 0.88 ML. The relatively low laser power ensures that the potassium coverage modulation is shallow, the

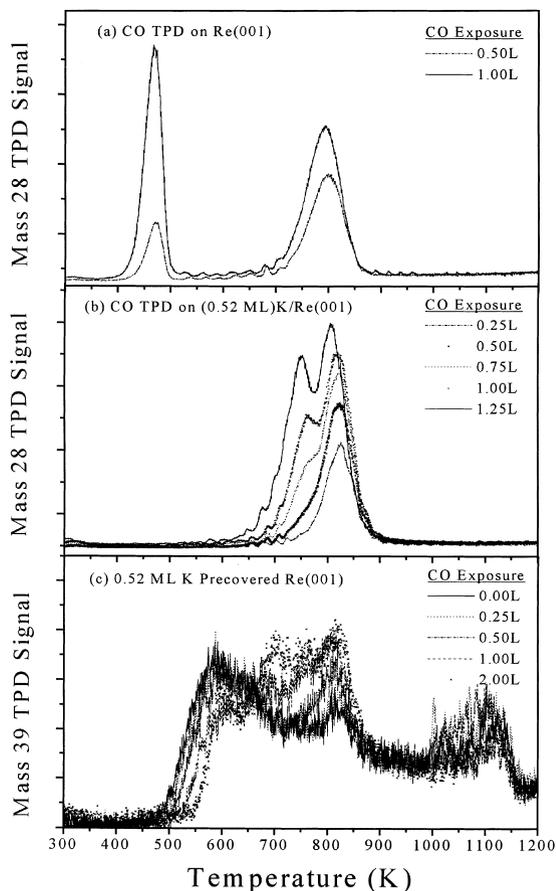


Fig. 2. (a) CO TPD spectra on clean Re(001) surface for two CO exposures of 0.5 L and 1.0 L. (b) CO TPD spectra on 0.52 ML potassium precovered Re(001) for various CO exposures. (c) 0.52 ML potassium TPD spectra for various CO exposures. All TPD are done at a heating rate of 6 K/s.

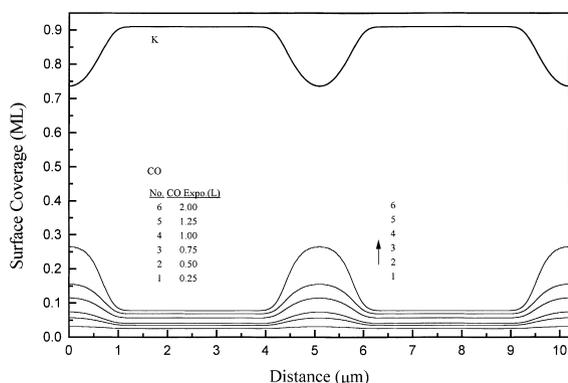


Fig. 3. The potassium and CO surface coverage profiles as obtained from LITD simulations, see text. The initial potassium coverage was 0.9 ML and the different CO coverage profiles are obtained at the indicated CO exposures.

according to the simulation results in Fig. 3. Since the most important density of the CO molecules is this inside the grating troughs, we introduce the effective average coverage, which is obtained by integrating over the CO coverage inside the grating troughs. Fig. 4 shows the CO effective average coverage as a function of CO exposure, potassium coverages (initial, average and grating trough) are indicated here as well. The inset displays the surface coverage profiles of CO in one grating period. The relatively shallow potassium modulation minimizes the potassium coverage effect on the diffusion rate coefficient.

maximum depth of the grating is less than 0.15 ML. This modulation is enough to generate a corresponding CO modulation depth of 0.3 ML.

The definitions of the CO surface coverages are displayed in Fig. 4. The average coverage is defined as the mean coverage along the entire grating. One has, therefore, to integrate the full grating period

3.3. CO quenching of the zero-order and first-order SHG diffractions

Fig. 5 displays how CO quenches the zero-order and first-order SHG diffractions starting from various potassium coverages on Re(001). The solid square curves are the zero-order decay, which can be fitted quite well by a single exponential decay. The quenching becomes more efficient at lower potassium coverages. The up triangle curves

