The adsorption and decomposition of acetylene on clean and K-covered Co(0001)

J. Vaari, J. Lahtinen * and P. Hautojärvi

Laboratory of Physics, Helsinki University of Technology, Otakaari 1 M, 02150 Finland
E-mail: Jouko.Lahtinen@hut.fi

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We have studied the adsorption of acetylene on clean and K-covered Co(0001) by XPS, TDS and XPD. Acetylene is adsorbed molecularly at room temperature on clean Co(0001) with its molecular axis lying in the plane of the surface. The decomposition takes place at 410 K and goes likely via a vinylidene intermediate. Further heating results in the decomposition of the molecule to "graphitic" and "carbidic" carbon via the desorption of hydrogen. Potassium induces an additional acetylene adsorption state which is filled after the one found on clean Co(0001). The desorption of molecular acetylene and ethylene is induced by potassium. The desorption temperature of potassium is increased by 80 K due to acetylene when compared to the desorption of pure potassium monolayer. The decomposition of acetylene leads again to graphitic and carbidic carbon, but the relative amount of carbidic carbon is increased due to the presence of potassium.

Keywords: acetylene, cobalt, potassium, promotion, carbon residues

1. Introduction

The adsorption of acetylene on metal surfaces has been studied as a case study of the interaction of hydrocarbons with the catalyst surfaces. The adsorption and decomposition of acetylene has been extensively characterized by vibrational spectroscopy (for a compilation of data see ref. [1]), but also thermal and electronic properties have been reported on metals used either for Fischer–Tropsch synthesis or hydrogenation/dehydrogenation reactions. Recently, also semiquantitative structural information has been reported on Ni(110) [2] and a full structural analysis on Ni(111) [3].

Generally, below room temperature acetylene is adsorbed molecularly with its C–C axis parallel to the surface. The thermal decomposition may take several routes depending on the initial coverage and the substrate, and a variety of hydrocarbon intermediates have been reported. Only small amounts of carbon are desorbed as hydrocarbons, and a carbonaceous overlayer is left on the surface after the completion of hydrogen desorption, typically around 500–600 K.

Much of the surface studies dealing with potassium deposition on transition metals derive their motivation from the use of potassium in the hydrogenation catalysts. The bulk of these studies have focussed on the effects of potassium on CO adsorption, but one cannot ignore the interactions between potassium and hydrocarbons when formulating a complete picture of the hydrogenation reactions on promoted catalysts. These studies are, however, very limited in number. The coadsorption of acetylene and cesium has been studied on a Pd(110)(2×2) surface [4]. The authors report a cesium-induced stabilization of vinylidene species, attributed to the formation of (111) facets upon the adsorption of cesium onto the missing-row reconstructed Pd surface. Furthermore, ethylene formation is promoted by cesium. The coadsorption of ethylene and potassium on Pt(111) has been studied to some extent [5–8]. These studies reveal that in the presence of potassium a new, loosely bound (π-bonded) adsorption state for ethylene is created at the expense of the di-σ-bonded ethylene found on the clean surface. The decomposition path of ethylene is also affected, including stabilization of an ethylidene ($=CH-CH_3$) species.

It has been proposed [9,10] that potassium increases the resistivity of a catalyst surface towards poisoning by inactive carbon species. The inactive carbon is sometimes termed "graphitic" since it exhibits similar characteristics to bulk graphite. Another form of carbon is often named "carbidic" due to similar analogy to metal carbides. The carbidic carbon is also called the "active" form of carbon since it will react with hydrogen to form hydrocarbons [11].

In this paper we report on studies of acetylene adsorption and decomposition on clean and K-covered Co(0001) surfaces. We will show that after the acetylene decomposition the clean surface is partially covered with a carbonaceous overlayer composed mainly of "graphitic" carbon. On the potassium-covered surface, the relative amount of "carbidic" carbon after the acetylene decomposition has increased compared to the case of clean surface. The results are compared to post-reaction surface studies on K-covered Co

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* To whom correspondence should be addressed.

