

INTERACTION OF CARBON MONOXIDE WITH CLEAN AND OXYGEN COVERED Cu(111)-Ni SURFACE ALLOYS

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Cu(111)-Ni surface alloys were prepared by dissociation of nickel carbonyl on clean Cu(111). The adsorption of CO is studied with AES and ellipsometry. At pressures higher than 10^{-2} Pa CO, migration of Ni to surface layers occurs, which makes it impossible to measure adsorption isotherms. The removal of preadsorbed oxygen on Cu(111)-Ni with CO is also studied with AES and ellipsometry. A reaction scheme is proposed to describe the two different types of reaction curves. At temperatures below 200 °C, the overall apparent activation energy is 40 kJ/mol, at higher crystal temperatures this value drops to 10 kJ/mol. CO is found to react with oxygen on the surface, which is replenished by incorporated (subsurface) oxygen.

1. Introduction

Copper and nickel are frequently used as catalysts, nickel especially for methane steam reforming and the synthesis of methane from hydrogen and carbon monoxide, and copper based catalysts for the conversion of carbon monoxide with steam to hydrogen and carbon dioxide. Single crystals have been used to study plane specific interactions of hydrogen, oxygen and carbon monoxide with copper and nickel surfaces.

In this paper investigations on the adsorption of carbon monoxide on Cu(111)-Ni surfaces are described. It is well known that carbon monoxide does not adsorb on pure copper surfaces above room temperature [1] or on Cu(100)-Ni [2]. Adsorption is measured on Cu(110)-Ni [3-5]. Pure copper and nickel single crystals exhibit a pronounced difference in the reactivity of preadsorbed oxygen with carbon monoxide: carbon monoxide reacts readily

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with oxygen adsorbed at copper surfaces [6] almost independent of the surface orientation, whereas the reduction of preadsorbed oxygen on nickel single crystal surfaces with carbon monoxide appears to be plane specific. Detailed reaction kinetics have been proposed for CO–O/Ni(111) [7], whereas O/Ni(100) cannot be reduced with carbon monoxide [8]. Kinetic data for the reaction of carbon monoxide with O/Ni(110) are unknown, although the reduction by CO is reported [9]. In the present paper we consider the reduction of Cu(111)–Ni alloy surfaces by CO.

2. Experimental

The experiments were carried out in a standard UHV system, equipped with facilities for AES, LEED and ellipsometry. The Auger spectra were recorded with a four-grid retarding field analyser. From the low energy part of the spectrum (95–110 eV), the amount of nickel in about the first two layers can be calculated with the equation given in ref. [10]:

$$x_L = 1.4h_{101}/(1.4h_{101} + h_{106}),$$

where h_{101} is the peak to peak height of the Ni 101 eV Auger transition in the second derivative spectrum and h_{106} is the height of the Cu 106 eV peak. From the high energy part of the spectrum (720–940 eV) the amount of nickel in the first 6–8 atomic layers can be calculated with:

$$x_H = 2.5h_{720}/(2.5h_{720} + h_{920}),$$

where h_{720} is the peak height of the Ni 720 eV signal and h_{920} is the height of the Cu 920 eV signal.

Cu(111)–Ni alloys were prepared by dissociation of nickel carbonyl on a clean Cu(111) surface at a crystal temperature of 220 °C [2,11]. The dissociation of Ni(CO)₄ on the surface was followed continuously with ellipsometry, and stopped at $\delta\psi = 0.4^\circ$. The surfaces thus prepared are denoted as Cu(111)–Ni(0.4°).

The interaction of carbon monoxide with oxygen covered Cu(111)–Ni(0.4°) was monitored continuously with an automatic nulling ellipsometer [10]. The CO was continuously renewed during the measurement by pumping with the turbo-molecular pump. The adsorption of CO on a clean Cu(111)–Ni(0.4°) surface was studied with off-null irradiance measurements [12]. To obtain pressures higher than 1 Pa, the UHV system was not pumped during the experiment and CO was exposed in a static atmosphere. Before deposition of nickel, the original copper surface was cleaned by sputtering with Ar⁺ ions for 80 min ($P = 8 \times 10^{-3}$ Pa, 800 eV, 6 $\mu\text{A}/\text{cm}^2$, angle of incidence 45°) and annealing at 450 °C for 70 min.

