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Enhanced reactivity of pseudomorphic Co on Cu(111)

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The reactivity of Co deposited on Cu(111) is determined using the dissociation of CH_4 as a test reaction. The CH_4 molecules are produced in a supersonic molecular beam expansion and dissociate on Co but not on Cu under the experimental conditions used here. It is found that the dissociation probability of CH_4 on a few layers of pseudomorphic Co adsorbed on noble Cu(111) is larger than that of pure Co. The apparent CO binding energy is, however, not shifted as measured using thermal desorption. A model of this surprising behavior is presented using information on the structure and theoretical calculations on the shift of the d-band of Co adsorbed on Cu(111).

Keywords: Co, Cu, single crystal, CH_4, supersonic molecular beam, temperature-programmed desorption, modified reactivity, bimetallic systems

1. Introduction

The fundamental investigation of modified reactivity of bimetallic systems is a promising area where new properties are discovered and models and possible applications are proposed both from experimental and theoretical studies [1,2]. In catalysis, such a knowledge of trends in both chemical and thermal properties of bimetallic systems will open for new detailed insight into the surface properties determining chemical reactivity. Combined with the existing experience, obtained mainly by the method of trial and error, new and more efficient catalysts can be developed.

In this paper, we investigate the question of modified reactivity in bimetallic systems by probing a single dissociative reaction step on a well defined surface. Previously, in the investigation of properties of bimetallic surfaces, a correlation between the shift in the CO desorption temperature and the core level shift of the adsorbate has been shown by Rodriguez and Goodman [1]. Additional density functional calculations propose that the shift in the entire d-band is also proportional to the shift in the CO desorption temperature [3]. Recently, d-band shifts have been tabulated for a number of combinations of late transition metals [4]. The correlation in [1] is tested for the bonding of CO. It is, however, not known nor obvious if the shift of the d-band can be used as a measure of change in reactivity in general. In the following we show that a few layers of Co adsorbed on the more noble Cu(111) is more reactive than that of pure Co. To our knowledge, this work is the first molecular beam investigation of a bimetallic surface showing an enhanced reactivity that is not just a combination of the reactivity of each of the two components. We also show that the enhanced reactivity is not necessarily probed by measuring the desorption temperature of CO [1].

It is known that some bimetallic surfaces show superior properties towards certain reactions but most of these investigations monitor the final product of a reaction without detailed knowledge of the intermediate reaction steps and their dependence on the new surface structure [5–9]. In such experiments it is difficult to distinguish the effect of a changed bonding of one of the intermediates from, e.g., a modified dissociation or recombination barrier. The rate-limiting step could also change for a bimetallic system compared to those of the pure components. An increased reactivity or selectivity can be caused both by an electronic effect and an ensemble effect [6,8]. In some cases a decreased reactivity is even acceptable if accompanied by an increased selectivity [10–12].

In order to conclude on the origin of the modified reactivity, we set out to use the single dissociative reaction of CH_4 as a test reaction of the Co reactivity.

Co is a well known Fischer–Tropsch catalyst, and much work has been performed in order to understand and improve this system [13]. Co overlayers on Cu have also drawn much attention due to its magnetic properties. The structure of the adsorbed Co layers has been investigated in great detail [14–18]. Using low-energy ion scattering the bimetallic surface was reported not to be in thermal equilibrium at room temperature (RT) with Cu segregating to cover the Co islands with a timescale of hours [16]. From the analysis of extended X-ray absorption fine structure data, it is concluded that the Co–Co nearest neighbor distance in Co layers up to several atomic layers is 2.54 Å which is very close to that of bulk Cu (2.55 Å) [17]. Recent STM data show that the large Co islands are formed with no defects and that they are three-layered with the lowest layer incorporated into the Cu substrate. At RT, all the Co islands are surrounded by double-layered Cu brims, thus eliminating the existence of Co steps [18]. Calculations in [18] on the thermodynamics of Co/Cu support the experimental observations of RT instability [16,18].