[9,10], Fe [12] and Ni [13] model catalysts after CO hydrogenation reactions.

2. Experimental

The experimental setup has been described previously [14]. Briefly, the experiments were performed in an ion-pumped UHV chamber equipped with facilities for X-ray photoelectron spectroscopy (XPS), X-ray photoelectron diffraction (XPD), low-energy ion scattering spectroscopy (LEIS), thermal desorption spectroscopy (TDS), low-energy electron diffraction (LEED) and metal depositions. Mg K_α radiation was used throughout the XPS measurements in this paper. The hemispherical electron analyzer was typically operated at 18 eV pass energy to obtain the best possible resolution when measuring the C 1s line. For XPD measurements the pass energy was set to 75 eV to reduce data collection time.

Potassium deposition was accomplished by a standard getter source. Before each deposition the K flux was allowed to stabilize for 4 min. Acetylene (99.5% purity) was admitted to the chamber through a leak valve. Exposures were monitored by a quadrupole mass spectrometer and calibrated against an ion gauge reading assuming a sensitivity factor of 2.0 relative to nitrogen, as suggested by Takaoka et al. [4].

The Co(0001) sample had a nominal purity of 99.999%. The initial preparation and cleaning have been documented elsewhere [15,16]. Routinely, the sample was cleaned by 1 hour sputtering with 1 keV Ar^+ ions followed by 5 min annealing at 650 K.

3. Results and discussion

3.1. The adsorption of acetylene on clean and K-covered Co(0001)

Fig. 1 displays the intensity of the C 1s photoelectron line as a function of exposure on clean and K-covered ($\theta_K = 0.3$) Co(0001) surface at 320 K temperature. We found that the C 1s line intensity saturated already after 3 L exposure. The main impurities during the gas exposure were H_2 and CO, probably resulting from the exchange reactions on the chamber walls and in the ion pump. The impurity exposures remained, however, below 0.1 L. The small exposure required for saturation suggests a high initial sticking coefficient, and potassium preadsorption does not affect the uptake rate. A small increase (about 25%) in the adsorption capacity is caused by potassium.

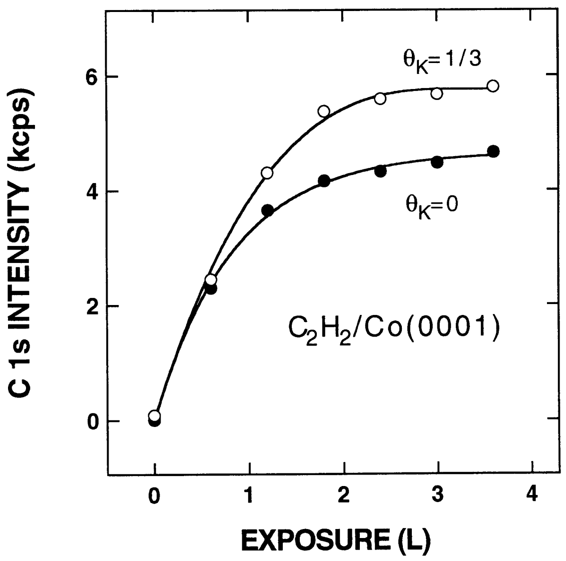

Fig. 1. The intensity of the C 1s photoelectron line versus the C_2H_2 exposure on clean ($\theta_K = 0$) and K-covered ($\theta_K = 1/3$) Co(0001) surface.

To estimate the acetylene coverage, we may compare the C 1s intensities measured from the surfaces saturated with C_2H_2 and CO. In the latter case the CO molecules form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer corresponding to a coverage of 1/3 [17,18,16], and the comparison yields a saturation coverage of 1/3 also for acetylene assuming the adsorption is molecular. Scaling of the K 2p and C 1s intensities in the coadsorption case by the sensitivity factors is in support of this, suggesting approximately one acetylene molecule per one potassium atom.