3. Interaction of CO with clean Cu(111)-Ni(0.4°)

3.1. Results

The change in the ellipsometric parameter Δ ($\delta\Delta = \bar{\Delta} - \Delta$, $\bar{\Delta}$ is the value for the clean Cu(111)-Ni(0.4°) surface) was used to monitor the CO adsorption [5] in the temperature range 22–150 °C. The pressure was raised stepwise from about 5×10^{-6} Pa up to 10^2 Pa. After every increase in the pressure, the ellipsometric signal stabilised after a few minutes. In fig. 1, the value of $\delta\Delta$ after saturation at each pressure, $\delta\Delta_s$, is plotted versus the pressure at two different crystal temperatures. It can be seen that at a crystal temperature of 150 °C the maximum value of $\delta\Delta_s$, $\delta\Delta_m$, is larger than the maximum value at a crystal temperature of 30 °C, and that at 150 °C CO adsorbs already at lower pressures at the surface. After evacuation, Auger spectra showed an increased amount of Ni in the surface layers. Table 1 gives some data on the CO induced Ni enrichment. At high CO pressures ($P > 10^{-3}$ Pa) Ni migrates to the surface,

Table 1
CO induced Ni segregation to the surface of Cu(111)-Ni(0.4°) alloys

Crystal temperature (°C)	CO pressure (Pa)	Before CO exposure		After CO exposure	
		x_L	x_H	x_L	x_H
30	40	0.06	0.21	0.25	0.31
50	30	0.02	0.27	0.22	0.34
150	40	0.06	0.20	0.41	0.39

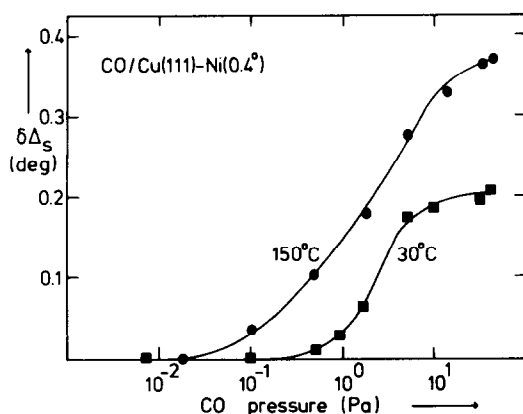


Fig. 1. Saturation value of $\delta\Delta$, $\delta\Delta_s$, as function of the CO pressure for CO adsorption on Cu(111)-Ni(0.4°) at two different crystal temperatures.

and the composition of the surface layers changes considerably. Thus it is impossible to measure a reliable adsorption isotherm, because the observed change in $\delta\Delta$ is composed of two different contributions: both CO adsorption and Ni segregation contribute to the ellipsometric signal.

In a new series of experiments, the clean Cu(111)-Ni(0.4°) surface was exposed to CO at a pressure of about 10^2 Pa. After a fast increase in $\delta\Delta$, due to CO adsorption, a slow increase followed, ascribed to Ni enrichment in the surface layers. After stabilisation of the signal, the pressure was decreased stepwise in the hope that the surface composition would not change. Surprisingly, sometimes an increase in $\delta\Delta$ was found after decreasing the pressure. Fig. 2 shows the saturation values of $\delta\Delta$, after a pressure change, versus the pressure for an adsorption and a desorption experiment at the same crystal temperature. A comparison of the two isotherms shows a large hysteresis. In case of desorption experiments, it was also not possible to measure reproducibly CO isotherms, because of apparent changes in the surface composition. Differences up to 0.25° in $\delta\Delta$ were found (compared to a maximum value of $\delta\Delta_m \sim 0.4^\circ$) at the same pressure and crystal temperature in two separate desorption experiments. Due to this irreproducibility, no isosteric heat of adsorption can be calculated.

