FEM STUDY OF CO AND H_2 INTERACTION WITH A SUPPORTED BIMETALLIC CATALYST: Mo–Pd/Al_2O_3/W

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Dedicated to Professor Otto Wichterle on the occasion of his 80th birthday.

Palladium and molybdenum were deposited onto a continuous layer of Al_2O_3 covering a tungsten field emitter. The adsorption of CO at 300 K on such a model system shows unexpected increase in the electron emission from both metals. This effect can either be understood in terms of a resonance enhancement of electron tunneling, or it can result from specific interactions of CO with supported clusters as compared to CO interaction with bulk metals. Coadsorption of CO and H_2 on the mixed molybdenum and palladium surface exhibits features different from coadsorption on the individual metals.

Recently we have proved that the system metal–alumina–metal can be successfully used for modelling of supported bimetallic catalysts in FEM. The interactions of N_2 and of CO with metallic catalysts were investigated. The results of the study of nitrogen interaction corresponded to the results obtained with different model systems (see refs[1,2] and quotations therein). However, the interaction of CO with Pd and Mo clusters deposited on an alumina layer differed qualitatively from the interaction on bulk metals.

EXPERIMENTAL

The experiments were performed in a commercial stainless steel UHV apparatus. The residual pressure was ≈ 2 . 10^{-8} Pa. Gases were introduced via a saphire leak valve from an all-glass gas-handling system. Purity of gases was checked by a Finnigan quadrupole mass spectrometer. All the experiments were performed under dynamic conditions. The gas mixtures were prepared in the gas-handling system and thereafter dosed into the vacuum chamber.

The tungsten tips were etched electrochemically in solution of KOH and NH_4OH applying 2 to 5 V a.c.. The tips were cleaned by short flashing to about 2 500 K in vacuum, the residual gas pressure being lower then 10^{-7} Pa.

The tip temperature was estimated by measuring the heating current through the tungsten loop (calibrated with an optical pyrometer). Pyrometer measurements were corrected to true temperatures by using reported emissivity values for tungsten. The error in the temperature estimation was about ±50 K in the range of 900 to 2 600 K.

RESULTS AND DISCUSSION

Formation of the Pd–Mo/Alumina System

A tungsten tip (Fig. 1*a*) was cleaned by flashing to ≈ 2 500 K and thereafter covered by aluminum succesively from the front, the right and the left side (Fig. 1*b*). Oxidation was performed by heating the tip to 1 200 K in the atmosphere of $1 \cdot 10^{-4}$ Pa of oxygen for 30 s. The tip was then heated several times to 1 200 K in vacuum (Fig. 1*c*). Molybdenum was deposited from the left side (Fig. 1*d*) and Pd was subsequently evaporated from the right side (Fig. 1*e*). It is evident that the emission current from the particullar zone of the deposited metal depends on the local radius of curvature, related to the thickness of the layer. After subsequent deposition of molybdenum (Fig. 1*f*) the contributions to the emission current from both metals are comparable, the brightest region being the zone where Pd and and Mo overlap.

Adsorption of CO at 300 K

Figure 2*a* shows the Mo–Pd system after heating to 1 100 K (Mo and Pd on the left and right side of the picture, respectively). At this temperature molybdenum as well as palladium partially evaporate. This process can be used for cleaning the surface. The picture in Fig. 2*b* was taken after 10 min of exposure to $5 \cdot 10^{-6}$ Pa of CO (≈ 30 Langmuir) at 300 K.

The negative images taken at a constant voltage were digitalized and the intensity profiles along a chosen line were plotted (Fig. 2). The curves in Fig. 2*c* represent the density of the black colour in the negative image. This density is considered to be proportional to the emission current giving thus the qualitative information about the work function changes of the particular surface region. The dashed and full curves represent the intensity profiles of the Figs 2*a* and 2*b*, respectively.

Comparison of these two curves shows that the work function decreases during the CO adsorption both on the molybdenum and on the palladium surfaces. This is an unexpected result, because it is known (e.g. refs[3 – 7]) that on the bulk samples of palladium and molybdenum the adsorption of a sufficient amount of CO causes an increase in work function of about 1 eV and 0.2 – 0.4 eV, respectively.