2. Experimental

The experiments were performed under ultra-high vacuum with a base pressure below 1×10^{-10} Torr. Both the initial and the routine cleaning of the Cu(111) surface was done by Ar^+-sputtering at RT and at 773 K. The supersonic molecular beam source is aligned with a time of flight system for the analysis of the translational energy of the molecular beam molecules. Further details on this experimental setup have been described previously [19,20]. The evaporation of Co took place at RT, and the quantification of the Co amount is given as a non-linear ratio of the I_{Co} (656 eV) and the I_{Cu} (920 eV) Auger intensities, $I_{\mathrm{Co}}/I_{\mathrm{total}}$, where $I_{\mathrm{total}} = I_{\mathrm{Co}} + (I^{\infty}_{\mathrm{Co}}/I^{\infty}_{\mathrm{Cu}})I_{\mathrm{Cu}}$ is a factor nearly-independent of the amount of Co adsorbed. I^{∞} refers to the intensity of the clean material. For pure Co, this ratio is equal to 1.0.

3. Results

3.1. CH4 dissociation

The reactivity of the Co/Cu surface towards the dissociation of CH_4 is found using a supersonic molecular beam of 3% CH_4 seeded in helium with a nozzle temperature of 1050 K giving a translational energy of 74 kJ/mol. The CH_4 molecules dissociate on Co but not on Cu under these experimental conditions. A beam exposure of 600 s at RT is chosen as standard in order to remain in the low-coverage regime of the adsorbates and to maintain an unchanged structure of the bimetallic surface.

By using a short beam exposure, the resulting amount of carbon adsorbed is directly proportional to the initial CH_4 sticking coefficient and, thereby, also the reactivity of the surface. After the beam exposure, the crystal is heated to 453 K in order to desorb hydrogen adsorbed from the dissociated CH_4 molecules and CO adsorbed from the background. This annealing procedure will change the surface composition but not the amount of carbon already adsorbed [21]. The small amount of carbon was quantified by measuring the recombination area of carbon and oxygen at 500 K [22]. This is below the temperature where carbon-bulk diffusion will occur [21]. The oxygen was dosed (7 L) at RT and followed by the temperature-programmed desorption (TPD) where mass 28 was the only mass to show a signal above the background level. Initially, it was checked that the carbon signal measured with Auger electron spectroscopy was directly proportional to the recombination area. After the TPD experiment, no carbon was ever detected and excess oxygen was always measured using Auger electron spectroscopy. This indicates that all the carbon was removed and that there was no subsurface carbon present. The maximum amount of recombined CO for $I_{\mathrm{Co}}/I_{\mathrm{total}} \approx 0.6$ corresponds to 4% of the saturation CO desorption signal on clean Cu(111). This method is indeed sensitive down to 0.1% of a saturation CO signal. To check the initial cleanness of the deposited Co films, several blind experiments without the beam exposure but following the exact same procedure were also performed. This showed a linearly increasing background from 0.4 to 1.6% of the saturation CO signal. This background is subtracted from the measured area and the resulting carbon deposited is shown in figure 1 as a function of the Co amount. The behavior of this reactivity will be discussed later.