3.2. Discussion

The first point we like to discuss is the irreproducibility of the observed adsorption isotherms. It is commonly accepted that at temperatures above 200°C and high CO pressures, segregation of Ni to the surface of Cu-Ni alloys occurs [13]. For Cu(110)-Ni(1°) single crystal surface alloys, prepared

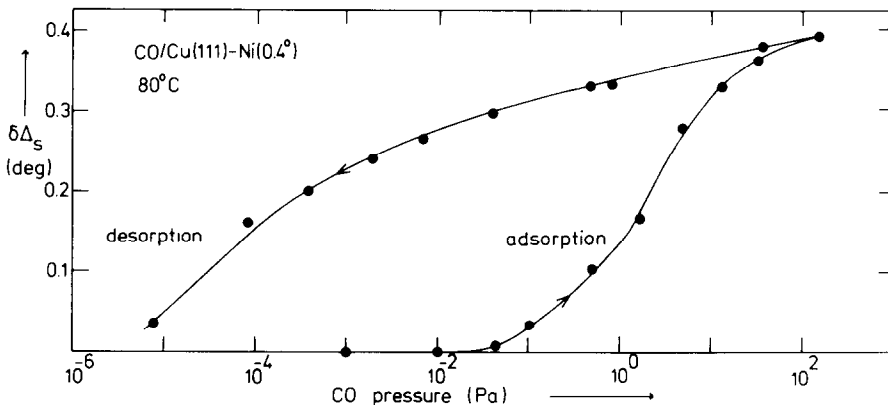


Fig. 2. Saturation values of $\delta\Delta$, $\delta\Delta_s$, as function of the CO pressure during adsorption and desorption of CO on Cu(111)-Ni(0.4°).

by $\text{Ni}(\text{CO})_4$ dissociation, it was found that segregation takes place at room temperature for CO pressures above 0.2 Pa [5].

Fig. 3 shows AES spectra recorded before and after CO exposure. In the low energy part of the spectrum, the Ni 101 eV peak is hardly visible before CO adsorption. After the desorption experiment, a large Ni 101 eV peak is present, and also the high energy peaks of Ni (720, 780 and 850 eV; some of these peaks overlap with copper peaks) are increased. The surface is thus enriched in Ni. Since CO adsorbs more easily at pure Ni surfaces than at pure Cu at the same pressure and crystal temperature, this segregation causes an increase in the amount of CO adsorbed. At higher crystal temperatures, Ni is more mobile, so segregation occurs at relatively lower pressures. At lower crystal temperatures, there is less segregation of Ni but more adsorption due to the low temperature. As a result of this, a larger maximum change in $\delta\Delta$ is recorded at 150°C than at 22°C.

For an adsorption experiment, the experiment starts with a "normal" Cu-Ni surface composition, and ends with a Ni enriched surface. When the pressure is stepwise decreased, the initial pressure of 10^2 Pa causes a large enrichment of Ni at the surface. The experiment starts with an appreciably enriched surface, and should end with a "normal" surface composition, if thermodynamic equilibrium in both adsorption and segregation were established. If this is not the case, the surface will contain more Ni and thus adsorb more CO than in the case where adsorption is performed by increasing the CO pressure.

The next point of discussion is the occasional observation of an increase in $\delta\Delta$ after decreasing the pressure. The surface alloy Cu(111)-Ni(0.4°) is made