The evolution of the C 1s lineshape during acetylene adsorption is shown in fig. 2a for clean Co(0001) and 2b for K-covered Co(0001). On clean Co(0001), the C 1s line has only one asymmetric component whose binding energy is 283.6 eV at low coverages and 0.2 eV higher at saturation coverage. We attribute these binding energy values to the molecularly adsorbed C_2H_2. On K-covered Co(0001), a 0.6 L exposure gives rise to a C 1s line with a similar shape as with clean Co(0001). The binding energy is now 283.3 eV, i.e. there is a 0.3 eV downshift due to potassium. This binding energy coincides with the one corresponding to carbidic C on cobalt, and it could thus imply acetylene dissociation. We, however, attribute it to potassium-affected molecular acetylene, since an increase in the exposure causes the line to shift smoothly to 283.7 eV. Together with the shift, a tail on the high binding energy side evolves which can be explained by a broad C 1s component centered at 285.3 eV. Since a higher binding energy for an adsorbed gas molecule corresponds to less electronic perturbation compared to gas phase, the tail most likely results from potassium-affected acetylene molecules which are loosely bound to the surface. This interpretation is in accordance with acetylene adsorption on Cs/Pd(110) [4] and with ethylene adsorption on K/Pt(111) [5–7] and Cs/Pt(111) [5]. In all of these cases, the alkali metal induced a new adsorption state for the hydrocarbon exhibiting a smaller interaction energy with the substrate.

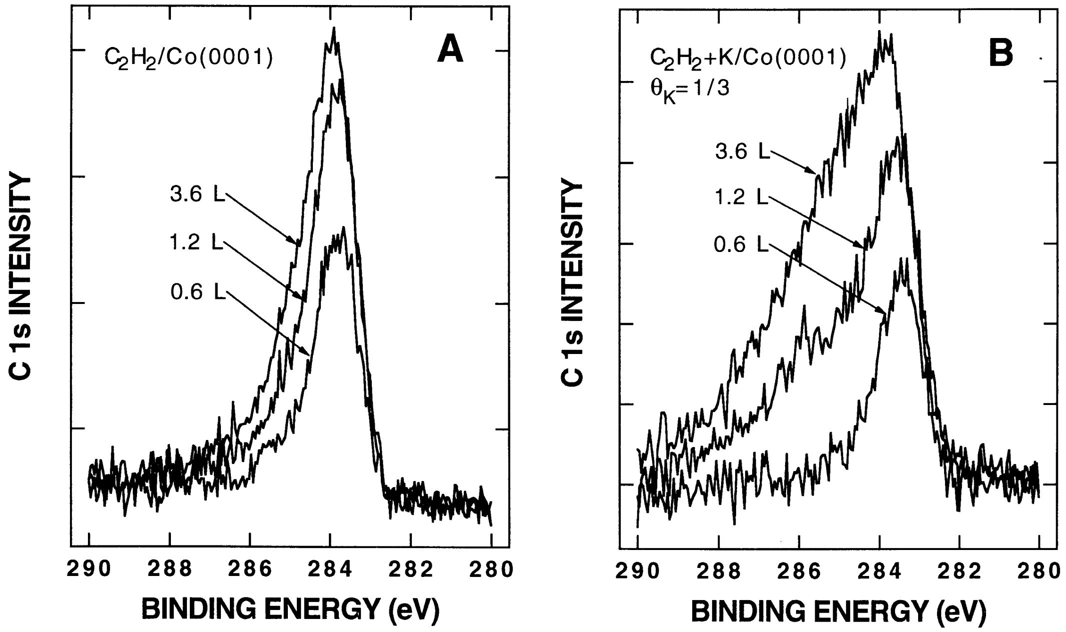

Fig. 2. The evolution of the C 1s lineshape during acetylene adsorption on the clean (A) and K-covered (B) Co(0001).

3.2. The decomposition of acetylene on clean Co(0001)

Fig. 3 shows the XP spectra of the C 1s region after a saturation exposure of C_2H_2 at 320 K and after heating to 570 K in 50 K steps. At 320 K the C 1s spectrum consists of a single peak at 283.8 eV. Heating to 420 K causes the C 1s line to shift to 0.7 eV upwards. Further heating splits the line into two distinct components at 283.3 and 284.6 eV. The total intensity of the C 1s line remains constant suggesting no significant desorption of hydrocarbons or bulk diffusion of carbon atoms.