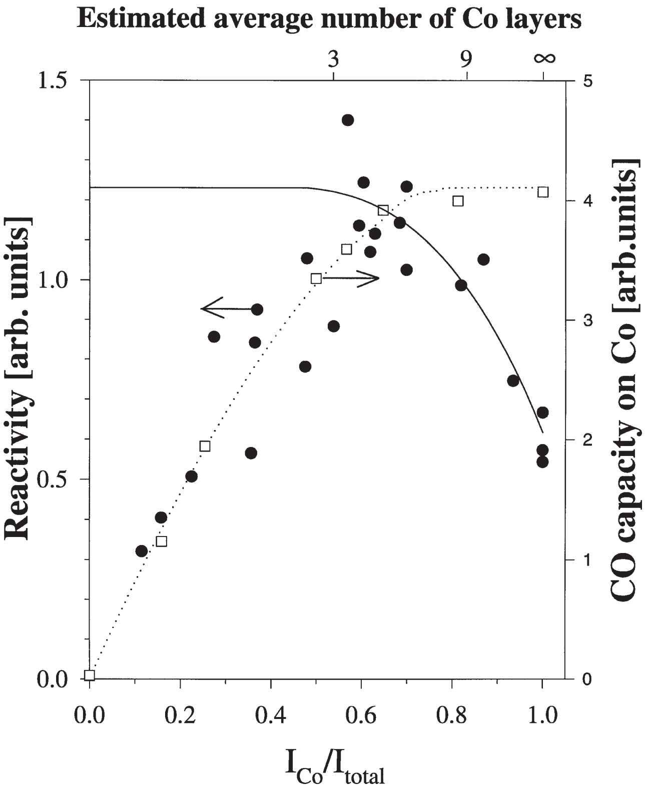

Figure 1. The reactivity measured as the recombination area of carbon from dissociatied CH_4 (circles), as a function of the Co amount. The oxygen was dosed (7 L) after the short beam exposure. On a different scale is the CO capacity on Co shown as squares with the dashed line to guide the eye. The solid line indicates the reactivity per Co reaction site as a function of the amount of Co. Uppermost, the corresponding average number of Co layers as a result of a simple layer attenuation calculation is indicated.

3.2. Temperature-programmed desorption of CO

Information on the surface composition corresponding to the intensity ratio, $I_{\mathrm{Co}}/I_{\mathrm{total}}$, can be obtained from the TPD spectra of CO for different amounts of Co. The desorption measurement followed a saturation dose of CO of 18 L at 103 K and the resulting spectra are shown in figure 2. The heating ramp was 2 K/s. The TPD position of the crystal surface, which was less than 0.5 mm from the orifice of the quadrupole mass spectrometer, was very well reproduced, so that absolute intensities can be compared from different spectra. Desorption experiments using small CO doses at RT were also performed on the Co/Cu(111) surface. The TPD spectra showed no differences in desorption temperature.

4. Discussion

The recombination area which as mentioned above is a measure of the total surface reactivity increases with the amount of Co up to $I_{\mathrm{Co}}/I_{\mathrm{total}} \approx 0.6$, as shown in figure 1. When increasing the amount of Co beyond this value the reactivity decreases. In order to determine whether this behavior is related to the effective Co area, information on the surface composition is extracted from the CO desorption spectra in figure 2. The desorption below 200 K is from pure Cu sites [23,24]. Cu defects have been shown to give CO desorption around 220 K [25] which can be seen as a small shoulder on the pure Cu spectrum. CO desorbs from Co(0001) and polycrystalline Co around 400 K. These experiments [26] were performed at RT, and no information on desorption below RT was reported. In figure 2, the desorption above 300 K is therefore from Co sites, and we suggest that the desorption down to 250 K originates from a compressed structure of CO also on Co. From the area of the temperature regime above 300 K we now have a measure of the number of available Co sites. This area, shown as squares in figure 1, becomes constant for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ values larger than 0.6. The same behavior is seen for the features in the temperature regime between 250 and 300 K. Therefore, we can conclude that for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ less than 0.6, the Cu surface is partially covered with Co, and above 0.6, the Co grows on top of Co as seen by STM [18]. The average number of Co layers corresponding to a few $I_{\mathrm{Co}}/I_{\mathrm{total}}$ values have been calculated and shown in figure 1. The calculation is based on an exponential attenuation of the Auger electron intensities for a simplified layer-by-layer structure of Co on Cu. It should be stressed that this is just to give a feeling for the amount of Co deposited.

As already discussed, this bimetallic surface is not in thermal equilibrium. By keeping the surface at RT on the timescale of hours, the Cu will segregate to the surface covering the Co [16,18]. This effect is more readily seen when heating the surface to higher temperatures. All the Co sites disappear when flashing a surface with, e.g., $I_{\mathrm{Co}}/I_{\mathrm{total}} \approx 0.6$ to 673 K. This is shown as the dashed upper curve in figure 2. Only Cu sites and many Cu defects are seen after the annealing.