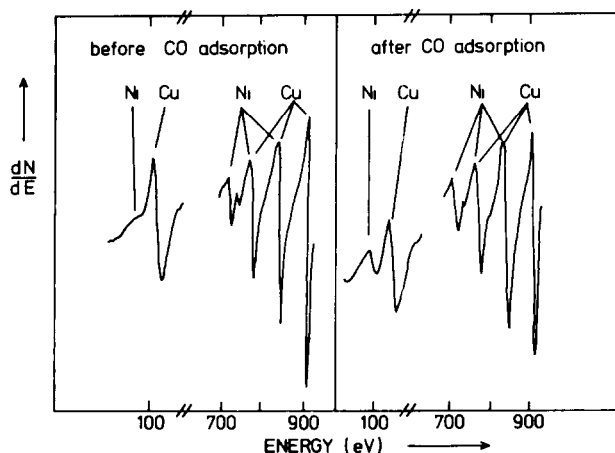


Fig. 3. Auger spectra of a Cu(111)-Ni(0.4°) surface before and after a CO exposure, at a crystal temperature of 30°C and pressure of 40 Pa.

by dissociation of nickel carbonyl, Ni deposition being stopped at $\delta\psi = 0.4^\circ$. It was observed [11] that immediately after exposing the Cu(111) surface to a mixture of CO and $\text{Ni}(\text{CO})_4$, $\delta\psi$ increases linearly with the total exposure. At the same time $\delta\Delta$ first decreases till a minimum is reached, and then also increases. This minimum in $\delta\Delta$ occurs around $\delta\psi = 0.4^\circ$. This implies that a minor change in the amount of Ni, or a minor redistribution of the Ni, can give either an increase or a decrease in $\delta\Delta$, depending on the initial position near the minimum. When the minimum was not reached during Ni deposition, Ni enrichment causes a negative change in $\delta\Delta$; when the minimum had been reached or passed, it causes a positive change in $\delta\Delta$.

4. Reaction of CO with oxygen sorbed on Cu(111)-Ni(0.4°)

4.1. Results

Clean Cu(111)-Ni(0.4°) surfaces were exposed to oxygen at crystal temperatures between 160 and 340°C . The details of the adsorption of oxygen on Cu(111)-Ni(0.4°) will be described in the subsequent paper [14]. Fig. 4 shows the change of $\delta\Delta$ when a surface, which had previously adsorbed oxygen up to $\delta\Delta = 1^\circ$, was exposed to CO, at pressures ranging from 10^{-3} Pa up to 8×10^{-2} Pa, at the same temperature as where the oxygen adsorption had taken place. During CO exposure, the ionisation gauge was switched off in order to prevent any influence of the operating gauge on the reaction rate [15]. Fig. 4 shows that two different types of $\delta\Delta$ versus time curves can be observed. Type 1 is characterised by an immediate maximum reaction rate, $d(\delta\Delta)/dt$, after admitting CO. The reaction rate decreases until no further change in $\delta\Delta$ is observed.

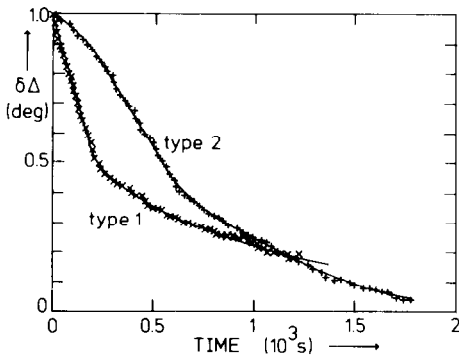
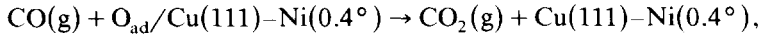


Fig. 4. $\delta\Delta$ versus time during CO exposure to a Cu(111)-Ni(0.4°) surface with preadsorbed oxygen ($\delta\Delta = 1^\circ$) at two different crystal temperatures. The solid lines represent the numerical integration of eqs. (4)-(6).

This type of curve is only observed at crystal temperatures above 300 °C. Type 2 curves, observed between 160 and 260 °C, show an initial increase in reaction rate up to a maximum value, after which the rate of change of Δ steadily decreases.

In order to calculate the apparent activation energy of the reaction



an Arrhenius plot was made by plotting the logarithm of the maximum slope versus the reciprocal temperature. This Arrhenius plot shows that the data obtained are irreproducible.

