### Molecular Beam and Time-of-Flight Studies of Catalytic Model Reactions on Two-Component Surfaces

R. Schennach, G. Krenn, K.D. Rendulic, G. Pauer, M. Kratzer and <u>A. Winkler</u> Institute of Solid State Physics, Graz University of Technology, Petersgasse 16, A-8010 Graz, Austria a.winkler@tugraz.at

### **1. Introduction**

The tailoring of catalytic reactions by specific modifications of the catalyst surfaces is a key objective of heterogeneous catalysis. Surface science can significantly contribute to reach this goal because all (or most) of the parameters determining a particular reaction can be controlled. In this work we have focused on two aspects, the influence of surface modifications as well as the effect of changing the gas properties (energy, molecular or atomic species) on some model reactions. A supersonic molecular beam source and a time-of-flight spectrometer were the main techniques to control and analyse the translational energies of the impinging reactants and desorption reaction products, respectively. As model reaction systems we have chosen the dehydrogenation of methanol on palladium and rhodium single crystal surfaces, as well as the water formation reaction on palladium. Vanadium and potassium were used to modify the surfaces.

### 2. Experimental

All experiments were done under ultra-high vacuum conditions. The molecular beam apparatus was equipped with AES, a rotatable quadrupole mass spectrometer in goniometer configuration, an electron beam evaporator and a quartz microbalance. For the methanol studies the nozzle in the molecular beam apparatus was kept at room temperature, yielding a measured translational energy of 105 meV for methanol, due to a considerable relaxation of internal energy into translational energy during expansion. Higher translational energies of 250 meV were achieved by seeding the methanol in helium. The given energies were obtained from time-of-flight measurements on the beam. The Pd(111) and Rh(111) samples were cleaned and characterised by standard methods, the surface alloys were prepared by following special procedures as described in the literature<sup>1,2</sup>. The studies of water formation on palladium were performed in a second UHV apparatus, equipped with AES, LEED, QMS and a time-of-flight spectrometer for determining the energy distribution of the reaction products. The TOF apparatus consisted of two differentially pumped chambers, one containing a chopper and the other a QMS detector<sup>3</sup>. Water reaction experiments were either

done using a conventional Pd(111) sample or using a palladium permeation source, with a Pd(111) or a polycrystalline palladium terminating surface. This allowed the supply of hydrogen either in molecular form from the gas phase or by diffusion of hydrogen atoms through the bulk. In addition to that, a specially designed doser allowed also hydrogen supply from the gas phase in atomic form<sup>4</sup>. Potassium was evaporated onto the palladium samples by an SAES getter source.

### **3. Results**

## **3.1** Controlling the methanol dissociation on palladium: Influence of surface alloying and translational energy of the molecules

The interaction of methanol with metal surfaces is of interest due to its importance in petrochemical industry. It has been shown that bimetallic surfaces can have quite different catalytic properties than either monometallic component. This can be due to electronic and/or geometric changes of the surface. We have investigated the combination of the reactive metal vanadium with the less reactive metal palladium. Using a special preparation technique, evaporated V on Pd(111) occupies subsurface states<sup>5</sup>. In this case the electronic structure but not the geometric structure of the surface is altered. On the clean Pd(111) surface methanol adsorption at 100 K in the sub-monolayer regime leads to molecular adsorption. During heating of the sample about 75% of adsorbed methanol desorbs intact at around 190 K, whereas the rest dehydrogenates, leading to hydrogen (around 320 K) and CO (around 490 K) desorption<sup>6</sup>. At coverage of 1 monolayer hydrogen bonds between the dense packed molecules lead to a special bi-layer formation on the surface, similar to the case of bi-layer water<sup>7</sup>. The

hydrogen bonding leads to а lowering of the C-O bond in the adsorbed methanol, and finally to some C-O bond opening during desorption, resulting in the partial formation of water and methane. On the Pd/V alloy, on the other hand, no such C-O bond breaking could be independent observed. of the methanol coverage (Fig.1). This is a result of the decreased reactivity of the alloy due to the downshift of the d-band caused by the alloyed vanadium<sup>8</sup>. Similarly, the adsorption energy for hydrogen and CO is also decreased on the Pd/V allov compared with the pure Pd(111)surface.

An interesting observation has been made with respect to the C-



Fig.1 Mass 16 signal during thermal desorption of one monolayer of methanol on Pd(111) and Pd(111)/V. The peaks around 190 K are cracking products of methanol. Methane desorbs only from the clean Pd(111) surface around 250 K.

