SURFACE INTERACTIONS IN Pd–Nb SYSTEM AND THEIR RELATION TO BASIC QUESTIONS AND PRACTICAL CATALYSIS

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Room temperature adsorption–desorption properties of Pd overlayers of various thicknesses were studied by thermal desorption spectroscopy of carbon monoxide. Pd overlayers were deposited on clean and oxidized Nb foil (NbO_x/Nb). Adsorption properties of Pd overlayers deposited on clean Nb at temperature 350–400 K were not influenced by annealing in the temperature range 400 K to 600 K. Annealing above this temperature caused the decrease in the area of the Pd surface. It became probably smoother, exhibiting lower number of adsorption sites for CO. Non-annealed Pd overlayers deposited on the oxide carrier (NbO_x/Nb) at temperatures between 350 and 400 K possessed the same adsorption capability as Pd deposited directly on Nb. Pd atoms thus neither massively penetrated into the oxide layer nor were encapsulated by NbO_x.

Key words: Thermal desorption spectroscopy; Carbon monoxide chemisorption; Supported catalysts; Pd/Nb; Pd/NbO_x/Nb.

Understanding surface phenomena is crucial point for several fields of practical importance *e.g.* heterogeneous catalysis, electrochemistry or electronics. Most of the commercially interesting metallic heterogeneous catalysts are transition metals, dispersed as small particles on oxide carriers. However, the chemical and catalytic properties of highly dispersed metals differ from those of bulk metals. This is probably due to the interaction of metallic clusters with the underlying substrate.

Relationship between catalytic properties and electronic or geometric structure has been already extensively studied in the past. Many experimental techniques and approaches have been used to improve the understanding of this phenomena; however, the full knowledge has not been attained[1].

Large perturbation of metal–metal bonds was found when an early transition metal was covered by about one monolayer of a late transition metal[1–6]. Under such conditions electronic structure of the surface layer differed from electronic structure of both metal constituents. Moreover, the overlayer has grown usually in a pseudomorphic mode, *i.e.*, overlayer fitted the geometrical structure of the underlying metal which was different from that of the overlayer[1,2].

Additionally, strong metal–substrate interaction was also found with metal overlayers deposited on the oxide substrates. Depending on the type of the used carrier, this effect – Strong–Metal–Substrate–Interaction (SMSI) – was responsible for the increased catalytic activity[7]. In other cases metal clusters deposited on the oxide surfaces exhibited the tendency to diffuse into the oxide bulk or to be encapsulated partially or fully by a thin oxide layer[8]. In the latter case, the catalytic activity of the metal particles was decreased or even eliminated.

In this study we focus on a combination of niobium and palladium as examples of an early and late transition metal which represents a good model system for the investigation of some fundamental problems like the influence of a metallic (Nb) or of an oxide (NbO_x) carrier on the surface properties of the catalyst (Pd), SMSI effect, diffusion of metallic atoms through an oxide support, *etc*. Moreover, these metals are important in practical catalysis as well: Pd, *e.g.*, in a three-way catalyst for an automotive exhaust convertor[9]. From the latter fact followed also the choice of carbon monoxide as an interesting reactant. Nb and Nb compounds are interesting catalytic materials, both as carriers and/or promotors, exhibiting redox and acid properties and even the photosensitivity[10].

EXPERIMENTAL

Experiments were carried out in an ultrahigh-vacuum apparatus with a base pressure 10^{-8} Pa, described in detail elsewhere[11]. A recrystallized Nb foil (13 × 3.5 × 0.115 mm) of purity 99.9% (Leybold–Heraeus) was a sample. It was resistively heated and its temperature was followed by W–Ta thermocouple. Standard procedure[11–14] was used to outgas and clean the sample surface (this procedure included repeated heating of the sample in oxygen at pressure $\approx 10^{-5}$ Pa for half an hour and flashing to the temperature 2 500 K). Measurements of the work function changes ($\Delta\phi$) were used to control the state of the sample surface and its modification by oxidation, Pd deposition and CO adsorption. Morphology of oxidized Nb was checked by *ex-situ* atomic force microscopy (AFM). It was found that Nb surface recrystallized to microscopic domains of tens μm in diameter after heating to 2 500 K in vacuum and that temperature during oxidation did not significantly influence the domain size[15]. All the oxide layers were prepared in the same way: by exposure of Nb at temperature 700 K to oxygen at a pressure of 10^{-4} Pa (purity 99.999%, Linde) for 10 min (oxygen exposure ≈600 L). Pd was deposited from an electrically heated Pd wire (purity 99.9975%, Johnson–Matthey). Carbon monoxide (purity 99.97%, Linde) was adsorbed to saturation coverage (30 L) under dynamic conditions by means of a pseudomolecular beam, directed to the sample surface. Thermal desorption spectroscopy (TDS) with quadrupole mass spectrometer was used to monitor desorption of mass 28 (formed exclusively by carbon monoxide) from Pd overlayers. The rate of the temperature sweeps was ≈11 K/s.