In order to get more reproducible measurements, the CO exposure was started exactly 10 min – a rather arbitrary time – after the oxygen exposure. Exactly 30 min after finishing the first reduction experiment, the crystal was exposed to oxygen for further experiments. In the periods of 10 and 30 min delay, Auger spectra were recorded. The results of this new set of experiments are used to construct a new Arrhenius plot. Again the maximum slope of the $\delta\Delta$ versus time curve is assumed to be proportional to the maximum reaction rate (see fig. 5). At each pressure, the curve can roughly be divided in two regions. At crystal temperatures below 220 °C, there is an appreciable temperature dependence; the slope of the Arrhenius plot yields an activation energy of about 40 kJ/mol. For temperatures above 260 °C, the maximum reaction rate

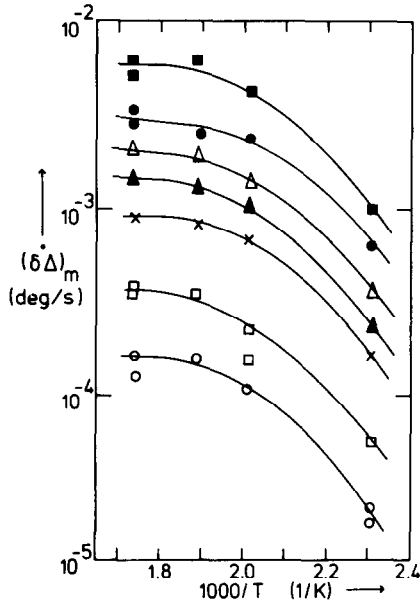


Fig. 5. Arrhenius plot of the maximum slope for the removal of oxygen by CO.

becomes nearly independent of the crystal temperature; the slope of the curves in fig. 5 yield an activation energy of about 10 kJ/mol. These values are of course somewhat arbitrary, since the slope of the curves changes with temperature. Nevertheless, they are representative of the high ($> 260^\circ\text{C}$) and low ($< 220^\circ\text{C}$) temperature values.

In fig. 6 the logarithm of the maximum reaction rate is given versus the logarithm of the CO pressure. The order of the reaction rate in the CO pressure can be calculated from the slope of these curves. The order turns out to be 0.95 ± 0.2 in the temperature range of 160 to 340°C , and is independent of the crystal temperature.

After the first reduction of the surface and removal of the CO gas phase, the ellipsometric signal stabilised at a positive value of $\delta\Delta$. At this point the oxygen concentration was below 5% of a monolayer, as observed with Auger spectra. Thus all the surface oxygen must have been removed by CO, but there remains some oxygen in deeper layers, outside the escape depth of Auger electrons, as evidenced by the ellipsometric signal. The second oxygen exposure was stopped after Δ had decreased by 1° , so that after the second oxygen uptake more oxygen was present than after the first oxygen exposure. After two cycles of oxidation and reduction, the surface was cleaned by sputtering and annealing and a fresh alloy surface was prepared.

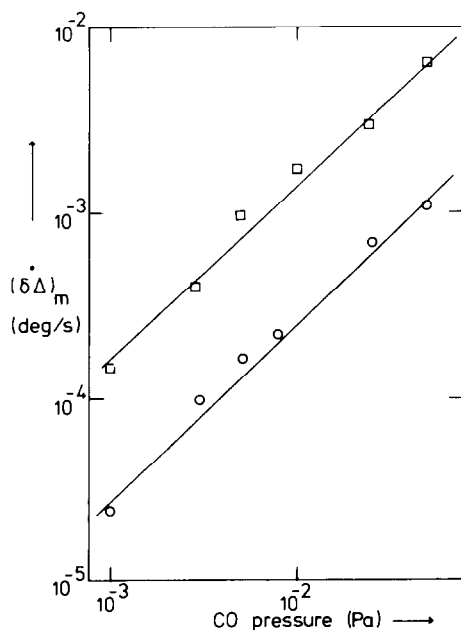


Fig. 6. Pressure dependence of the maximum reaction rate during the reduction of O/Cu(111)-Ni(0.4°) with CO.