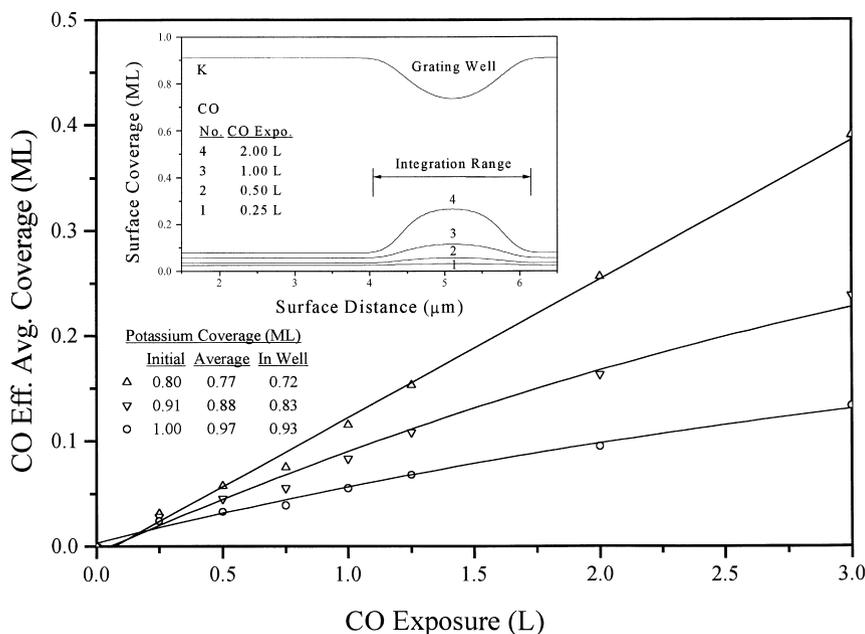


Fig. 4. CO effective average coverage (for definition see text) vs. CO exposure for various potassium coverages. The initial, average and within grating trough coverages are indicated in the figure. The inset shows the CO and K surface coverage profiles.

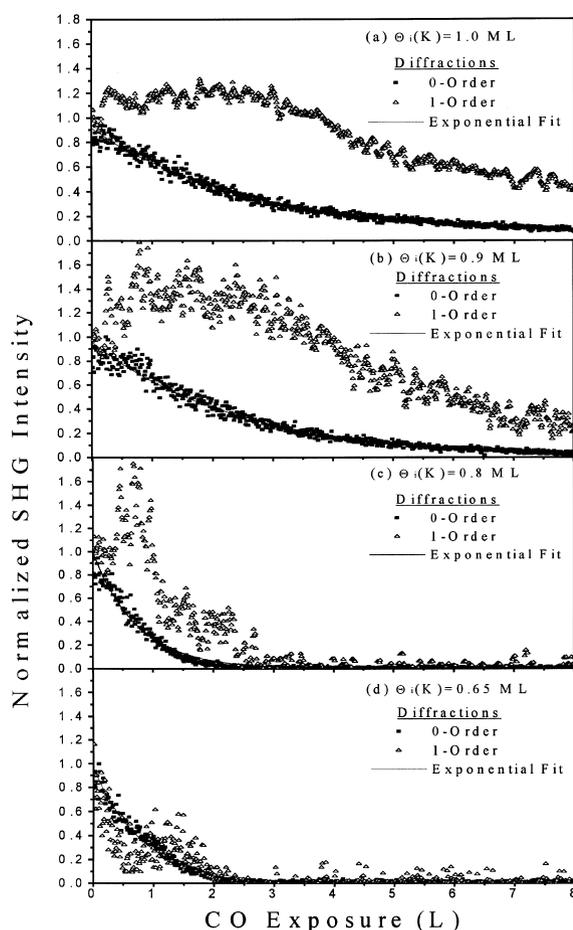


Fig. 5. (a) CO quenching of the zero-order and first-order SHG diffraction signals at an initial K coverage of 1.0 ML, the LITD laser power density was 7.0 MW/cm^2 . (b) The same for initial K coverage of 0.9 ML, the LITD laser power density was 7.6 MW/cm^2 . (c) Initial K coverage of 0.8 ML, the LITD laser power density was 8.9 MW/cm^2 . (d) Initial K coverage of 0.65 ML, the LITD laser power density was 10.3 MW/cm^2 .

represent the change of the first-order diffraction with CO exposure. It reveals a rather high sensitivity to the potassium coverage, as indicated by its different behavior. For potassium initial coverage of 1.0 ML (Fig. 5a), the first-order diffraction peak slightly increases at low CO exposure, then remains unchanged up to 3 L CO exposure, and then slowly quenches. Due to the small sticking probability of CO on 1.0 ML potassium, one can measure the first-order diffraction even after 8 L CO exposure. With 0.9 ML initial potassium coverage (Fig. 5b),

the first-order signal initially grows by about 30% and then stays constant almost until 3 L CO exposure, followed by a decrease at higher CO exposure, which is faster than in the case of 1.0 ML potassium. At 0.8 ML initial potassium coverage (Fig. 5c), the first-order peak significantly increases by 60% at 0.75 L CO exposure, followed by a rapid decay immediately after, to a complete quenching at 3 L CO exposure. In the 0.65 ML initial potassium coverage, the first-order decays immediately with the exposure to CO, going through a minimum at about 0.75 L CO, then its intensity oscillates once before the complete quenching is reached above 2.5 L CO exposure.

3.4. Effects of coadsorbed CO on potassium surface diffusion

The surface diffusion of potassium on Re(001) in the presence of CO has been examined as a function of the CO exposures. Shown in Fig. 6 are the decay curves of the first-order SH diffraction peak with time at different surface temperatures for the initial potassium surface coverage of 1.0 ML followed by 0.5 L CO exposure. Coverage grating as in Fig. 3 has been obtained using LITD laser power density of 7.6 MW/cm^2 . Ideally, if the