O bond breaking as a function of the methanol translational energy. On the pure Pd(111) surface adsorbing methanol with a mean translational energy of 250 meV (seeded in He) did not lead to a C-O bond breaking during subsequent heating. The reason for this behaviour is partial C-H dissociation taking place already during adsorption, which in turn suppresses the formation of the molecular bilayer, and hence the C-O dissociation. An activation barrier of 410 meV for the first dehydrogenation step has been calculated by density functional theory (DFT), which can be surmounted with higher probability using higher methanol translational energies. On the Pd/V alloy the increased translational energy of methanol has no influence. While a bi-layer can be formed again, there is no C-H bond breaking during adsorption on the Pd/V alloy, due to the much higher activation barrier for dehydrogenation of 910 meV. However, the reduction of the bond energy between C and O due to the bi-layer formation is not strong enough to overcome the much higher C-O dissociation energy for methanol on the Pd/V alloy, according to DFT calculations<sup>6</sup>.

# **3.2 Reaction of methanol with rhodium: Influence of surface alloying and oxygen**

The interaction of methanol with rhodium is also of great importance for many catalytic processes, e.g. for methanol powered fuel cells. In this work we will focus on the reactivity of Rh(111) and vanadium modified rhodium. We have prepared a Rh/V subsurface alloy by evaporation of 0.3 monolayers vanadium at 823 K onto the Rh(111). In addition to that we have prepared vanadium islands on the surface by evaporation of 0.3 ML V at room temperature. The experimental details are described elsewhere<sup>1</sup>. Fig. 2 compiles the sticking (reaction) coefficients of methanol on Rh(111), Rh(111)+V(subsurface) and Rh(111)+V(subsurface). On the clean Rh(111) surface the initial sticking coefficient

is close to unity at low surface temperature but decreases rapidly at surface temperatures for which methanol desorption takes place. For a proper interpretation of the result we have to take into account that these experiments were done by the King and Wells method<sup>9</sup>. In the case of "zero initial sticking" and at temperatures above the desorption temperature one cannot distinguish between true zero sticking and finite sticking with immediate desorption. However, if a "finite sticking" is measured above the desorption temperature (removal of methanol from the gas phase) then this is a clear



Fig. 2 Sticking (reaction) coefficients of methanol on A: Rh(111), B: Rh(111) + V(subsurface) and C: Rh(111) + V(islands). Curve D represents the data for Rh(111) + 0.5 ML oxygen pre-coverage

indication of methanol dehydrogenation during adsorption and desorption of reaction products (CO, H<sub>2</sub>). This is indeed the case for the subsurface alloy and even more pronounced for the rhodium with vanadium islands on the surface (Fig. 2). Apparently, the reactivity for methanol dehydrogenation is increased on the latter surfaces with respect to the clean Rh(111) surface. Unfortunately, the high reactivity of the Rh/V(island) surface diminishes after a few adsorption/desorption cycles, most probably due to poisoning of the V-islands by CO dissociation.

The reason for the apparent contradiction to the previously described decrease of the activity for alloys is the different density of states (DOS) for Pd and Rh. Rhodium has one electron less in the d-band compared with palladium. Although the alloying of Rh with V again leads to a downshift and narrowing of the d-band, there is still quite a significant DOS at the Fermi level. Therefore the reactivity of the alloy is rather increased than decreased. However, one should have in mind that a complete description of the reactivity of a metal surface has to include not only the Fermi level DOS but also the unoccupied d-states, the centroid of the d-band and the hybridisation between bonding and anti-bonding adsorbate states and the metal d-states<sup>10</sup>.

Pre-adsorbed oxygen (0.5 ML) on the individual surfaces has a quite different effect on methanol adsorption. On the Rh(111)+O surface the probability for dehydrogenation increases, resulting in a significant initial reaction coefficient well above the desorption temperature (see Fig. 2). This is most probably due to the additional bonding between the hydroxyl group and the pre-adsorbed oxygen, leading to O-H bond breaking more easily<sup>11</sup>. Interestingly, for the Rh/V subsurface alloy and the Rh/V(island) surface with pre-adsorbed oxygen we obtain a similar temperature dependence of the initial sticking/reaction coefficient as for the clean surface. But this means that in this case pre-adsorbed oxygen decreases the reactivity relative to the surfaces without oxygen. One possible explanation is that now the true sticking coefficient is reduced, i.e. the activation barrier for molecular methanol adsorption is increased.