The number of CO molecules bonded to the surface is not expected to depend on the strength of the bond itself. The amount of CO bonded is therefore a chemically neutral probe, indicating that the number of Co sites on the surface remains constant for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ larger than 0.6, as seen from the dashed curve in figure 1. From being a measure of the reactivity of the entire surface, the recombination area for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ larger than 0.6 becomes a measure of the reactivity of the individual Co dissociation site. This is seen even more clearly if we calculate the reactivity per reaction site, i.e., per Co atom, by dividing the recombination area with the number of Co atoms given by the CO saturation area. A guideline to these values is shown as the solid line in figure 1. The reactivity per Co site remains high and constant in the low and pseudomorphic coverage regime where we have detailed STM information. But for many Co layers, i.e., for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ larger than 0.6, the reactivity per site drops off to a lower value corresponding to that of bulk Co.

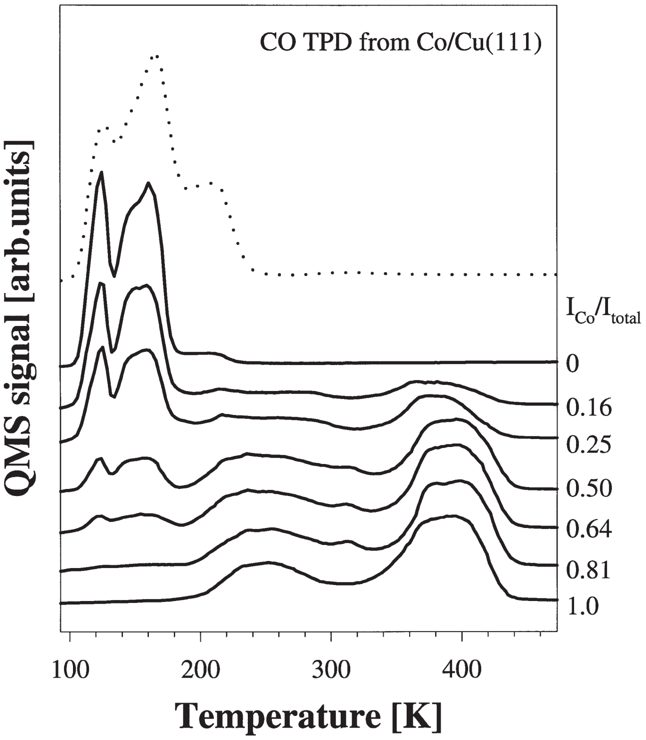

Figure 2. TPD spectra of CO from various Co amounts with the corresponding $I_{\mathrm{Co}}/I_{\mathrm{total}}$ values indicated to the right of the spectra. The Co evaporation took place at RT and the surface was saturated with CO at 103 K. The dashed curve at the top is also a CO TPD spectrum but for a surface flashed to 673 K. Before flashing, $I_{\mathrm{Co}}/I_{\mathrm{total}}$ was approximately 0.6.

There is some scattering in the experimental data, but it is unambiguously found that the Co dissociation site corresponding to $I_{\mathrm{Co}}/I_{\mathrm{total}}$ less than 0.6 is more reactive than a site on top of very many (in the limit of an infinite number of) layers of Co ($I_{\mathrm{Co}}/I_{\mathrm{total}} = 1.0$). From figure 1 it is seen that the sticking coefficient of the $I_{\mathrm{Co}}/I_{\mathrm{total}} \approx 0.6$ surface is approximately a factor of 2 higher than that of the pure Co surface ($I_{\mathrm{Co}}/I_{\mathrm{total}} = 1.0$).