There are two possible explanations of this effect: (i) chemical properties of small clusters supported on alumina may significantly differ from the bulk metal properties; (ii) the observed increased electron emission after CO adsorption on the sample surface can be due to the resonance enhanced tunneling (if there exists an electron state in the

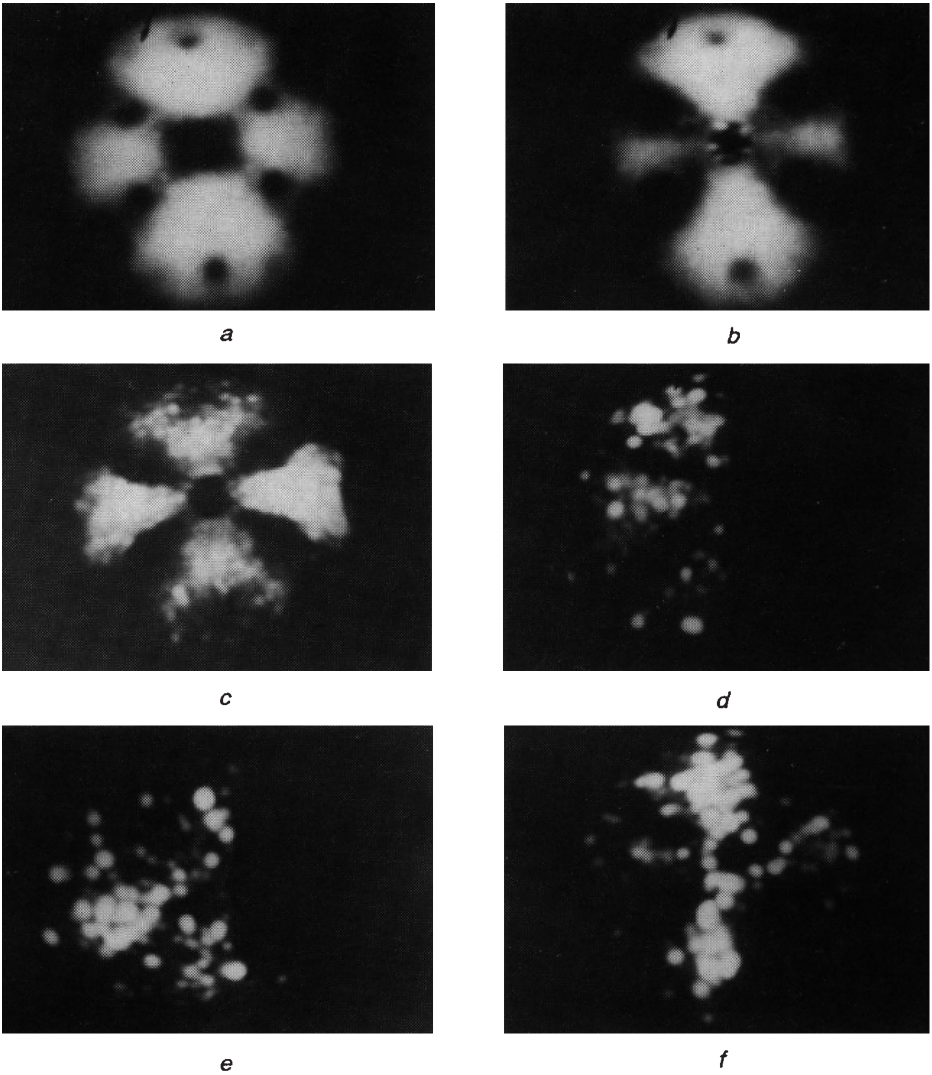


FIG. 1

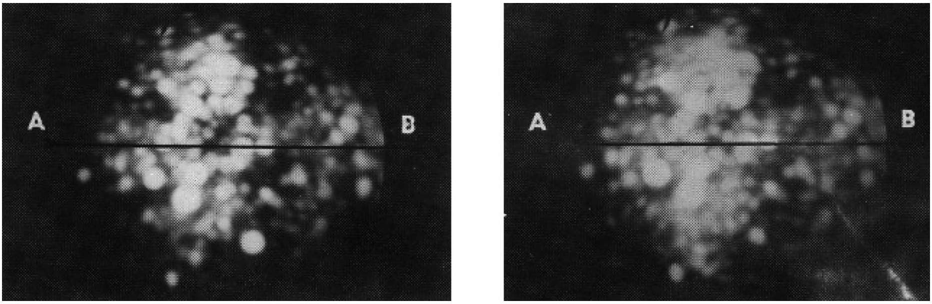
FEM images of: *a* a clean tungsten tip (image conditions: U = 4.2 kV, T = 300 K, I = 0.20 μA); *b* aluminum deposited onto a tungsten tip (U = 4.3 kV, T = 300 K, I = 0.12 μA); *c* a clean alumina layer after heating to 1 200 K in vacuum (image conditions: U = 5.8 kV, T = 300 K, I = 0.04 μA); *d* molybdenum deposited onto the alumina from the left side (image conditions: U = 4.4 kV, T = 300 K, I = 0.03 μA); *e* palladium deposited additionally to molybdenum from the right side (image conditions: U = 3.8 kV, T = 300 K, I = 0.04 μA); *f* some more molybdenum additionally deposited from the left side (image conditions: U = 3.6 kV, T = 300 K, I = 0.17 μA)

CO molecule having energy close to the Fermi energy of the underlying tungsten, the probability of electron tunneling can increase by an order of magnitude[8,9]).