RESULTS AND DISCUSSION

Thermal stability of metal clusters on oxide supports is one of important problems in catalytic studies. Figure 1 demonstrates several examples of carbon monoxide desorption spectra from annealed and non-annealed Pd–Nb systems. Pd was deposited on cleaned Nb surface at temperature of 350–400 K. The amount of deposited Pd ranged between 6 and 10 monolayers[11] (Pd_{6-10} – subscript at palladium symbol denotes value of the surface coverage in monolayers of Pd). Such layers exhibited identical adsorption properties as those of bulk Pd[11,12]. After thermal treatment, carbon monoxide at pressure $6.7 . 10^{-5}$ Pa was introduced into the apparatus for 1 min (corresponding to the exposure of 30 L). This resulted in saturation coverage of carbon monoxide at 330 K. Thermal desorption was applied within several minutes after CO adsorption.

Curve *1* in Fig. 1 presents desorption from the non-annealed Pd surface. Curves *2–5* show CO desorption from Pd/Nb surface annealed to different temperatures. It can be seen that both temperature of the peak and its area are decreasing with increasing the annealing temperature. These data are shown in detail in Figs 2 and 3. Low temperature shoulder on curve *1* (non annealed Pd overlayers exhibiting bulk Pd properties) is attributed to desorption of compressed CO layer (which is formed at saturation CO coverage) with lateral interactions[16].

Figure 2 shows temperature of the desorption peak for carbon monoxide desorbed from Pd_{6-10}/Nb and from non-annealed surfaces as a function of the annealing temperature. It can be seen that the temperature of CO desorption peak (T_{max}) remains nearly constant (within the experimental error) up to the annealing temperature ≈550 K. Then T_{max} starts to decrease rapidly. Similar course is observed also for the area of CO desorption peak, namely A_{CO}. At a constant pumping speed, the area is related to the desorbed amount of carbon monoxide. This is shown as a function of the amount of deposited palladium in Figure 3. One can see that the desorbed amount of CO starts to decrease above the annealing temperature of ≈600 K. Clearly, adsorption properties of Pd overlayers do not change up to the annealing temperature 550–600 K. Above this temperature both parameters characterizing the desorption peak decrease.

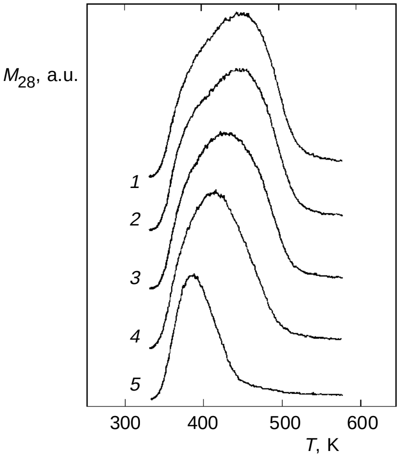

FIG. 1
Thermal desorption spectra of carbon monoxide (partial pressure of mass 28 – M_{28}) from annealed Pd_{6-10}/Nb system. After the palladium deposition the sample was annealed for 2 min at a given temperature: *1* without annealing, *2* 450 K, *3* 600 K, *4* 700 K, *5* 800 K

Morphology changes can be qualitatively judged on the basis of the presented TDS data. We have found[11,12] that Pd overlayers grow on Nb mainly in Stranski–Krastanov mode[7] (formation of 3-dimensional (3D) clusters on top of the first completed monolayer). Thus 3D islands with relatively high number of adsorption sites were exposed to the gas phase in contrast to layer-by-layer growth mode (Frank–van der Merve mode[7]). Moreover, Nb sample was polycrystalline and its surface was not smooth. We have found domains having the size of tens of μm on the foil surface[15]. The decrease in the desorbed amount of CO indicated lowering of the number of adsorption sites. Since the saturation coverage of CO has been attained in all experiments it could be concluded that Pd surface became smoother under these conditions (*i.e.*, the sample surface decreased). Consequently, it exhibited lower adsorption capacity and also weaker CO chemisorption bond could be expected. Moreover, our previous experiments revealed that the decrease in the deposited amount of palladium caused weakening of CO–Pd bonds (*i.e.*, T_{max} decreased[11,12]). Since Pd desorbed from refractory metals such as Nb,

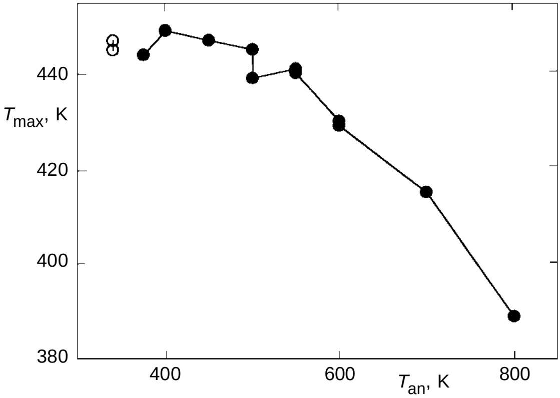

FIG. 2
Temperature of the carbon monoxide desorption peak (T_{max}) from annealed Pd_{6-10}/Nb as a function of annealing temperature (T_{an}). Data for non-annealed Pd overlayers are included (❍)