Having established that the surface area of Co is constant for $I_{\mathrm{Co}}/I_{\mathrm{total}}$ larger than 0.6, the observed variations in reactivity most likely relate to the pseudomorphic nature of the Co layers on Cu(111). From EXAFS data Le Fevre et al. conclude that the in-plane lattice constant for several layers of Co is close to that of Cu, i.e., larger than the Co bulk value [17]. Density functional calculations by Ruban et al. [4] on pseudomorphic overlayers propose that the entire d-band of the surface atoms will shift in energy depending on the difference in lattice size of the adlayer and the substrate material. In cases where a pseudomorphic adlayer is forced to have a larger lattice constant than that of its bulk value, the embedding density is smaller thus resulting in a narrowing of the d-band. In the case of an adsorbate with a nearly-filled d-band, the narrowing will be accompanied by a shift in the d-band towards the Fermi level, and this is predicted to result in an increased CO binding energy [3]. We take issue in the three-layer Co/Cu structure recently proposed by Pedersen et al. [18]. For three Co layers pseudomorphically adsorbed on Cu an upshift of the d-band of 0.30 eV is calculated [27]. The largest site reactivity is obtained for surfaces with $I_{\mathrm{Co}}/I_{\mathrm{total}}$ less than 0.6, corresponding to the Cu surface being covered with three layers of Co with an enlarged lattice constant and therefore with a d-band center shifted towards the Fermi level. Eventually, the lattice constant and, thereby, the position of the d-band will return to that of bulk Co as more Co is evaporated. The reactivity is correspondingly seen to decrease. Hence, it appears that the shift in the d-band is not only related to the shift in the desorption temperature of a simple molecule like CO [3] but also to the ability of the surface to dissociate, e.g., CH_4.

A calculation of the change in dissociation barrier for CH_4 on a Co substrate with different lattice constants is not available. It is, however, possible to give a plausible estimate of the change in sticking coefficient of CH_4 on Co/Cu(111) using existing calculated data for the d-band shift and the following change in dissociation barrier for CH_4 on the Ni/Cu system. Here the shift of the d-band for a Ni impurity in a Cu substrate amounts to 0.27 eV [4], and the decrease in CH_4 dissociation barrier is found by density functional calculations to be 0.05 eV compared to that of pure Ni [12]. Assuming that the change in barrier scales linearly with the d-band shift, the predicted d-band shift of three Co layers on Cu of 0.30 eV should correspond to a decrease in the CH_4 dissociation barrier on Co/Cu of 0.06 eV. In order to transform this change in barrier height to a change in sticking coefficient, we simply use the measured data for the Ni(111) surface [11]. Assuming that a change in barrier of CH_4 dissociation corresponds to a similar change in translational energy of the CH_4 molecule keeping the vibrational energy fixed, a relative sticking coefficient for an increased translational energy of 0.06 eV (5.4 kJ/mol) is estimated to be 1.6 compared to that of the beam energy used (74 kJ/mol). This number should be compared to the factor of 2 found from the experimental data shown in figure 1. Taking the rather crude assumptions of this calculation into account and the scattering of the experimental data the agreement is satisfactory.

One could also argue that the change in reactivity is an effect of the surface morphology (steps, kinks, etc.) and not of an electronic effect as proposed here. At low Co coverage, the defect concentration is very low as seen from recent STM investigations. The Co steps of the rather large and smooth Co islands are eliminated by the double-layered Cu brim [18]. For increasing number of Co layers, the tensile stress in the pseudomorphic Co layers must eventually be relieved by introducing defects [28]. One would therefore expect the high Co coverage regime to be more reactive if the surface reactivity were governed by Co defects, opposite of the effect observed.

One would expect CO to be bonded more strongly to the Co/Cu surface than to pure Co [1,3,4]. This effect is, however, not observed using thermal desorption of CO. As mentioned before, energy is gained when Cu segregates to the Co surface [16,18]. We suggest that the segregation of Cu to the surface will force the CO to desorb at a temperature indicative of the thermodynamics of the bimetallic surface and not of the bonding strength of CO to the surface. This segregation will result in an apparently unchanged binding energy of CO to Co. This is a very important point to take into account when using TPD in the investigation of bimetallic surfaces which are not in thermal equilibrium.