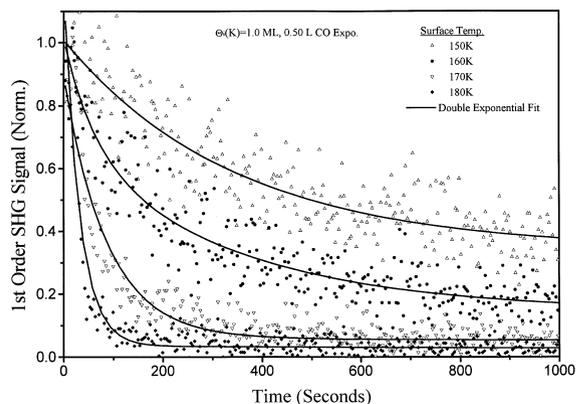


Fig. 6. First-order SHG diffraction signal as a function of time during the diffusion of potassium at the indicated surface temperatures. The signal has been normalized to the same zero-time signal in each case. The initial potassium coverage was 1.0 ML, exposed to 0.5 L CO the LITD laser power density was 7.0 MW/cm^2 . The solid lines through the data points are obtained from double exponential fits.

diffusion coefficient is independent of surface coverage, and the SH signal is directly proportional to the coverage squared [3–7,10], then the decay of the diffracted SH signal should be a single exponential. This is not expected to be the case in the presence of coadsorbed CO which quenches the SH response of the K adsorbate. Even if the above conditions do not strictly hold, the decay of the SH signal can be very close to an exponential as long as the coverage modulation depth (determined by the LITD laser intensity) is shallow. We have carefully chosen for each of the initial potassium surface coverages the appropriate desorption laser power such that the diffraction signal is still measurable, but the modulation is shallow. Even after taking these precautionary measures, the decay curves in Fig. 6 are clearly non-exponential. In order to obtain diffusion coefficients from Fig. 6, we had to fit each of the decay curves with a double exponential, and use the decay constant of the initial ‘fast’ exponential only. The validity of this assumption has been examined and discussed in the case of pure potassium diffusion on Re(001) [10]. The slow component of the first-order decay at longer times is believed to originate from background CO accumulation, resulting in a gradually higher activation energy for diffusion, as will be discussed below. The resulting Arrhenius plots are shown in Fig. 7, as obtained from the data in Fig. 6.

Similar measurements were performed at other

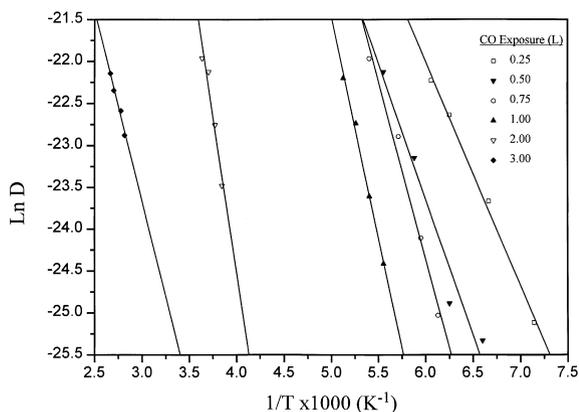


Fig. 7. Arrhenius plots for the diffusion data shown in Figs. 6 and 7. Here the initial potassium coverage was 1.0 ML and the CO coverages are indicated in the figure.

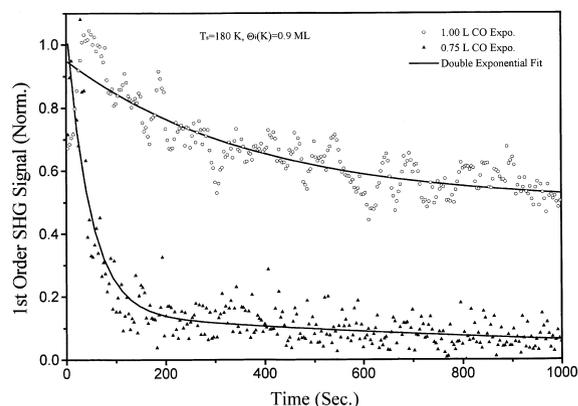


Fig. 8. The effect of the indicated CO coverage on potassium diffusion rate at surface temperature of 180 K. The potassium coverage was 0.9 ML.

initial potassium coverages of 0.9 ML and 0.8 ML. Lower potassium coverage could not be studied due to the severe quenching of the first-order diffraction signal in the presence of coadsorbed CO. The decay of the first-order SH diffraction at initial potassium coverage of 0.9 ML vs. the CO exposure of 0.75 L and 1 L at 180 K is shown in Fig. 8. Finally, the resulting activation energies for potassium diffusion and the corresponding pre-exponential factors in the presence of CO are presented in Fig. 9.

4. Discussion

4.1. CO and K interaction

Studies of CO and K coadsorption over transition metals [20,24–29] have shown that the initial sticking coefficient of CO on potassium covered metal surfaces slightly increases or remains approximately constant for potassium coverages up to 0.66 ML. At higher K coverage there is a gradual decrease in the sticking probability. In the case of potassium on rhenium as shown in Fig. 1, the sticking of CO is practically constant up to potassium coverage of 0.52 ML, and then gradually decreases with faster decay for coverages over 0.8 ML. The mechanism of CO adsorption on alkali metal covered surfaces is complicated. At lower potassium coverages, the adsorption of CO