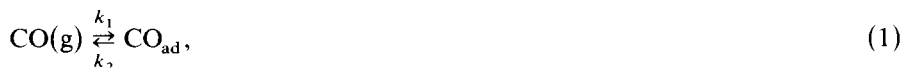
In order to investigate the mechanism of the reduction reaction quantitatively, the plots of $\delta\Delta$ versus time during removal of oxygen from (sub)surface layers, have to be corrected for the adsorption of CO. In a separate experiment, the UHV system was evacuated at intermediate oxygen coverages. After stabilisation of the ellipsometric parameter $\delta\Delta$, the surface was again exposed to CO. Fig. 7 shows the decrease in $\delta\Delta$ due to CO desorption after every evacuation. At $\delta\Delta = 0.75^\circ$ no CO desorption is observed after evacuation, the amount of CO desorbed increases with decreasing $\delta\Delta$. From these data one may construct the "true" $\delta\Delta$ due to sorbed oxygen only.

4.2. Discussion

The removal of preadsorbed oxygen on Cu(111)-Ni(0.4°) with CO has two major characteristics;

- (1) There are two different types of reaction curves.
- (2) The Arrhenius plot shows no linear relation between the logarithm of the maximum slope and the reciprocal temperature.

An overall reaction scheme according to a Langmuir-Hinshelwood mechanism is:



As described in the subsequent paper [14], the total amount of oxygen sorbed can be divided into an amount adsorbed θ_{ad} and an incorporated amount θ_{inc} ,

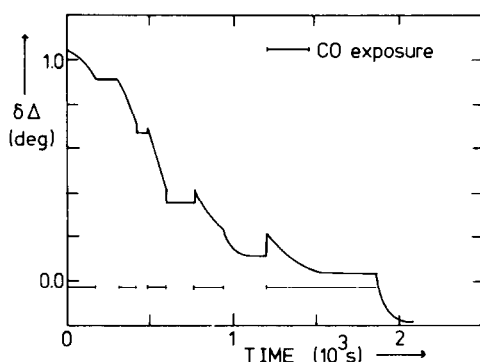


Fig. 7. Effect of evacuation during the reduction by CO at 220 °C. CO exposures are at $P_{\text{CO}} = 3.6 \times 10^{-2}$ Pa during the intervals denoted by —|—| .

respectively, given by the number of oxygen atoms at the surface per surface atom, and the number of oxygen atoms in deeper layers per surface atom. Whereas at Cu(111) only half a monolayer of oxygen can be chemisorbed at the surface [15,16], corresponding to $\delta\Delta = 0.7^\circ$, there is also an amount of oxygen, at least corresponding to $\delta\Delta = 0.3^\circ$, which has migrated to deeper layers of the Cu(111)–Ni(0.4°) alloy surface. The ellipsometric signal $\delta\Delta$ is a function of both θ_{ad} and θ_{inc} , because the penetration depth of the laser light (wavelength 632.8 nm) is very large. A numerical integration is used to calculate the observed total oxygen concentration, $\theta_{ad} + \theta_{inc}$, from:

$$d\theta_{ad}/dt = -k_5\theta_{ad} + k_6\theta_{inc} - k_3\theta_{ad}\theta_{CO}, \quad (4)$$

$$d\theta_{inc}/dt = k_5\theta_{ad} - k_6\theta_{inc}. \quad (5)$$

This model describes type 1 curves, in which the rate of change of $\delta\Delta$ has its maximum value at the beginning of the reaction, quantitatively, but is incompatible with type 2 curves, which show an initial increase in reaction rate. If we assume in addition to eqs. (4) and (5) that CO molecules, which are able to react with adsorbed oxygen, adsorb only on oxygen free parts of the surface, we should take:

$$k_1 = k_1'(0.5 - \theta_{ad}), \quad (6)$$

where the value of 0.5 corresponds to the maximum coverage of chemisorbed oxygen. A numerical integration of eqs. (4)–(6) reproduces also type 2 curves.