5. Conclusions

We have shown results from a molecular beam study of a well characterized bimetallic surface. The Co coverage is the only parameter changed in the experiment. For a few Co layers on Cu, we find a chemical behavior of Co which is not intermediate between the behaviors of Co and Cu separately. The probability of CH_4 dissociating on Co deposited on Cu is enhanced by approximately a factor of 2. This synergetic effect between Co and Cu is suggested to be a pure electronic effect, caused by a shift in the center of d-band of Co forced to a larger neighbor distance by the substrate. This opens up a very promising path for understanding and predicting trends in modified reactivity of bimetallic surfaces.

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References

[1] J.A. Rodriguez and D.W. Goodman, Science 257 (1992) 897.
[2] J.A. Rodriguez, Surf. Sci. Rep. 24 (1996) 223.
[3] B. Hammer, Y. Morikawa and J.K. Nørskov, Phys. Rev. Lett. 76 (1996) 2141.
[4] A. Ruban, B. Hammer, P. Stoltze, H.L. Skriver and J.K. Nørskov, J. Mol. Catal. A 115 (1997) 421.
[5] J.H. Sinfelt, Science 195 (1977) 641.
[6] W.M.H. Sachtler and R.A. van Santen, Adv. Catal. 26 (1977) 69.
[7] V. Ponec, Adv. Catal. 32 (1983) 149.
[8] C.T. Campbell, Annu. Rev. Chem. 41 (1990) 775.
[9] G.A. Somorjai, *Introduction to Surface Chemistry and Catalysis* (Wiley, New York, 1994).
[10] J.R. Rostrup-Nielsen, J. Catal. 85 (1984) 31.
[11] P.M. Holmblad, J.H. Larsen and I. Chorkendorff, J. Chem. Phys. 104 (1996) 7289.
[12] P.M. Holmblad, J.H. Larsen, I. Chorkendorff, L. Pleth Nielsen, F. Besenbacher, I. Stensgaard, E. Lægsgaard, P. Kratzer, B. Hammer and J.K. Nørskov, Catal. Lett. 40 (1996) 131.
[13] R.W. Joyner, in: *The Chemical Physics of Solid Surfaces*, Vol. 6, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1993) chapter 8.

[14] M.T. Kief and W.F. Egelhoff, Jr., Phys. Rev. B 47 (1992) 10785.
[15] J. de la Figuera, J.E. Prieto, C. Ocal and R. Miranda, Phys. Rev. B 47 (1993) 13043.
[16] A. Rabe, N. Memmel, A. Steltenpohl and Th. Fauster, Phys. Rev. Lett. 73 (1994) 2728.
[17] P. Le Fevre, H. Magnan, O. Heckmann, V. Briois and D. Chandesris, Phys. Rev. B 52 (1995) 11462.
[18] M.Ø. Pedersen, I.A. Bönicke, E. Lægsgaard, I. Stensgaard, A. Ruban, J.K. Nørskov and F. Besenbacher, Surf. Sci. 387 (1997) 86.
[19] P.M. Holmblad, J. Wambach and I. Chorkendorff, J. Chem. Phys. 102 (1995) 8255.
[20] B. Ølgaard Nielsen, A.C. Luntz, P.M. Holmblad and I. Chorkendorff, Catal. Lett. 32 (1995) 15.
[21] J. Vaari, J. Lahtinen and P. Hautojärvi, Catal. Lett. 44 (1996) 43.
[22] M. Valden, J. Pere, N. Xiang and M. Pessa, Chem. Phys. Lett. 257 (1996) 289.
[23] J. Pritchard, Surf. Sci. 79 (1979) 231.
[24] W. Kirstein, B. Krüger and F. Thieme, Surf. Sci. 176 (1986) 505.
[25] I.A. Bönicke, W. Kirstein, S. Spinzig and F. Thieme, Surf. Sci. 313 (1994) 231.
[26] M.E. Bridge, C.M. Comrie and R.M. Lambert, Surf. Sci. 67 (1977) 393.
[27] A. Ruban, private communications.
[28] B. Müller, B. Fischer, L. Nedelmann, A. Fricke and K. Kern, Phys. Rev. Lett. 76 (1996) 2358.