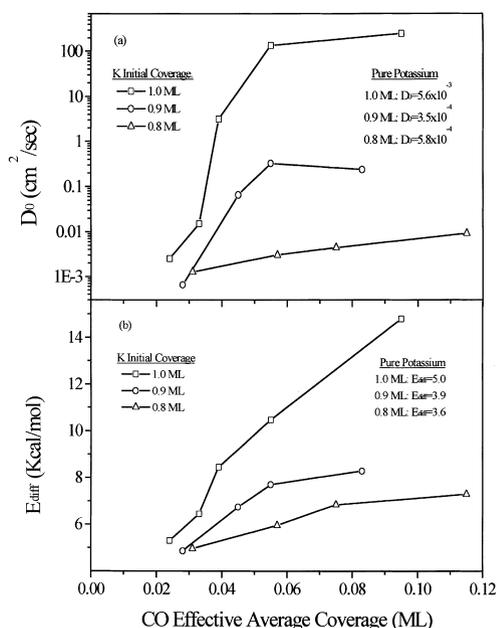


Fig. 9. (a) The pre-exponentials for diffusion as a function of CO effective average coverage for the initial potassium coverages of 1.0, 0.9 and 0.8 ML. (b) The activation energies for diffusion as a function of CO effective average coverage for the initial potassium coverages of 1.0, 0.9 and 0.8 ML.

follows a precursor mechanism [30], but for $\theta_K > 0.66$ ML different kinetics dominate. The conversion from ionic to a neutral species as potassium coverage increases, significantly decreases the electric field exerted by the dipoles on the surface [31]. This, together with simple site-blocking effect, results in a reduced sticking coefficient [20]. As shown in Fig. 3, CO sticking and therefore its coverage changes along the surface, exactly opposite to the potassium coverage modulation. It is likely therefore that on top of occupied metallic potassium sites, CO does not stick.

Potassium thermal desorption from clean Re(001) has been studied in detail using TPD, work function and SHG methods [22], revealing a rather similar behavior to that of potassium on other transition metals, e.g. Ru(001) [23]. TPD of potassium (and other alkalis) from transition metals shows a number of common features. One is a dramatic decrease in the peak desorption temperature with increasing coverage [22,32–37], which is attributed to the existence of strong

repulsive interactions between the highly polarized alkali adatoms on the surface. CO adsorption and desorption kinetics on Re(001) reveal different behavior. There are two thermal desorption peaks at 475 K and 800 K, unlike the desorption from Ru(001) [16] and Ni(110) [26], where only a single low temperature desorption peak exists. The high temperature peak has been attributed to CO partial dissociation on the relatively active Re surface. This assumption is supported by the effect of coadsorbed potassium on Re(001) which causes complete elimination of the low temperature peak while enhancing the partial dissociation peak near 800 K. The formation of $K_x\text{-CO}$ ($x \geq 1$) complexes is expected to weaken the intramolecular C–O bond and thus enhance its partial dissociation. A similar example was demonstrated in the case of CO on clean and K-covered Fe(110) surface [38–40]. Adsorption of CO near room temperature is molecular on Fe(110) but after a brief annealing to 390 K most of the CO desorbs and about 20% dissociates. In contrast, a monolayer potassium promoted Fe(110) can increase the fraction of CO dissociation from 20% to nearly 100% at 500 K annealing temperature. Similar results were reported for Fe(100) [41] and Fe(111) [42].

Potassium TPD peak temperature was shown to be influenced by the presence of CO as well (Fig. 2c). The 585 K peak diminishes while the peaks of 680–800 K gain in intensity, the overall peak area remains constant. On Ru(001) [8,9], the potassium TPD peak at 495 K, observed at a coverage of 0.8 ML, shifts gradually to 655 K as the CO coverage approaches 0.4 ML, in a rather similar way to that shown here for Re(001).

TPD and surface diffusion results of CO and K coadsorbed on Re(001) both show a mutual stabilization and attractive interaction between CO and K. Fig. 2b and c displays coincident thermal desorption, which emphasizes the attraction between the two adsorbates. A large number of studies correlating the basic interaction of alkali metals with CO to Fischer–Tropsch catalysis [43] have demonstrated that the dominant interaction between CO and K is strongly attractive and rather short range. Surface complexes having some degree of charge transfer to form $K_x^{\delta+}\text{-CO}^{\delta-}$ have been proposed based on spectroscopic evidence. The

exact nature of the K_x -CO surface compound is a subject of further investigation and is definitely substrate specific [19,21,25,44]. In particular, the claim that there is a unique 'coincident desorption temperature' of CO and K on all metal substrates has been reviewed [44] and was shown to be incorrect. A coadsorbed $K_x^{\delta+}-CO^{\delta-}$ surface complex with direct or indirect electronic interaction (including electron transfer between CO and K through surface) is considered to be the more likely and general case [44]. Such a complex would also cause coincident K and CO desorption spectra because of their mutual stabilization.

The optical second harmonic (SH) response of a solid surface is typically sensitive to changes in adsorbate-surface electronic structure via the second-order susceptibility of the substrate [45–48]. On a clean substrate the strong SH response of the potassium covered surface is due to the particularly large second-order susceptibility of the alkali-metal complex at the fundamental laser wavelength of 1.064 μm . Electron transfer between K-4s to the antibonding $CO-2\pi^*$ is therefore expected to significantly influence the SH response of the K-metal complex. Shown in Fig. 5 are the zero-order and the first-order diffraction decays from potassium coverage grating on Re(001) as a function of CO exposure.