# 3.3 Water formation reaction on palladium: Influence of potassium and atomic hydrogen

The water formation reaction on palladium has been studied extensively in the past and can be regarded as a model system. In this work we have focused on two aspects: a) How can we influence the water reaction rate on Pd(111) by different types of hydrogen supply? b) What is the effect of potassium on palladium on the water formation? In both cases we have measured the translational energy of the reaction products by time-of-flight spectroscopy. With respect to hydrogen supply from the gas phase we have either used Maxwellian beams of molecular hydrogen at room temperature or Maxwellian beams of atomic hydrogen, as produced in a special doser at 2000 K<sup>12</sup>. In addition to that we have supplied hydrogen to the palladium surface by permeation through the bulk in a special permeation device<sup>13</sup>. In all cases molecular oxygen was supplied to the surface from the isotropic gas phase. For the reaction of molecular

hydrogen with molecular oxygen we have measured the water formation rate for a large variation of the  $H_2/O_2$  ratio and over a wide temperature range, in order to find the optimum pressure and impingement ratios, respectively<sup>14</sup>. It turned out that below 450 K surface temperature the optimum impingement ratio  $N_{H2}/N_{O2}$  is 2.7. With increasing surface temperature this ratio decreases linearly to 2.0 at around 900 K, from where it remains constant. The reason for this behaviour is the change of the sticking coefficients for oxygen and hydrogen as a function of temperature. Whereas the sticking coefficient for hydrogen remains nearly constant at 0.45 over the whole temperature range<sup>15</sup>, the sticking coefficient for oxygen decreases from 0.55 to 0.45 between 450 K and 650 K<sup>16</sup>. Time-of-flight measurements on the originating water molecules yielded a mean translational energy corresponding to the sample temperature (Fig. 3). This shows that the reaction is of Langmuir-Hinshelwood type.

We expected to be able to increase the water reaction rate by using atomic hydrogen instead of molecular hydrogen, due to the higher sticking coefficient for atomic hydrogen. Interestingly, the opposite is the case. At a surface temperature of 450 K the optimum impingement ratio is now increased to  $N_{\rm H}/(2N_{O2}) = 3.3$ . The reason for this peculiar result is the fact that atomic hydrogen, which can be considered as a hot atom on the surface<sup>17</sup>, not only reacts with oxygen to form water but also with adsorbed hydrogen. This reaction is of the Eley-Rideal type or Harris-Kasermo type, as observed for similar systems<sup>18</sup>. From a quantitative investigation it results that only about 20% of the impinging hydrogen reacts with oxygen to form water. However, the translational energy of the desorbing water

molecules, as measured with time-of-flight spectroscopy, is again thermalized to the surface temperature (Fig. 3). This shows that the water formation reaction, which actually proceeds via OH + H  $\rightarrow$  H<sub>2</sub>O, is again of Langmuir-Hinshelwood type.

Finally, we have studied the water formation by reaction of permeating hydrogen with adsorbing oxygen. In this case the surface is "exposed" to atomic hydrogen which comes from subsurface sites. If the oxygen impingement rate is sufficiently high, all the hydrogen approaching the



Fig. 3 Time-of-flight spectra for desorbing water after different types of hydrogen + oxygen reactions. In all cases thermalized water desorption is observed.

surface from the bulk side reacts with oxygen. No significant parallel associative hydrogen desorption was observed. That means that 100 % of the available hydrogen can be consumed to form water. The translational energy of the

desorbed water is again completely accommodated to the surface temperature (Fig. 3).

Modification of metal surfaces to change their reactivity or selectivity is a key aspect of heterogeneous catalysis. We have studied the influence of potassium adsorbed on a polycrystalline and a (111) single crystal palladium surface on the water formation reaction, using the permeation technique. The main results of these investigations are as follows: The water formation rate is significantly suppressed. This is most probably caused by the much smaller sticking coefficient of  $O_2$  on the potassium covered palladium surface, due to an increased activation barrier for dissociation, like in the case of dissociative hydrogen adsorption on potassium covered palladium<sup>19</sup>. However, the translational energy distribution of the produced water molecules is again Maxwellian, corresponding to the surface temperature.

Hydrogen desorbing from the clean palladium surface (without coexposure to oxygen) exhibits a Maxwellian energy distribution with  $\langle E \rangle = 2kT$ , whereas hydrogen desorbing from the potassium covered surface shows a clearly hyper-thermal energy distribution, with a mean translational energy of about 4kT. This corresponds nicely with experiments on dissociative hydrogen adsorption via detailed balancing<sup>19</sup>. Interestingly, when the potassium covered surface is exposed to oxygen, the mean translational energy of the permeated/desorbed hydrogen decreased almost to the thermalized value. This means that areas on the surface have to be created with reduced activation barriers for associative hydrogen desorption. Indeed, it has been shown recently that co-adsorption of potassium and oxygen on rhodium surfaces leads to the formation of stable islands of dense packed K+O layers, surrounded by oxygen and potassium free areas<sup>20</sup>.

