# Size Dependent CO Dissociation on Rh Particles Supported on Thin Alumina Films

J. Libuda<sup>1</sup>, M. Frank<sup>1</sup>, A. Sandell<sup>1</sup>, S. Andersson<sup>2</sup>, P.A. Brühwiler<sup>2</sup>, M. Bäumer<sup>1</sup>, N. Mårtensson<sup>2</sup>, and H.-J. Freund<sup>1</sup>

<sup>1</sup>Physical Chemistry 1, Ruhr-Universität Bochum,

D-44780 Bochum, Germany

<sup>2</sup>Department of Physics, Uppsala University, Box 530,

S-75121 Uppsala, Sweden

Small Rh particles are grown onto a well ordered alumina film which covers a NiAl(110) single crystal surface. Adsorption and dissociation of carbon monoxide is studied by means of photoelectron spectroscopy (XPS). The tendency to dissociate CO increases with increasing particle size. This statement is supported for the first time by a direct in-situ measurement, and is in partial contrast to literature data. It is speculated that the low tendency for dissociation on the small particles is connected with the spatial constraints of a dissociation reaction, i.e. it needs several separated sites to occur. Since the smallest particles contain less than ten Rh atoms these constraints may play an important role.

### **1. Introduction**

In many catalytic processes at present dispersed metal catalysts are being used [1,2]. Often the metal particle size plays an important role for the activity and selectivity of the reaction in question. For so called structure sensitive reactions the size dependent distribution of specific adsorption sites on small metal particles can affect the reaction [3]. In order to study the details of the interaction of molecules such as CO, as a prototype system, with small metal particles as a function of temperature we resort to the study of model systems. These model systems consist in our case of a thin well ordered Al<sub>2</sub>O<sub>3</sub> film grown on top of a NiAl(110) single crystal surface, onto which metal particles are deposited from the gas phase [4-13]. In the past we have studied various metal deposits, such as Pt, Pd, Ag, and Rh [4, 5, 8-13]. The different metals exhibit quite different growth behaviour which is due to the varying interaction strength between the metal and the oxide substrate. CO adsorption has been studied for almost all the different metal deposits. We have reported indications that e.g. for Pt particles dissociation occurs on very small particles [5]. The evidence was deduced from x-ray photoelectron spectroscopic measurements carried out for this system. However, it could not be finally excluded that this dissociation was photoinduced due to the rather extensive exposure times to x-rays in conventional x-ray spectrometers or was due to contaminations accumulating during the rather long accumulation times. Investigations carried out subsequently applying synchrotron radiation to record the corresponding spectra in short times indicated that this may in fact have been

> Springer Series in Solid-State Sciences, Volume 121 Elementary Processes in Excitations and Reactions on Solid Surfaces Eds. : A. Okij, H. Kasai and K. Makoshi © Springer-Verlag Berlin Heidelberg 1996

the case [4]. It was therefore important to investigate a system where there are strong indications from the literature that CO dissociation does take place and that this dissociation proceeds via a thermal mechanism. Rh is known to induce CO dissociation, and CO adsorption and reaction has been studied extensively in the literature for small deposited metal particles [14-17] as well as single crystal surfaces [18-25]. While for the single crystal systems XPS results have been reported, such reports for small particle systems have been very scarce. Whereas previous SIMS and TPD studies have shown that dissociation is more important for smaller than for larger metal particles [15], thermal desorption data recently published gives very indirect indication for lower activity for dissociation on smaller particles [14]. On the single crystal surfaces it appears that while the close packed surfaces do not seem to induce C-O bond breaking [18-21], the more open or stepped faces are very well capable for CO dissociation [22-25].

In the present study we report on a synchrotron based XPS study of dissociation as a function of temperature of small Rh particles interacting with CO., CO dissociation is observed and its dependence on the particle size is discussed.

#### 2. Experimental Aspects

The experiments have been performed in several ultrahigh vacuum systems located in Bochum and at beamline 22 located at Maxlab in Lund/Sweden. The setup contains a modified Zeiss SX-700 monochromator in conjunction with a large hemisperical electron energy analyser for photoemission and a multichannel plate with a retarding grid for x-ray absorption measurements by detection of secondary electrons. The C1s spectra were recorded with a total resolution of 0.4eV. All the XPS binding energies are referred to the Fermi level of the NiAl substrate. The absolute photonenergies were determined using photoemission spectra excited by first and second order radiation. The SPA-LEED measurements were carried out in a seperate ultrahigh vacuum system. From the SPA-LEED investigations the average island size could be determined from an analysis of the line profile.

The substrate oxide film has been prepared according to well known recipes. Rh was evaporated from a rod using a commercial evaporator based on electron bombardment. The evaporation rate was monitored using a quartz microbalance.