There are two conditions in which a single exponential decay of the first-order SH diffraction peak should be observed: coverage independent diffusion coefficient, which results in an exponential analytical solution of the second Fick's diffusion equation; coverage modulation sufficiently shallow to resemble diffusion under effectively constant coverage, where again the diffusion rate is expected to follow an exponential decay. Our experimental arrangement has been close enough to the second condition to observe an exponential decay during the initial decay time. The rate in which the zero-order SHG diffraction signal decreases due to the CO coadsorption therefore depends on the potassium coverage on Re(001). The potassium coverage determines the SHG signal on the one hand but also dictates the actual CO sticking probability and its final coverage, as demonstrated in Fig. 5a and b. As the potassium coverage decreases below 0.8 ML, the zero-order

SH diffraction peak decays much faster because more CO sticks and the actual CO coverage increases significantly. In a previous study, the SHG response of a Re(001) covered by NH_3 was shown to be very effectively quenched by minute amounts of coadsorbed CO [48], in a very similar way.

Unlike the zero-order diffraction peak, higher order peaks are determined by the Fourier components of the periodic coverage profile formed by the interference of the LITD grating formation laser pulse. The intensity ratio of the first-order signal to the zero-order should be dictated by the coverage modulation profile. Simulations of the dependence of the higher order diffraction peak intensities on the modulation profile suggest that the intensity ratio of the first-order SH diffraction peak to the zero-order should increase as the coverage modulation profile becomes closer to a square wave in shape [49]. The results shown in Fig. 5 suggest that at the lower potassium coverages, adsorbed CO effectively reshapes the potassium coverage profile on Re(001). The initial CO adsorbates (low exposures) preferentially stick to the area of lowest K coverages. The interaction at the bottom of the potassium troughs between CO and K are stronger and local SH quenching is more efficient. This causes the reshaping of the K coverage modulation from the point of view of SH response, thus enhancing the first-order diffraction peak, which significantly increases the magnitude of the ratio of first-order to zero-order diffraction intensity [49]. A similar behavior was predicted to be possible during diffusion, if lateral interactions among adsorbates are strongly repulsive [50].

4.2. Effect of coadsorbed CO on potassium surface diffusion

Fig. 8 demonstrates that the presence of low coverages of coadsorbed CO can significantly slow down the potassium surface mobility. Both the activation energy and the pre-exponential factor clearly increase as more CO is coadsorbed on the potassium grating. For potassium initial coverage of 1.0 ML, 0.065 ML effective average CO coverage leads to an increase of the activation energy

for surface diffusion of potassium on Re(001) from 5.0 kcal/mol on the clean metal up to 15.0 kcal/mol. The activation energy doubles for initial potassium coverage of 0.8 ML at the same effective average CO coverage. The fact that the activation energy and the pre-exponential increase simultaneously is a manifestation of the well-known compensation effect, which was observed in pure potassium diffusion on Re(001) as well [10]. Despite this compensation, however, the overall diffusion coefficient decreases with the increase in CO coverage, as shown in Fig. 8, where we depict decay curves of the first-order SHG diffraction peak as a function of time for the two CO exposures at the same initial potassium coverage of 0.9 ML and surface temperature.

The analysis of our results can be clarified and better understood by comparing it with the results reported by Westre et al. [16] and that of Xiao et al. [18], both studied the effect of coadsorbates on the surface diffusion of CO. In their work, Westre et al. [16] investigated in great detail the mutual effect of the coadsorbed CO and K on their surface diffusion on Ru(001). Using the hole-refilling LITD method they varied both the potassium and CO coverages over a wider range than that performed in the present study (we tried to avoid surface damage during the LITD process, therefore only high potassium coverages were studied – $\theta_K > 0.8$ ML, equivalent to $K/Re > 0.26$). While the coadsorption system studied by these investigators was assumed to be always homogeneous over the entire ~ 100 μm hole diameter [16], in our case the 5.1 μm grating period dictates a rather non-uniform coverage modulation of both the potassium diffusing atoms and the CO coadsorbates, as discussed above, and of course in our case the substrate is Re(001) and not Ru(001). In spite of these differences it is interesting to point out the similarities and differences found between these two systems.

The diffusion coefficient is typically expressed in an Arrhenius form, $D = D_0 \exp[-E_{\text{diff}}/RT]$ (cm^2/s), where E_{diff} is the activation energy for diffusion and D_0 is the pre-exponential factor. From Fig. 9 one can compute the diffusion coefficient at $\theta_K = 0.8$ ML ($K/Re = 0.26$), which is the closest to the high coverage value measured in

Ref. [16] of $K/Ru = 0.25$. At 240 K, the potassium diffusion coefficient changes from $5 \times 10^{-7} \text{ cm}^2/\text{s}$ without any CO coadsorption, to $(4 \pm 2) \times 10^{-9} \text{ cm}^2/\text{s}$ with coadsorbed CO at a coverage of 0.12 ML. The diffusion coefficient in the presence of CO is almost identical to that reported under very similar conditions in Ref. [16] ($K/Ru = 0.25$, $\theta_{\text{CO}} = 0.12$ ML) where $D = (7 \pm 3) \times 10^{-9} \text{ cm}^2/\text{s}$. The magnitude of the change, however, is different since the diffusion coefficient decreases by two orders of magnitude on Re(001) while only one order of magnitude change has been recorded on Ru(001). It is possible that while the diffusion of the clean potassium is strongly influenced by the substrate, in the presence of coadsorbed CO, it is the strong interaction between K and CO which dominates the diffusion kinetics, therefore the numbers are so similar on Re(001) and on Ru(001).