Fig. 4 displays the thermal desorption spectrum of

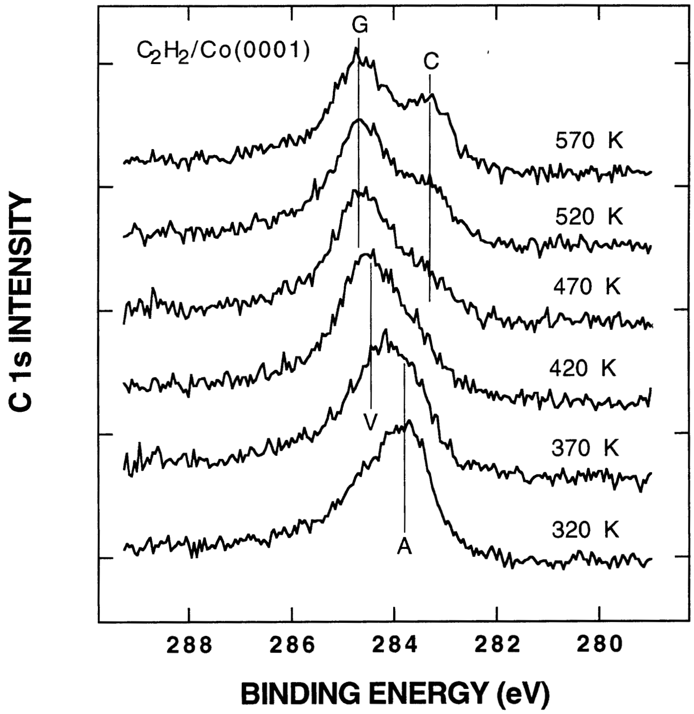

Fig. 3. The photoelectron spectra of the C 1s region after a saturation exposure of C_2H_2 at 320 K followed by heating to 570 K in 50 K steps. The various peak positions are labelled as A (molecular acetylene), V (the proposed vinylidene intermediate), G (graphitic carbon) and C (carbidic carbon).

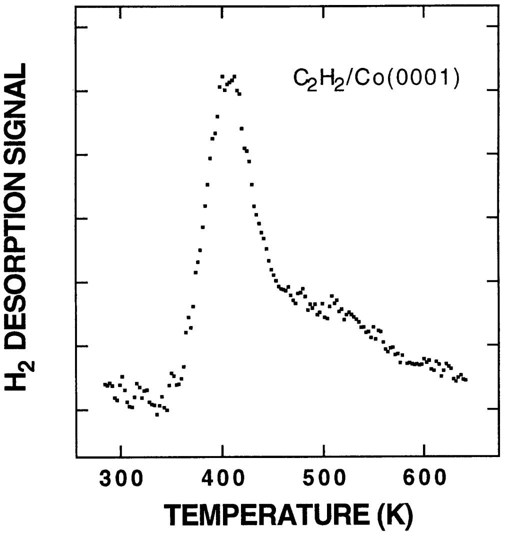

Fig. 4. The thermal desorption spectrum of hydrogen after a saturation exposure of C_2H_2 on Co(0001) at 320 K. The heating rate was 2 K/s. No other species were found to desorb.

hydrogen after a saturation exposure of C_2H_2 on Co(0001) at 320 K. The spectrum has a peak at 410 K, and above that, the desorption continues with a smaller rate up to 550 K. In agreement with XPS, no hydrocarbon desorption was observed. A similar hydrogen desorption spectrum has earlier been reported for acetylene on polycrystalline cobalt [19].