Coadsorption and Surface Reaction of CO and H_2 at 300 K

Figure 3*a* shows a clean Pd–Mo/Al_2O_3/W system. The photo in Fig. 3*b* was taken after 10 min of exposure to 5 . 10^{-6} Pa of the CO and H_2 mixture (the ratio approximately 1 : 1) (≈ 30 Langmuir).

Dashed and full curves in Fig. 3*c* represent the intensity profiles along the lines marked in Figs 3*a* and 3*b*, respectively. The photodensity curves show clearly that within the regions of clean molybdenum and clean palladium, electron emission increases after the CO and H_2 coadsorption, whereas the central zone of the overlapping metal layers exhibits a lowering of the field emission current.



a *b*

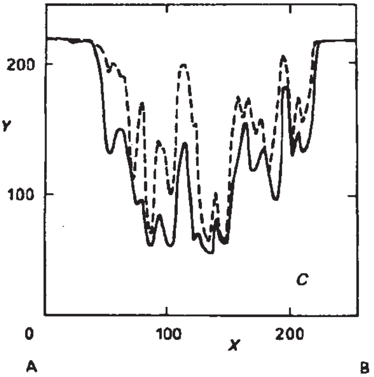


FIG. 2

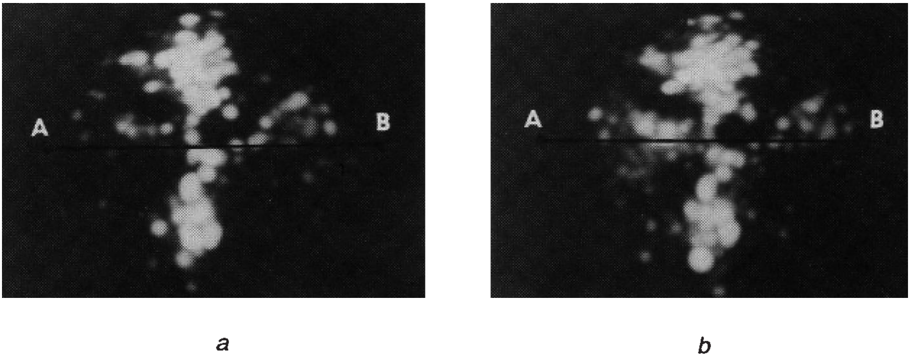
FEM image of Mo–Pd/Al_2O_3/W system: *a* cleaned by heating to 1 100 K (image conditions: U = 5.6 kV; T = 300 K; I = 0.13 μA); *b* after 10 min in 5 . 10^{-6} Pa of CO (image conditions: U = 5.6 kV; T = 300 K; I = 0.30 to 0.50 μA – flickering); *c* the dashed and full curves correspond to the intensity profiles of the Figs 2*a* and 2*b*, respectively. Zero on the Y-axis corresponds to a completely bright region in the image, the value 255 to zero emission. X-axis represents the coordinate along the line A–B in arbitrary units

This suggests, that at the region of mixed palladium and molybdenum surface a reaction occurs which is qualitatively different from the mere coadsorption of carbon monoxide and hydrogen on the islands of pure palladium and pure molybdenum.

CONCLUSIONS

After the adsorption of CO onto a Mo–Pd/Al_2O_3/W sandwich system at room temperature the emission current at a constant voltage from both metals increases. This effect can be due to: (i) the work function decrease which is, however, in contradiction to the behaviour of CO on the bulk molybdenum and bulk palladium; (ii) the resonance enhancement of the electron tunneling due to an appropriate state within the carbon monoxide molecule.

During the coadsorption of CO and H_2 mixture at room temperature a surface reaction occurs on the area where palladium and molybdenum are mixed or alloyed. This



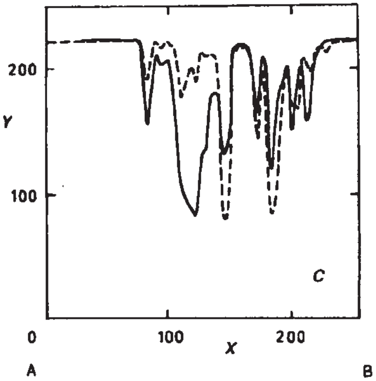


Fig. 3
FEM image of Mo–Pd/Al_2O_3/W system: *a* clean system (the same is in Fig. 1*f*) (image conditions: U = 3.6 kV; T = 300 K; I = 0.17 μA); *b* after 10 min in 5 . 10^{-6} Pa of CO + H_2 (1 : 1) mixture (image conditions: U = 3.9 kV; T = 300 K; I = 0.09 μA); *c* the dashed and full curves correspond to the intensity profiles in Figs 3*a* and 3*b*, respectively. Zero on the Y-axis corresponds to a completely bright region in the image, the value 255 to zero emission. X-axis represents the positional coordinate along the line A–B in arbitrary units

surface reaction differs qualitatively from the interaction of this gas mixture with islands of the individual metals.

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