At potassium coverages close to full monolayer ($K/Re > 0.25$), a range which was not studied on Ru(001), the most dramatic changes occur in both the activation energy for diffusion and in the pre-exponential factor, as the CO coverage increases. The way we define the coverages of the two coadsorbates prevents a clear conclusion as to the stoichiometry of the surface compound between K and CO which is responsible for the large changes in E_{diff} and D_0 . This is in contrast to the study on Ru(001), where a compound with a 1:1 ratio between K and CO has been concluded as the most stable and thus the one which is actually formed on the surface and causes the diffusion of both K and CO to slow down [16]. It is clear, however, that for each CO molecule there are on average two to five potassium atoms along the coverage troughs. The surface compounds $K_x\text{-CO}$, which are the result of strong attractive interactions, the nature of which has been extensively studied in the past [16,21,34], become a physical block for potassium atoms to thermally migrate on the surface. It is, therefore, reasonable to expect that this site-blocking effect will increase as the K/CO ratio increases at high potassium coverages. Moreover, as the number of potassium atoms which are attractively interacting with the CO coadsorbate increase, the barrier for surface diffusion of these atoms should increase. This is

indeed consistent with the experimental observations as seen in Fig. 9. It is interesting to note that the rate of change of the activation energy for diffusion with increasing CO coverage for each of the potassium coverages (0.8, 0.9, 1.0 ML) qualitatively changes as the ratio of the number density of CO molecules to potassium atoms at the grating troughs (effective average coverage): 1:1, 1:2, 1:4, respectively. It suggests that the initial slope in Fig. 9b correlates with the number of nearest neighbor potassium atoms which directly interact with a single coadsorbed CO molecule. This means that this slope can be used as a qualitative measure of the number of nearest neighbors which participate in the K_x -CO surface complex. As stated above, we cannot assign a precise number for x , which is probably greater than one even at the lowest potassium coverage studied here – only the relative numbers seem to correlate with our data.

The effect of site-blocking for the surface diffusion of the potassium atoms is indicated also by the four orders of magnitude increase in the pre-exponential factor with increasing CO coverage observed at the highest K density of 1.0 ML (shown in Fig. 9a). As discussed above for the effect of the number of nearest potassium neighbors on the activation energy for diffusion, so is the effect on the pre-exponential factor: it increases faster with CO coverage as the number of K atoms in direct interaction with CO increases.

Support for the explanation given above for the effect of site-blocking on surface diffusion could also be found in the measurements by Xiao et al. [18], who studied the effect of surface impurities (sulfur, oxygen and potassium) on the surface diffusion of CO on Ni(110). The interpretation for the slower diffusion of CO in the presence of sulfur or oxygen was also in terms of site-blocking, which causes an effective increase of the activation energy for CO diffusion. In the case of coadsorbed potassium, the attraction between K and CO has been suggested as the effective mechanism for increased barrier for diffusion [18].

Westre et al. have demonstrated the role of immobile site-blockers, in their case the stable K -CO complex, by modeling their system using Monte Carlo simulations [16]. Although the immobility of the K -CO complex is an assumption

in their model, it agrees well with previous observations from e.g. metal adatom diffusion measurements using FIM, that dimers are far less mobile than monomers [1,2]. With this assumption built into their model, the experimental results could be reproduced quite nicely by the Monte Carlo simulations [16]. In our case, the effective K_x -CO complexes probably consist on average of $x > 1$, therefore the mobility can certainly be ignored in all the surface temperature range of our measurements (which is much lower than that examined in the study by Westre et al.). Complexes which consist of about two potassium atoms ($x=2$) per single CO were previously reported for high potassium coverages on Ni(100) based on microcalorimetry measurements [51]. We conclude that these surface complexes are acting as site-blockers for the free potassium atom diffusion, with increased effect as the number of K atoms (x) interacting with CO increases at higher potassium coverages.

Finally, the strength of the attraction between the K atoms and the CO is consistent with the observations in the TPD spectra shown in Fig. 2, demonstrating the significant shift of the peak CO desorption to higher temperatures. Also here, the maximum effect is observed as the ratio K/CO reaches a maximum at full monolayer potassium coverage.

A summary of all the diffusion rates which have been measured is shown in Fig. 10 as a function of CO coverage and surface temperature. This is obtained by fitting both the activation energy for diffusion and the natural logarithm of the pre-exponential factor using a non-linear fitting procedure. From these fitted expressions, the diffusion rate has been determined as a function of CO effective average coverage for the three initial potassium coverages (0.8, 0.9 and 1.0 ML). The gradual changes in these curves are again consistent with the dependence of the activation energy for diffusion on the effective CO coverage shown in Fig. 9. The effect of surface temperature is interesting since it shows that at elevated temperatures beyond the experimental capability, the diffusion rates go through a maximum as a function of the CO coverage and not a smooth slowing down at all coverages, as seen experimentally at the lower temperatures.