The XPD measurements of the C 1s line are summarized in fig. 5. The measurements were performed after a saturation exposure of C_2H_2 at 320 K (corresponding to C 1s binding energy of 283.8 eV) and after heating to 420 K (corresponding to C 1s binding energy of 284.5 eV). The experimental angular dependencies were removed by measuring the XPD data of a potassium monolayer. At 320 K we find no forward focussing effects in the C 1s data within the angular range available. At 420 K, i.e. just above the maximum in the hydrogen desorption of fig. 4, the XPD data shows a forward focussing peak at normal emission with a signal-to-background ratio of 8%.

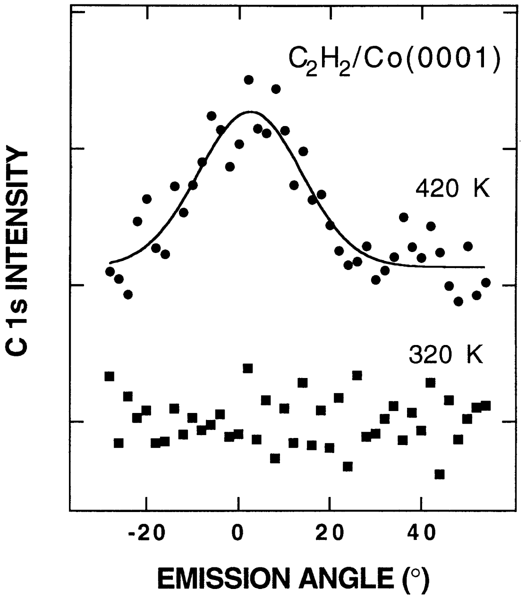

Fig. 5. The XPD data of the C 1s line after a saturation exposure of C_2H_2 at 320 K and after heating to 420 K.

The above observations are interpreted as follows. Starting from XPS at 320 K, we assign the binding energy of 283.8 eV to molecularly adsorbed C_2H_2 on Co(0001). This value falls between the two known states for atomic carbon on Co(0001), called "graphitic" (284.8 eV) and "carbidic" (283.1 eV) [20]. Since the C 1s line has only one component, there is but one chemical state for carbon. The XPD of the C 1s line shows no forward focussing peak, and we thus conclude that the 283.3 eV binding energy corresponds to a flat-lying C_2H_2 molecule on Co(0001) as is also observed on Ni(111) [3].

At 420 K, the C 1s line has shifted to 284.5 eV. Although the hydrogen desorption peak temperature of 410 K is close to the one reported earlier for H_2 on Co(0001) [21], the concomitant shift in the C 1s binding energy suggests acetylene decomposition. The XPD measurement now reveals enhanced C 1s emission along the sample normal, which is taken as evidence for a vertically bonded C_2 hydrocarbon fragment. Such a species could be, for example, vinylidene (=C=CH_2) which is formed from acetylene by isomerization. According to bond-order-conservation calculations [11] the isomerization of acetylene to vinylidene is exothermic in the chemisorbed state on transition metals. Note that the XPD data does not exclude other possible intermediates. On polycrystalline cobalt, a CH fragment has been suggested [19]. On Fe(100), CH and CCH as well as vinylidene intermediates have been claimed [22]. Since we do not observe ethylene desorption on clean Co (suggesting a reaction between acetylene molecules), we consider unlikely the formation of an ethylidyne intermediate, CCH_3.

Above 420 K the C 1s line splits into two components at 284.6 and 283.3 eV which we assign to graphitic and carbidic carbon, respectively [9,20]. The amount of carbidic carbon attains its maximum level at 570 K which, according to the TDS data of fig. 4, corresponds to the completion of the acetylene decomposition. We thus see that the decomposition of an acetylene monolayer on clean cobalt results mainly in graphitic carbon. Note that the terms "graphitic" and "carbidic" are used in the literature often because the two forms of atomic carbon give rise to similar electronic and chemical characteristics as bulk graphite or carbide [12,20,23]. The local structure around the surface carbon atoms remains, however, unclear.