### 4. Summary

We have investigated several model systems with respect to a tailoring of catalytic properties of metal surfaces. On a Pd(111) surface the C-O bond of methanol at high coverage is partially opened due to the formation of hydrogen bonds. This behaviour is suppressed in case of a subsurface vanadium layer on the palladium surface. This is a result of the decreased reactivity of the alloy due to the downshift of the d-band and lowering of the DOS at the Fermi edge caused by the alloyed vanadium. On the other hand the dehydrogenation reaction for methanol on Rh(111) can be enhanced by alloying the surface with vanadium. This is again a consequence of the altered density of states of the surface alloy. The reason for the opposite influence of surface alloying is due to the different DOS for Pd and Rh. In the latter case the downshift of the less filled d-band leads to an increase of the DOS at the Fermi energy. For the water formation reaction on Pd(111) we have studied the influence of the specific hydrogen supply. Reaction of oxygen with impinging molecular and atomic hydrogen, as well as with permeating hydrogen has been studied. Most interestingly, with atomic hydrogen the water reaction rate decreased, due to concomitant associative hydrogen desorption of the Eley-Rideal type. In all cases the translational energy

distribution of the formed water molecules obeyed a Maxwellian flux, corresponding to the surface temperature.

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### References

- <sup>9</sup> D.A. King and M.G. Wells, Proc. Royal Soc., London, Ser. A 339 (1974) 245.
- <sup>10</sup> B. Hammer and J.K. Norskov, Surface Sci. 343 (1995) 211.
- <sup>11</sup> F. Solymosi, T.I. Tarnoczi, and A. Berko, J. Phys. Chem. 88 (1984) 6170.
- <sup>12</sup> C. Eibl, G. Lackner, and A. Winkler, J. Vac. Sci. Technol. A 11 (1998) 2979.
- <sup>13</sup> G. Pozgainer, L. Windholz, and A. Winkler, Meas. Sci. Technol. 5 (1994) 947.
- <sup>14</sup> G. Pauer and A. Winkler, J. Chem. Phys. 120 (2004) 3864.
- <sup>15</sup> M. Beutl, M. Riedler, and K.D. Rendulic, Chem. Phys. Lett. 247 (1995) 249.
- <sup>16</sup> P. Sjövdall and P. Uvdal, Chem. Phys. Lett. 282 (1998) 355.
- <sup>17</sup> Th. Kammler, D. Kolovos-Vellianitis, and J. Küppers, Surface Sci. 460 (2000) 91.
- <sup>18</sup> A. Winkler, Appl. Phys. A67 (1998) 637.
- <sup>19</sup> C. Resch, H.F. Berger, K.D. Rendulic, and E. Bertel, Surface Sci. 316 (1994) L1105.
- <sup>20</sup> S. Günther, H. Marbach, R. Hoyer, R. Imbihil, L. Gregoratti, A. Barinov, and M. Kiskinova, J. Chem. Phys. 117 (2002) 2923.

<sup>&</sup>lt;sup>1</sup> G. Krenn and R. Schennach, J. Chem. Phys. 120 (2004) 5729.

<sup>&</sup>lt;sup>2</sup> M. Beutl, J. Lesnik, E. Lundgren, C. Konvicka, P. Varga, and K.D. Rendulic, Surface Sci. 447 (2000) 245.

<sup>&</sup>lt;sup>3</sup> C. Eibl and A. Winkler, J. Chem. Phys. 117 (2002) 834.

<sup>&</sup>lt;sup>4</sup> C. Eibl, G. Lackner, and A. Winkler, J. Vac. Sci. Technol. A 16 (1998) 2979.

<sup>&</sup>lt;sup>5</sup> C. Konvicka, Y. Jeanvoine, E. Lundgren, G. Kresse, M. Schmid, J. Hafner, and P. Varga, Surface Sci. 463 (2000) 199.

<sup>&</sup>lt;sup>6</sup> R. Schennach, A. Eichler, and K.D. Rendulic, J. Phys. Chem. B 107 (2003) 2552.

<sup>&</sup>lt;sup>7</sup> J.J. Chen, Z.C. Jiang, Y. Zhou, B.R. Chakraborty, and N. Winograd, Surface Sci. 328 (1995) 248.

<sup>&</sup>lt;sup>8</sup> J.C. Fuggle, F.U. Hillebrecht, R. Zeller, Z. Zolnierek, and P.A. Bennet, Phys. Rev. B 27 (1982) 2145.