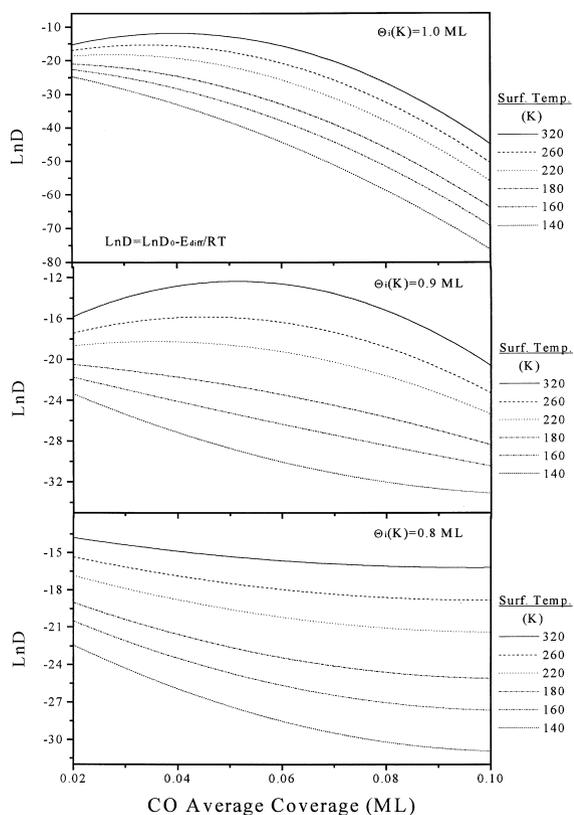


Fig. 10. Natural logarithm of the computed surface diffusion rates ($\ln D$) at three initial potassium coverages of 1.0, 0.9 and 0.8 ML as a function of CO effective average coverage at various surface temperatures, as indicated.

5. Conclusions

The mutual interaction and surface diffusion of potassium coadsorbed with CO in a template coverage grating has been studied on Re(001). Surface diffusion of potassium has been investigated in the presence of CO coadsorbate by using the coverage grating optical second harmonic diffraction method. Effective CO coverages at the grating troughs have been calculated based on the independently measured sticking of CO on the potassium covered surface. Significant change of the zero-order and first-order SHG diffraction peak intensities due to CO coadsorption emphasizes the complexity of this coadsorption system, as the attractive interactions between K and CO affect the SH response and the optical diffraction.

The activation energy for diffusion and the pre-exponential factor significantly increase with CO coverage. At potassium initial coverage of 1.0 ML, and an effective CO coverage of 0.065 ML, the activation energy for potassium diffusion on Re(001) has increased from 5.0 kcal/mol up to 15.0 kcal/mol, and the pre-exponential factor increases from 5.6×10^{-3} to 2.0×10^2 cm²/s. The activation energy doubles for potassium coverages of 0.9 ML and 0.8 ML with the same increase in the CO coverage. TPD measurements indicate that strong attractive interactions exist between CO and K on Re(001). Coadsorbed CO and K are likely to stabilize each other through the formation of K_x -CO surface complexes, consistent with studies of these coadsorbates on other transition metals. The exact number of potassium atoms interacting with a single CO cannot be determined from our measurements. Nevertheless, we conclude that these surface complexes act as site-blockers to impede the surface diffusion of potassium, resulting in the most significant increase of both the activation energy and the pre-exponential factor as the number of these complexes increases with CO coverage.

Acknowledgements

This work has been partially supported by the Israel Science Foundation, German-Israel Foundation. The Farkas Research Center for Light Induced Processes is supported by the Minerva Gesellschaft für die Forschung, GmbH, München.

References

- [1] G. Ehrlich, K.J. Stolt, *Ann. Rev. Phys. Chem.* 31 (1980) 603.
- [2] G. Gomer, *Rep. Progr. Phys.* 53 (1990) 917.
- [3] X.D. Zhu, Th. Raising, Y.R. Shen, *Phys. Rev. Lett.* 61 (1988) 2883.
- [4] G.A. Reider, U. Höfer, T.F. Heinz, *Phys. Rev. Lett.* 66 (1991) 1994.
- [5] X.D. Xiao, X.D. Zhu, W. Daum, Y.R. Shen, *Phys. Rev. Lett.* 66 (1991) 2354.
- [6] X.D. Zhu, A. Lee, A. Wong, U. Linke, *Phys. Rev. Lett.* 68 (1992) 1862.