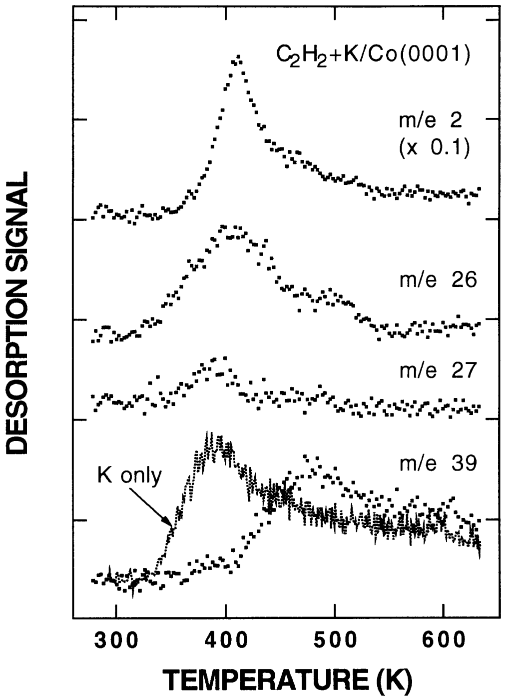

Fig. 6. The TDS spectra of H_2, C_2H_2, C_2H_3 and K from the coadsorption system. For comparison, the desorption spectrum of a pure potassium monolayer is included. The heating rate was 2 K/s.

3.3. The decomposition of acetylene on K-covered Co(0001)

The effect of potassium on the adsorption of acetylene was studied with a potassium coverage of 0.3, corresponding to one monolayer of adsorbate [14]. The TDS spectra of H_2, C_2H_2 and K from the coadsorption system are presented in fig. 6. The hydrogen desorption spectrum resembles the one measured without K. However, there is significant acetylene desorption at mass number 26. The qualitative behaviour of this spectrum follows the hydrogen desorption spectrum, with a main peak at 410 K and a shoulder around 500 K. We also observe ethylene formation, monitored by measuring the mass number 27 because of the CO background at mass number 28. According to the cracking pattern of ethylene, there are side peaks at mass numbers 27 and 26 with intensities of 63 and 61%, respectively. Since the peak for mass 27 is around 390 K, the desorption spectrum for mass 26 is slightly broadened on the low temperature side by ethylene desorption.

Potassium desorption sets on above 400 K and attains maximum rate at 480 K which means that a potassium monolayer is stabilized by about 80 K on the surface due to acetylene coadsorption. The loss of C 1s intensity upon heating is about 25% which approximately corresponds to the increase in the adsorption capacity induced by potassium. The hydrocarbon desorption may thus be assigned to the new, loosely bound adsorption state created for acetylene by potassium. An alkali-metal-induced (either K or Cs), loosely bound adsorption state for ethylene has been reported on Pt(111) [5,6]. This is attributed to a change in the bonding mechanism from di-σ-bonding to π-bonding.

Fig. 7 shows the XP spectra of the K 2p and C 1s region at various temperatures after the adsorption of a potassium coverage of 0.3 followed by a saturation exposure of C_2H_2 at 320 K. For reference, we also show the K 2p lineshape measured from a K monolayer without C_2H_2. It is clearly seen that C_2H_2 increases the K 2p