In order to calculate the theoretical reduction curves, the initial values of θ_{ad} and θ_{inc} are required. Using an initial value of θ_{ad} of almost 0.5, the maximum amount of half a monolayer at the surface, type 2 curves are obtained. This means that in the experiments at crystal temperatures below 260 °C, after 10 min waiting between oxygen adsorption and the reaction of sorbed oxygen with CO, still (nearly) half a monolayer of oxygen is present at the surface. When $\theta_{ad} < 0.5$ is used as an initial condition for the reduction, type 1 curves result. This implies that in the experiment at, or above, 300 °C, in 10 min a considerable amount of oxygen has migrated from the surface to deeper layers. This is in good agreement with the conclusions derived from oxygen adsorption measurements [14], where it was found that the oxygen Auger signal significantly decreases at crystal temperatures above 250 °C, after oxygen adsorption at room temperature and subsequently heating the crystal.

The overall reaction rate during reduction is the decrease of the total amount of oxygen, $\theta_{ad} + \theta_{inc}$, per unit time. From a detailed analysis of the computed reaction curves it follows that the maximum reaction rate is obtained during the removal of adsorbed oxygen, θ_{ad} , only, θ_{inc} being almost constant at this point. Assuming a steady state for the adsorption of CO, the maximum reaction rate r is given by:

$$r = -\frac{k_1 k_3}{k_2 + k_3 \theta_{ad}} (0.5 - \theta_{ad}) \theta_{ad} P_{CO}. \quad (7)$$

For $k_2 \ll k_3\theta_{\text{ad}}$ the maximum reaction rate is

$$r = -k_1(0.5 - \theta_{\text{ad}})P_{\text{CO}}, \quad (8)$$

whereas in the reverse situation we have

$$r = \frac{k_1 k_3}{k_2} (0.5 - \theta_{\text{ad}}) \theta_{\text{ad}} P_{\text{CO}}. \quad (9)$$

The former case (eq. (8)) implies that at low temperatures CO desorption is slow compared to CO oxidation, whereas at high temperatures desorption is rapid compared to the oxidation reaction.

From the observed Arrhenius plot we may deduce that the activation energy of k_1 (E_1) is 40 kJ/mol. The activation energy $E_3 - E_2$ is then ≤ -30 kJ/mol from the high temperature slope of fig. 5. Since the reaction takes place between adsorbed CO and oxygen, adsorbed on the surface which is mainly copper, it is reasonable to assume that E_3 will be similar to the value found for the same reaction on pure Cu(111), i.e. 75 kJ/mol [14]. The difference $E_2 - E_1$, which is just the heat of desorption of CO on Cu(111)-Ni(0.4°) is then equal to 65 kJ/mol, which compares nicely with the value of 63–75 kJ/mol found for Cu(110)-Ni [4,5]. An independent determination of this quantity by direct measurements was impossible, as shown in section 3.

Qualitatively our model for the CO oxidation with oxygen sorbed on Cu(111)-Ni(0.4°) is then as follows. After an oxygen exposure, the surface and near surface layers contain adsorbed and incorporated oxygen atoms, their ratio depends on the crystal temperature and the time during which the system is allowed to equilibrate. The surface oxygen is removed by CO, adsorbed initially on non-oxygen containing sites and replenished by the source of incorporated oxygen. However, not all oxygen sorbed can be removed by carbon monoxide. Compared with the removal of sorbed oxygen with CO on pure Cu(111), the reaction with chemisorbed oxygen also proceeds via a Langmuir-Hinshelwood mechanism. However, the rate at which empty sites at the surface are replenished by oxygen from deeper layers, is much higher on the pure copper surface. This has to be due to a stronger bond between oxygen and nickel atoms in deeper layers, compared with the bond strength of the oxygen copper bond. This was also concluded for oxygen sorbed on Cu(100)-Ni with respect to pure Cu(100) [2].

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