#### 3. Results and Discussion

Fig. 1 shows a set of C1s spectra taken on a Rh deposit of 4 Å as monitored by the quartz balance. In the SPA-LEED pattern such a deposit exhibits clear indications for island growths of the metal on the surface. As has been discussed in detail for Pt and Pd deposits, the (0,0) reflex shows a pronounced shoulder [8,13]. The profile analysis yields an average isand size of 20 Å for a film of 4 Å thickness of Rh. At low temperature, i.e. 90 K, a single C1s signal with binding energy 286.5 eV is measured. This binding energy is typical for molecularly bound CO. Upon heating the surface to room temperature the single line narrows and shifts to lower binding energy by 0.3 eV. The situation changes when the sample is heated to 400



Fig. 1 C1s photoelectron spectra of CO on Rh/Al<sub>2</sub>O<sub>3</sub>/NiAl(110) after heating to various surface temperatures. The Rh particles have been deposited at  $T_{dep}$  = 90 K.

K. At the expense of the molecular species a peak at 284 eV binding energy grows in, and at 600 K surface temperature the molecular peak has completely disappeared. By comparison with literature data it is quite obvious that the peak at 284 eV correponds to atomic carbon being formed on the surface. In Fig.2 the initial situation at low temperature and the final situation at 600 K are plotted together for the various Rh depositions investigated. The amount of deposited Rh is given as determined by the quartz balance. For these metal coverages the average particle size as determined from the SPA-LEED analysis varies by almost an order of magnitude, namely between about 5 Å and about 30 Å. The spectra at the smallest particle size must be taken with care because of the rather limited signal to noise ratio. Several trends may be observed. Firstly the C1s ionization of the molecular species shifts from higher to lower binding energy as the particle size increases. The corresponding shift of the C1s ionization of atomic carbon is considerably smaller but in the same direction. Secondly, the line widths increase systematically for decreasing particle size. Thirdly, and probably most importantly, for the present study, the amount of atomic carbon found on the surface varies with particle size. The last point, which we shall adress first, is highlighted in Fig.3a. In this figure the relative C1s intensity is decomposed into the three components,



Fig. 2 C1s photoelectron spectra of CO on Rh/Al<sub>2</sub>O<sub>3</sub>/NiAl(110) as a function of the amount of deposited Rh metal ( $T_{dep} = 90$  K). For each deposition the full line corresponds to the spectra taken after exposure to CO at 90 K. The dotted line represents the spectrum taken after heating the CO adsorbate to 600 K.

namely carbon stemming from CO dissociation after heating to 400 K, loss of signal due to CO desorption the amount of adsorbed CO, and a carbon contaminant being present on the surface as the CO is dosed. We do not use the data after heating to 600 K for this analysis because at that temperature CO starts to desorb via recombination with oxygen. [24,14,15]. Again, the data for the smallest particle sizes have to be taken with care. We shall therefore base the consecutive conclusions mainly on the data for coverages excluding those for the 0.2 Å deposit. The general result, independent of the temperature, once the dissociation temperature is crossed, is that the amount of dissociated CO increases with increasing Rh particle size. We note, however, that the analysis of the data after heating to 600 K yield the same result.

In order to discuss these findings we adress the three main observations as mentioned above: The first observation was the shift of the C1s ionization towards lower binding energies. This result for Rh clusters corroborates a similar result obtained for Pd clusters on the same substrate. This shift is accompanied by the decrease in width of the C1s ionization line, which was the second observation



(After heating to 400 K and partial desorption of CO)



Relative amounts of various sources of carbon on Rh/Al<sub>2</sub>O<sub>3</sub>/NiAl(110) as Fig. 3 a function of the amount of deposited Rh metal, after heating the system to 400 K.

CO dissociating

C(a) before heating

alluded to above. These two results are interrelated and connected with a change in the interaction strength between the adsorbed molecule and the particle as well as the screening abilities of the metal particle. The latter is strongly influenced by its size as also documented by our studies on Pd particles [12,13]. The presented data are compatible with the idea that the smaller CO-covered particles behave more like a molecular species than the larger particles. The third observation is the increasing tendency for CO dissociation as the size of the particle deposited increases.

Studies of the particle size dependence of CO dissiciation reported in the literature have come to different conclusions [14,15]. None of these investigations, however, has reported XPS data that directly measure the amount of dissociated CO staying on the particle. Studies based purely on the analysis of temperature programmed desorption spectra might lead to the conclusion that dissociation is indeed favoured by increasing the particle size [14]. The conclusions are somewhat indirect as they are based on the CO<sub>2</sub> production rate, resulting from the reaction adsorbed CO with oxygen produced by CO dissociation. In the present study the measurement of the amount of dissociated CO is direct.

One possiblity to interpret the present result is to assume that in order for dissociation to occur the particle has to have a minimal size. After all dissociated

CO needs at least two well separated sites into which the released carbon and oxygen atoms can be accomodated. Taking into account that our smallest particles only contain 10 or less Rh atoms it is quite conceivable that on the smaller particles there is simply not enough space for dissociation to occur. The results for the larger particles found in the present study are compatible with results reported in the literature for stepped and open face Rh single crystal surfaces. This is a quite expected result.