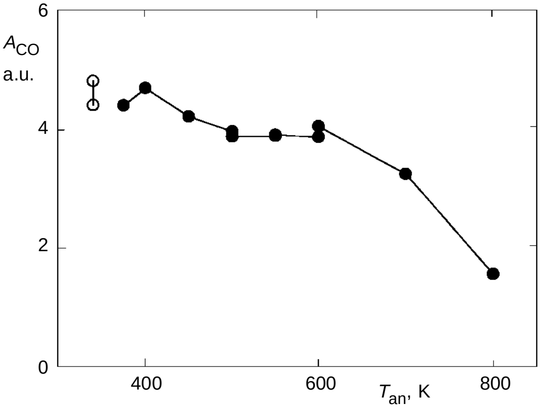

FIG. 3
Area of carbon monoxide TDS peak (A_{CO}) from annealed Pd_{6-10}/Nb as a function of annealing temperature (T_{an}). Data for non-annealed Pd overlayers are included (❍)

Ta, W, and Mo at temperatures above 1 100 K (refs[17,18]) one could not exclude the effect of smaller patches of palladium surfaces exposed to the gas phase which are due to the diffusion of a part of palladium into the subsurface region of Nb at temperatures above 550–600 K.

Figure 4 shows the amount of carbon monoxide (represented here as the area of CO desorption peak) desorbed from Pd/NbO$_x$/Nb as a function of Pd deposition time (which is used as a rough measure of the Pd amount). Oxide layers have been prepared by a standard routine which included exposure of Nb foil at temperature of 700 K to oxygen at a pressure of 10^{-4} Pa. The thickness of oxide layer prepared in this way is estimated, according to literature, to be between 1 and 2 nanometers[19,20]. These data are compared in Fig. 4 with our previous results on bimetallic system Pd/Nb (refs[11,12]). In both cases identical rates of Pd deposition and thermal desorption as well as identical substrate temperatures were used.

One can see in Fig. 4 that desorbed amount of carbon monoxide rises with increasing amount of deposited Pd to a saturation value at the longest deposition time. Both Pd/NbO$_x$/Nb and Pd/Nb exhibit the same amount of desorbed CO within the experimental error. It implies that the “identical” number of Pd adsorption sites is available on both surfaces. Moreover, Pd overlayers do not tend to diffuse into metals with high surface energies (such as Nb, Ta, W and Mo) at temperatures below 400 K (ref.[21]). Thus no formation of Pd–Nb alloy can be expected with non-annealed Pd overlayers deposited at 350–400 K.

CONCLUSIONS

Adsorption properties of Pd overlayers deposited on clean Nb are not influenced by annealing in the temperature range from 400 K to 600 K. Annealing above this temperature causes the decrease in both desorbed amount of Pd and temperature of the CO desorption peak. This behavior is interpreted as a consequence of smoothening of poly-

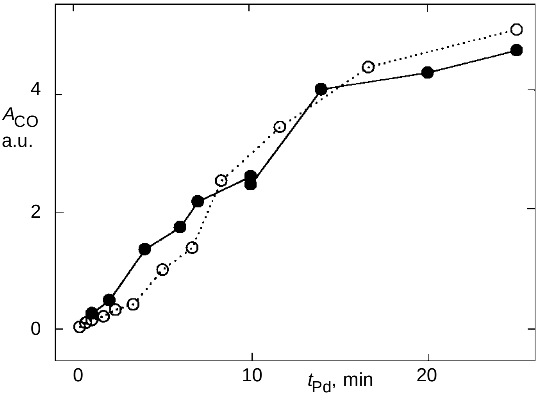

Fig. 4
Area of carbon monoxide TDS peak (A_{CO}) as a function of deposited Pd amount (expressed by deposition time, t_{Pd}) for Pd/NbO$_x$/Nb (●) and Pd/Nb (○) systems (see also ref.[15])

crystalline Pd overlayers (*i.e.*, lowering of the palladium surface). Some Pd atoms might also diffuse into the Nb subsurface region at higher temperatures (550–600 K).

Non-annealed Pd overlayers deposited on the oxide carrier NbO_x/Nb at 350–400 K exhibit identical adsorption properties as Pd on Nb. Thus we conclude that Pd atoms are neither massively lost in the oxide layer (due to diffusion into the NbO_x volume) nor they are encapsulated by NbO_x.

The oxide interlayer NbO_x (having different structure from that of the bare niobium surface) excludes direct structural influence of niobium on the morphology of the palladium overlayer. The observed identical behavior of Pd/Nb and Pd/NbO_x/Nb systems with respect to CO is obviously due to the electronic Pd–Nb interaction which is not hindered by the NbO_x interlayer (exhibiting electrical conductivity).

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