- [7] X.D. Zhu, *Mod. Phys. Lett. B* 6 (1992) 1217.
- [8] M. Asscher, Z. Rosenzweig, Optical second harmonic generation as a real time probe of gas-surface interactions, Chapter 4, Part 1, in: H.-L. Dai, W. Ho (Eds.), *Laser Spectroscopy and Photochemistry on Metal Surfaces*, Advanced Series in Physical Chemistry, Vol. 5, World Scientific, Singapore, 1995.
- [9] Z. Rosenzweig, I. Farbman, M. Asscher, *J. Chem. Phys.* 98 (1993) 8277.
- [10] W. Zhao, R.W. Verhoef, M. Asscher, *J. Chem. Phys.* 107 (1997) 5554.
- [11] P.A. Williams, G.A. Reider, L. Li, U. Höfer, T. Suzuki, T.F. Heinz, *Phys. Rev. Lett.* 79 (1997) 3459.
- [12] C.H. Mak, B.G. Koehler, J.L. Brand, S.M. George, *J. Chem. Phys.* 87 (1987) 2340.
- [13] D.E. Brown, D.S. Sholl, R.T. Skodje, S.M. George, *Chem. Phys.* 201 (1995) 273.
- [14] J.L. Brand, A.A. Deckert, S.M. George, *Surf. Sci.* 194 (1988) 457.
- [15] C.H. Mak, A.A. Deckert, S.M. George, *J. Chem. Phys.* 89 (1988) 5242.
- [16] E.D. Westre, D.E. Brown, J. Kutzner, S.M. George, *J. Chem. Phys.* 104 (1996) 7313.
- [17] X.D. Xiao, Y.L. Xie, C. Jakobsen, H. Galloway, M. Salmeron, Y.R. Shen, *Phys. Rev. Lett.* 74 (1995) 3860.
- [18] X.D. Xiao, Y.L. Xie, C. Jakobsen, Y.S. Shen, *Phys. Rev. B* 56 (1997) 12529.
- [19] H.P. Bonzel, *Surf. Sci. Rep.* 8 (1988) 43.
- [20] H.P. Bonzel, G. Pirug, D.A. King, D.P. Woodruff (Eds.), *The Chemical Physics of Solid Surfaces: Coadsorption, Promoters and Poisons*, Vol. 6, Elsevier, Amsterdam, 1993.
- [21] H.P. Bonzel, A.M. Bradshaw, G. Ertl (Eds.), in: *Physics and Chemistry of Alkali Metal Adsorption*, Material Science Monographs, Vol. 57, Elsevier, Amsterdam, 1989.
- [22] R.W. Verhoef, W. Zhao, M. Asscher, *J. Chem. Phys.* 106 (1997) 9353.
- [23] E.D. Westre, D.E. Brown, J. Kutzner, S.M. George, *Surf. Sci.* 294 (1993) 185.
- [24] D. Heskett, *Surf. Sci.* 199 (1988) 67.
- [25] M.P. Kiskinova, *Poisoning and Promotion in Catalysis Based on Surface Science, Concepts and Experiments*, Studies in Surface Science and Catalysis, Vol. 70, Elsevier, Amsterdam, 1992.
- [26] L.J. Whitman, W. Ho, *J. Chem. Phys.* 83 (1985) 4808.
- [27] L.Q. Jiang, B.E. Koel, J.L. Falconer, *Surf. Sci.* 273 (1992) 273.
- [28] J.J. Weimer, E. Umbach, D. Menzel, *Surf. Sci.* 159 (1985) 83.
- [29] J.J. Weimer, E. Umbach, D. Menzel, *Surf. Sci.* 155 (1985) 132.
- [30] P. Kisliuk, *J. Phys. Chem. Solids* 3 (1957) 95.
- [31] R.W. Verhoef, M. Asscher, *Surf. Sci.* 391 (1997) 11.
- [32] J.E. Crowell, E.L. Garfunkel, G.A. Somorjai, *Surf. Sci.* 121 (1982) 303.
- [33] T.E. Madey, C. Benndorf, *Surf. Sci.* 164 (1985) 602.
- [34] R.H. DePaola, J. Hrbek, F.M. Hoffman, *J. Chem. Phys.* 82 (1985) 2484.
- [35] S.B. Lee, M. Weiss, G. Ertl, *Surf. Sci.* 108 (1981) 357.
- [36] E.L. Garfunkel, G.A. Somorjai, *Surf. Sci.* 115 (1982) 441.
- [37] J. Hrbek, M.-L. Shek, T.K. Sham, G.-Q. Xu, *J. Chem. Phys.* 91 (1989) 5786.
- [38] G. Brodén, G. Gafner, H.P. Bonzel, *Nederl. Tijdschr. Vacuumtechn.* 16 (1978) 160.
- [39] G. Brodén, G. Gafner, H.P. Bonzel, *Surf. Sci.* 84 (1979) 295.
- [40] L. Zhu, S. Bao, C.Y. Xu, Y.B. Xu, *Surf. Sci.* 260 (1992) 267.
- [41] J. Benzigrer, R.J. Madix, *Surf. Sci.* 94 (1980) 119.
- [42] U. Seip, I.C. Bassignana, J. Kupperts, G. Ertl, *Surf. Sci.* 160 (1985) 400.
- [43] R.W. Joyner, in: W.G. Frankenburg (Ed.), *Advances in Catalysis* Vol. 4 Academic Press, New York, 1952..
- [44] F. Solymosi, A. Berko, *Surf. Sci.* 201 (1988) 361.
- [45] Y.R. Shen, in: M.A. Van Hove, S.Y. Tong (Eds.), *The Structure of Surface* Springer Series in Surface Science Vol. 2, Springer, Berlin, 1985, p. 77. and references cited therein.
- [46] H.W.K. Tom, X.D. Zhu, Y.R. Shen, G.A. Somorjai, *Surf. Sci.* 167 (1986) 167.
- [47] T.F. Heinz, H.W.K. Tom, Y.R. Shen, *Phys. Rev. A* 28 (1983) 1883.
- [48] Z. Rosenzweig, M. Asscher, *Surf. Sci.* 240 (1990) L583.
- [49] R.W. Verhoef, M. Asscher, *Surf. Sci.* 376 (1997) 389.
- [50] R.W. Verhoef, M. Asscher, *Surf. Sci.* 376 (1997) 395.
- [51] N. Al-Sarraf, J.T. Stuckless, D.A. King, *Nature* 360 (1991) 243.