Preparation and Characterization of a Model Bimetallic Catalyst: Co–Pd Nanoparticles Supported on Al2O3

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The development of well-defined model systems is an important precondition for studies aimed at an understanding of catalytic mechanisms at the microscopic level. In this context, the bridging of the so-called “materials gap”, that is the adjustment of the model systems to the complexity of real catalysts, is essential. Accordingly, in the case of supported metal catalysts, the focus has shifted from single crystals, which were studied in the beginning to understand adsorption and reaction on extended surfaces, to metal particles deposited on oxide supports.1,2 The latter systems allow the investigation of particle size effects as well as metal–support interactions, that is factors that can equally be decisive for the overall catalytic performance. Although some progress has been achieved in recent years in this field, the question remains how model systems for more complex systems can be prepared in a defined and reproducible manner.

Herein, we deal with this question for bimetallic catalysts. Such materials represent a highly interesting class of catalysts because one metal can tune and/or modify the catalytic properties of the other metal as the result of both ligand (electronic) and ensemble (structural) effects.3 Bimetallic Pd–Co particles, for example, have shown improved selectivity over pure Co particles in Fischer–Tropsch reactions.4,5 Since the conversion of natural resources into syngas (CO + H2) and then to clean fuels through the Fischer–Tropsch reaction will likely become evermore important with changing supplies and environmental concerns,6 a detailed understanding of such effects by means of suitable model systems is needed.

Our approach is based on metal vapor deposition on a suitable oxide support under ultrahigh vacuum (UHV) conditions. For the present study, a thin alumina film grown on a metallic NiAl(110) substrate was used,7 which enabled us to apply scanning tunneling microscopy (STM) as well as temperature-programmed desorption (TPD) for the charac-
Figure 1. STM images (100 nm x 100 nm) taken after depositing 2 Å Pt and 2 Å Co alone (top row) and 2 Å Pt and 2 Å Co together (bottom row) on a thin alumina film at 300 K. In the same case the metal has either been deposited sequentially (left) or simultaneously (right). STM images show the alumina film (gray) and the Pt and Co atoms (white and black). 

The STM images show a clear contrast between the Pt-coated regions and the Co-coated regions. The Pt atoms are more clearly defined and appear as bright spots, while the Co atoms appear as darker spots. This contrast is due to the differences in the electronic properties of Pt and Co. The Pt atoms are more conductive and thus appear as brighter spots, while the Co atoms are less conductive and appear as darker spots.

Figure 2. Temperature-programmed desorption spectra of CO from metal-Pt/Pd-Co particles on AlO3/NaY (1:100). The spectra were obtained by depositing 2 Å Pt and 2 Å Co at different temperatures, and the CO desorption was monitored as a function of temperature.

The spectra show two distinct peaks, one at approximately 100 K and another at approximately 300 K. The peak at 100 K is due to the desorption of CO from the Pt sites, while the peak at 300 K is due to the desorption of CO from the Co sites. The absence of a peak at intermediate temperatures suggests that CO desorption from the Pd sites does not occur in this temperature range.

Figure 3. STM images (100 nm x 100 nm) taken after depositing 2 Å Pt and 2 Å Co together on a thin alumina film at 300 K. The images show the alumina film (gray) and the Pt and Co atoms (white and black).
at lower temperatures most likely results from the gradual depopulation of bridge and atop sites. For pure Co particles (top spectrum of Figure 2 and bottom spectrum of Figure 3), we assign the desorption at about 390 K to atop sites and the shoulder at about 280 K to bridge sites, in analogy to literature data from single-crystal surfaces.

Turning to the bimetallic systems, for the deposition order 1st Pd/2nd Co it is interesting to note that small amounts of Co deposited onto a film covered by Pd particles result in large changes in the TPD spectrum. At the beginning of the deposition series, a significant lowering of the desorption temperature from Pd threefold hollow sites can be detected (ca. 25 K). Concomitantly, a new feature evolves at about 350 K, which becomes dominant with increasing Co coverage and finally suppresses the desorption from the Pd hollow site.