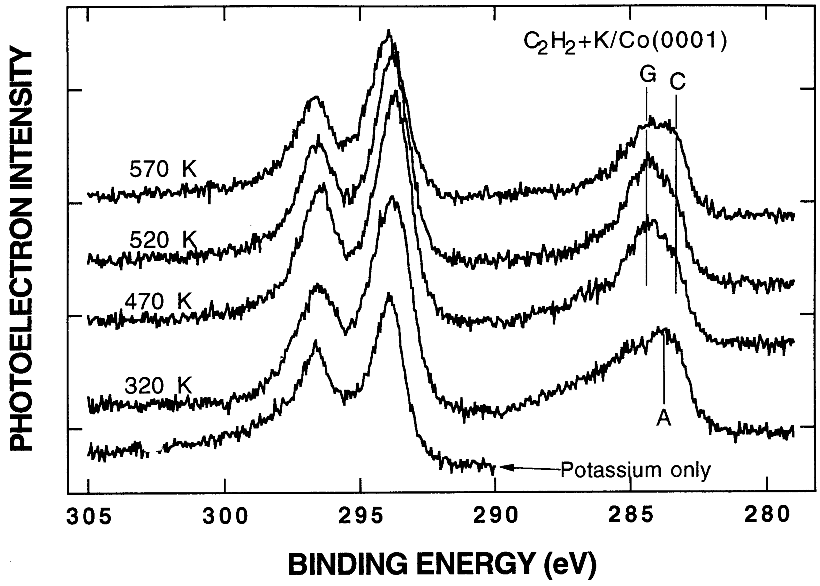

Fig. 7. The XPS spectra of the K 2p and C 1s region at various temperatures after the deposition of a potassium coverage of 0.3 followed by a saturation exposure of C_2H_2 at 320 K. Peak labelling as in fig. 3.

linewidth as well as removes the asymmetry indicative of a purely metallic monolayer, but no binding energy shift is observed. These effects are taken as evidence of a K–C_2H_2 interaction. We may note that quite similar effects on the K 2p lineshape were also observed due to CO [14], and it was suggested that the role of CO was to act as a buffer for the K–K repulsion. Acetylene may also act as such a buffer, and the energy gain from this buffering could give an explanation for the potassium-induced slight increase in the adsorption capacity for acetylene (which was also observed for CO).

The XPS and TDS data suggest that acetylene molecules are attached to the Co substrate rather than directly to the K promoter. This is because there is only a minor decrease in the C 1s binding energy due to K, and because the hydrogen desorption spectrum is almost identical whether K is present or not. Furthermore, a matrix-isolation study involving acetylene and alkali metals [24] suggests only a van der Waals type interaction between acetylene and potassium, which would lead to no adsorption at room temperature.

The C 1s binding energy undergoes an upshift of 0.8 eV upon heating to 470 K, just as in the case of K-free surface. We also observe a loss of intensity in the high energy tail of the C 1s line, which suggests hydrocarbon desorption. Upon further heating, some intensity evolves around 283.3 eV, which is visually observed as a broadening of the line. The total intensity of the C 1s line decreases continuously as a function of temperature, and at 570 K it has dropped nearly by a factor of two. Comparing the C 1s lineshapes of the clean and K-covered surfaces at 570 K, one observes that potassium significantly alters the chemical state of carbon resulting from acetylene decomposition. In the case of clean Co, the intensity ratio of the graphitic component to the carbidic component is about 2 : 1. With K added onto the surface, the intensity ratio changes to 1 : 1.

Our measurements thus support the idea that one of the promoter effects of potassium in hydrogenation catalysts is the prevention of surface poisoning by inactive carbon layers. The decrease in the C 1s line intensity as a function of temperature, especially above the desorption region of acetylene and ethylene, suggests potassium-induced subsurface penetration of carbon atoms.

A similar potassium-induced effect is observed in a CO hydrogenation study by Wesner et al. on potassium-covered Co foil [9]. Using 100 kPa total pressure and temperatures between 523 and 548 K, these authors found after the reaction a predominantly graphitic carbon layer over an initially clean Co surface. With potassium added on the surface, the hydrogenation reaction led to enhanced carbon deposition, but the chemical state of the carbon had changed to predominantly carbidic. As a possible reason for this, the authors mention a geometrical site-blocking by potassium, since on a clean Co(0001) surface graphite can grow almost epitaxially. An electronic effect on carbon by potassium was, however, not excluded. On Ni [13], Campbell and Goodman find that potassium decreases the activation energy for carbidic carbon buildup, which leads to more carbon on the K-promoted surface during reaction as compared to clean Ni. As a contrast to Co and Ni, hydrogenation reactions by Wesner et al. on Fe foils [12] revealed that the formation of graphitic carbon was enhanced by the presence of potassium.

4. Conclusions

Acetylene adsorbs molecularly on clean and K-covered Co(0001) at 320 K. The saturation coverage on clean Co(0001) is about 0.3 and it is increased by 25% by a monolayer of potassium. The initial sticking coefficient is not altered by potassium.