#### 4. Ackowledgements

This work was funded by: The Deutsche Forschungsgemeinschaft, Ministerium für Wissenschaft und Forschung des Landes Nordrhein-Westfalen, Fonds der Chemischen Industrie, the Swedish Natural Science Research Council (NFR) and the Swedish National Board for Industrial and Technical Development. A.S. wishes to acknowledge NFR for a fellowship and J.L. finally thanks the Studienstiftung des Deutschen Volkes for financial support.

## 5. References

- [1] A.B. Stiles (Ed) "Catalyst Supports and Supported Catalysts" Butterworth, Boston (1987).
- [2] B.C. Gates, C. Guli, H. Knözinger (Eds.) "Metal Clusters in Catalysis" in "Studies in Surface Science and Catalysis", Vol. 29 Elsevier Publ. Cong., Amsterdam (1986).
- [3] G.A. Somorjai, J. Carazza, Ind. Eng. Chem. Fundam. 25, 63 (1986).
- [4] a) H.-J. Freund, Ber. Bunsenges. Phys. Chem. <u>99</u>, 1261 (1995)
  b) H.-J. Freund, B. Dillmann, D. Ehrlich, M. Haßel, R.M. Jaeger, H. Kuhlenbeck, C.A. Ventrice Jr., F. Winkelmann, S. Wohlrab, C. Xu, Th. Bertrams, A. Brodde, H. Neddermeyer, J. Mol. Catal. <u>82</u>, 143 (1993)
- [5] F. Winkelmann, S. Wohlrab, J. Libuda, M. Bäumer, D. Cappus, M. Menges, K. Al-Shamery, H. Kuhlenbeck, and H.-J. Freund Surf. Sci. <u>307 - 309</u>, 1148 (1994).
- [6] J. Libuda, F. Winkelmann, M. Bäumer, H.-J. Freund, Th. Bertrams, H. Neddermeyer, and K. Müller, Surf. Sci. <u>318</u>, 61 (1994)
- [7] R.M. Jaeger, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, and H. Ibach, Surf. Sci. <u>259</u>, 253 (1991)
- [8] J. Libuda, M. Bäumer, and H.-J. Freund, J. Vac. Sci. Technol. <u>A 12</u>, 2259 (1994)
- [9] S. Wohlrab, F. Winkelmann, H. Kuhlenbeck, and H.-J. Freund, to appear in: Springer Proceedings in Physics, Springer, Berlin 1995
- [10] A. Sandell, J. Libuda, P. Brühwiler, S. Andersson, A. Maxwell, M. Bäumer, N. Mårtensson, and H.-J. Freund, to appear in: J. Electron Spectrosc. Relat. Phenom.

- [11] A. Sandell, J. Libuda, M. Bäumer, and H.-J. Freund, submitted to Surf. Sci.
  A. Sandell, J. Libuda, P.A. Brühwiler, S. Andersson, A.J. Maxwell, M. Bäumer, N. Mårtensson, H.-J. Freund, submitted to J. Vac. Sci. Techol. M. Bäumer, J. Libuda, A. Sandell, H.-J. Freund, G. Grow, Th. Bertrams, H. Neddermeyer, Ber. Bunsenges. Phys. Chem. <u>99</u>, 1381 (1995)
  [14] V. Nehasil, I. Stavá, V. Matolin, Surf. Sci. <u>331</u>, 105 (1995)
- [15] V. Matolin, K. Masek, M.H. Elyakhloufi, E. Gillet, J. Catal. <u>143</u>, 492 (1993)
- [16] E.I. Altman, R.J. Gorte, Surf. Sci. <u>195</u>, 392 (1988)
- [17] D.N. Belton, S.J. Schmieg, Surf. Sci. 202, 238 (1988)
- [18] J.T. Yates, E.D. Williams and W.H. Weinberg, Surf. Sci. <u>91</u>, 562 (1980)
- [19] D.G. Castner, B.A. Sextonand G.A. Somorjai, Surf. Sci. 71, 519 (1978)
- [20] P.A. Thiel, E.D. Williams, J.T. Yates and W.H. Weinberg, Surf. Sci. 84, 54 (1979)
- [21] Y. Kim, H.C. Peebles and J.M. White, Surf. Sci. <u>114</u>, 363 (1982)
- [22] R.A. Marbrow, R.M. Lambert, <u>67</u>, 489 (1977)
- [23] D.G. Castner, G.A. Somorjai, Surf. Sci. 83, 60 (1979)
- [24] M. Rebholz, R. Prins, and N. Kruse, Surf. Sci. Lett. 259, L 797 (1991)
- [25] M. Rebholz, R. Prins, and N. Kruse, Surf. Sci. Lett. <u>269/270</u>, 293 (1992)