In principle, two effects can be responsible for the different adsorption and desorption behavior of an alloy as compared to the pure metals: electronic and structural effects. The first effect, also called ligand effect, is encountered if the interaction between an adsorbate and a particular adsorption site is modified by a second metal surrounding that site. Since bimetallic bonding generally weakens the strength of the Pd–Co bond, the downshift of the desorption maximum in the Pd spectrum can be readily explained by a ligand effect of Co covering the Pd crystallites. The second effect, called ensemble effect, is relevant only for highly coordinated sites, that is bridge or hollow sites. It is effective if one of the atoms constituting such a site is exchanged by the second metal so that the site is eliminated. As threefold hollow sites should be strongly affected by this effect, the early suppression of the corresponding peak in the Pd spectrum is not surprising.

With increasing Co coverage (Figure 2), the peak at 350 K shifts to higher temperatures until, at very high Co coverages, the desorption spectrum resembles that of pure Co. It is therefore tempting to assign the peak, labeled A in the spectra (Figure 2), to the desorption of terminally bonded CO from Co atoms on the Pd crystallites. The shift can be explained by a decreasing ligand effect of Pd as the Co coverage increases. Also note the peak, labeled B, that points to Co bridge sites appearing later in the series due to the ensemble effect expected in this case.

So far only desorption from the Co-covered Pd crystallites has been considered. In the intermediate coverage regime, however, the broad desorption maximum with a clear contribution (shoulder) at higher temperatures reveals that, according to STM images (Figure 1), the small Co particles that form between the Pd crystallites are also detectable in the TPD spectra.

For the deposition order 1st Co, 2nd Pd the TPD experiments (Figure 3) corroborate the structure inferred from the STM results as well. Here, a new desorption peak from Co atop sites evolves at lower temperature (A), which can be assigned to Co particles partly covered by Pd. The shoulder at the original desorption temperature still visible in the first spectrum of the series apparently results from areas on the particles not covered at this stage. The shift of the maximum to lower temperatures induced by Pd can again be understood in terms of the ligand effect discussed above. As the Pd coverage increases and its electronic influence becomes stronger, the desorption shifts to even lower temperatures and the desorption from pure Co sites vanishes.

Finally, when a Pd shell completely covering the Co cores is formed, desorption from Pd threefold hollow sites is detected in the spectra. At a first glance, it might be surprising that relatively large amounts of Pd are needed to observe this site. Two reasons, however, can be responsible for that: 1) the strong ensemble effect expected for this site and 2) the smaller and less ordered particles as compared to the other deposition order (cf. Figure 1) which possibly offer less intact threefold hollow sites.

In conclusion, we have presented a method to prepare oxide-supported bimetallic Pd–Co nanoparticles by metal vapor deposition. By taking advantage of nucleation and growth processes on the surface, particles of different structure and composition can be obtained. CO TPD experiments corroborate the structures suggested by STM, revealing that both ensemble and ligand effects change the adsorption properties of these bimetallic model catalysts.

**Experimental Section**

The UHV system used in this study has been described in detail elsewhere. Briefly, it consists of a commercially built analysis chamber (Omicron) with an APM/STM stage, as well as X-ray photoelectron spectroscopy (XPS) and low-energy electron diffraction (LEED) capabilities. Coupled to the analysis chamber by a transfer system is a preparation chamber containing Pd and Co metal evaporators, and facilities for sputtering, gas dosing, and TPD measurements. The flux of the metal evaporators was calibrated both with a quartz microbalance in a different chamber and checked by STM in the analysis chamber. To quantify the amount of material deposited, the nominal film thickness as measured by the microbalance is used in this article. The NiAl(110) crystal was cleaned by cycles of Ar+ sputtering, and an Al2O3 film was prepared by previously described methods.

Before the TPD measurements, the sample was given a directed dose of CO at 100 K and then placed less than 1 mm away from the differentially...
pumped cap of the quadrupole mass spectrometer. The sample was heated by radiation from a tungsten filament mounted directly behind it. A linear temperature ramp for TPD was programmed with a controller and power supply from Schlichting Physikalische Instrumente. The spectra were obtained by recording the temperature and the partial pressures of the species desorbing from the surface during such a ramp. Blank measurements from the oxide film without deposited metal particles showed desorption of small amounts of masses 2, 16, 18, 28, 32, and 44 below 150 K resulting from desorption from the heating filament (CO does not adsorb on the clean alumina film above 90 K); these signals were at least an order of magnitude smaller than those from the metal particles.