The decomposition of acetylene occurs at 400 K on both clean and K-covered Co(0001). On the clean surface, the decomposition may occur via a vinylidene intermediate without hydrocarbon desorption. On the K-covered surface hydrocarbon desorption is observed, consisting of acetylene and a small amount of ethylene. The origin of the hydrocarbon desorption is a new, loosely bound adsorption state for acetylene created by potassium.

The final product of acetylene decomposition is a carbonaceous overlayer. On the clean surface this layer consists mainly of "graphitic" carbon with a small amount of "carbidic" carbon. Potassium alters the decomposition in such a way that the relative amount of carbidic carbon is higher. This implies a greater resistivity towards poisoning by inactive carbon of a potassium-promoted catalyst surface.

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References

[1] N. Sheppard, Annual Rev. Phys. Chem. 39 (1988) 389.

[2] M. Weinelt, W. Huber, P. Zebisch, H.-P. Steinrück, P. Ulbricht, U. Birkenheuer, J.C. Boettger and N. Rösch, J. Chem. Phys. 102 (1995) 9709.

[3] S. Bao, Ph. Hofmann, K.-M. Schindler, V. Fritzsche, A.M. Bradshaw, D.P. Woodruff, C. Casado and M.C. Asensio, Surf. Sci. 323 (1995) 19.

[4] T. Takaoka, T. Sekitani, T. Aruga and M. Nishijima, Surf. Sci. 306 (1994) 179.

[5] A. Cassuto, M. Mane, M. Hugenschmidt, P. Dolle and J. Jupille, Surf. Sci. 237 (1990) 63.

[6] X.-L. Zhou, X.-Y. Zhu and J.M. White, Surf. Sci. 193 (1988).

[7] R.G. Windham, M.E. Bartram and B.E. Koel, J. Phys. Chem. 92 (1988) 2862.

[8] R.G. Windham, G. Linden and H.P. Bonzel, Appl. Surf. Sci. 26 (1986) 335.
[9] D.A. Wester, G. Linden and H.P. Bonzel, Appl. Surf. Sci. 26 (1986) 335.
[10] J. Lahtinen and G.A. Somorjai, unpublished.
[11] A.T. Bell and E. Shustorovich, Surf. Sci. 235 (1990) 343.
[12] D.A. Wesner, F.P. Coenen and H.P. Bonzel, Langmuir 1 (1985) 478.
[13] C.T. Campbell and D.W. Goodman, Surf. Sci. 123 (1982) 413.
[14] J. Vaari, J. Lahtinen, T. Vaara and P. Hautojärvi, Surf. Sci. 346 (1996) 1.
[15] J. Lahtinen, J. Vaari, A. Talo, A. Vehanen and P. Hautojärvi, Surf. Sci. 245 (1991) 244.
[16] J. Lahtinen, J. Vaari, A. Talo, A. Vehanen and P. Hautojärvi, Vacuum 41 (1990) 112.
[17] M.E. Bridge, C.M. Comrie and R.M. Lambert, Surf. Sci. 67 (1977) 393.
[18] H. Papp, Surf. Sci. 129 (1983) 205.
[19] P. Tiscione and G. Rovida, Surf. Sci. 154 (1985) L255.
[20] J. Nakamura, I. Toyoshima and K. Tanaka, Surf. Sci. 201 (1988) 185.
[21] M.E. Bridge, C.M. Comrie and R.M. Lambert, J. Catal. 58 (1979) 28.
[22] W.-H. Hung and S.L. Bernasek, Surf. Sci. 339 (1995) 272.
[23] E.L. Garfunkel, J. Parmeter, B.M. Naasz and G.A. Somorjai, Langmuir 2 (1986) 105.
[24] L. Manceron and J.P. Perchard, in: *Physics and Chemistry of Alkali Metal Adsorption*, eds. H.P. Bonzel, A.M. Bradshaw and G. Ertl (Elsevier, Amsterdam, 1989).