

Beneficial interaction of gold and palladium in bimetallic catalysts for the selective oxidation of benzyl alcohol

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Bimetallic nanoparticles often exhibit advantageous properties in catalysis compared to those of their pure constituent metals. In this work, a series of Au/Pd nanoparticles with different compositions have been prepared and tested as catalysts in the aerobic oxidation of benzyl alcohol. We found that the selectivity towards benzaldehyde in the oxidation reaction depends strongly on the Pd content. Depending on the catalysts composition a selectivity of 98% towards benzaldehyde at full conversion could be achieved.

To elucidate the origin of the superior behaviour of the bimetallic nanoparticles in catalysis the structural and electronic properties of the particles have been characterized with X-ray absorption techniques. The structural properties, like interatomic distances and coordination numbers, were investigated with EXAFS while the electronic configuration was examined with XANES. Both techniques were used to correlate the change in the catalytic performance. Upon admixing Pd to the Au nanoparticles a change of the interatomic distances occurs in accordance to Vegard's law^[1], which leads to a proper distance of the adsorption sites and facilitates the chemical conversion step. On the other hand alloying Pd to Au nanoparticles might cause electronic perturbations, which result in a change of the energy and filling of the d-bands of the metals.

The experiments were performed at the beamline X1 (energy range: 7 – 100 keV) and C (energy range: 5 – 43keV). The monochromator was a Si (111) double crystal for the measurement of the Au-L_{III} edge (11.918 keV) and a Si (311) double crystal for the Pd-K edge (24.35 keV). The samples were pressed into a pellet and measured in transmission mode. The scans were energy referenced to Au or Pd foil. The Fourier transformed Au L_{III} EXAFS spectra of the catalyst series (pure Au, 7:1, 1:1, 1:9) are shown in Figure 1a. All catalysts exhibited a feature in the region between 1.7 – 3.5 Å due to the first shell Au-Au backscatter contributions. For the nanoparticles with a Au/Pd composition of 1:1 and 1:9 a second backscatter contribution at shorter R-values became visible. This contribution was assigned to Au-Pd scattering paths, indicating that Au atoms are surrounded not only by Au but also by Pd atoms. Moreover we found that the total coordination number of the gold atoms is always bigger than the total coordination number of the Pd-atoms. The lower coordination number of the Pd atoms indicates that Pd is mainly located at the surface of the particles and we concluded that the particles have a core shell structure (with a Au rich core and a Pd enriched shell) and are not homogeneously alloyed. Moreover the Au-Au distance shrinks with increasing Pd-content in accordance to Vegard's law from 2.86 Å in pure Au nanoparticles to 2.79 Å in the Au/Pd 1:9 system.

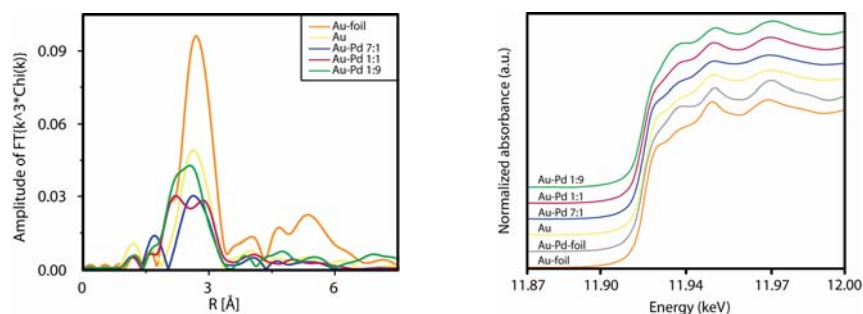


Figure 1: a) Fourier transformed Au L_{III} EXAFS spectra (k^3 -weighted),
b) Stacked plot of the XANES spectra at the Au L_{III} edge

In Figure 1b the Au L_{III} XANES spectra of the nanoparticles are depicted. The L_{III} edge probes the transition of 2p electrons to the empty density of states that have mainly d character. Hence, the intensity of the white line in the L_{III} spectrum is directly linked to the number of holes in the d-band. Comparing the white line

intensity of the Au reference foil (bulk gold) with the one of the pure Au nanoparticles, a clear decrease of the intensity is visible. When going from the bulk to nanosized particles the number of atoms forming a lattice decreases and therefore the width of bands will decrease, too. The decrease in bandwidth results in a less pronounced overlap of bands leading to a rehybridization of the s, p and d orbitals. In the concrete case of gold the ideal electron configuration for a single atom is $5d^{10}6s^1$. With increasing number of atoms the overlap of bands becomes significant and leads to hybridization of the 5d, 6s and 6p band. The electron count of 5d and 6s orbitals is depleted while the 6p orbitals are occupied upon an increase in the number of neighbors, resulting in a electron configuration of $5d^{10-x}6s^{1+x}$ for bulk gold. This depletion of the d-band for bulk gold is reflected as a small white line in the Au-foil XANES spectrum.

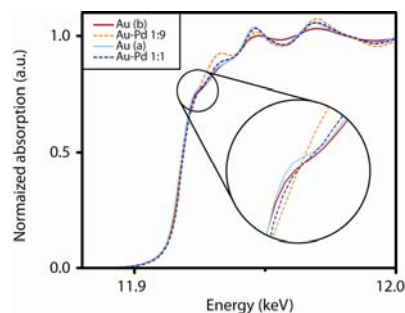


Figure 2: Comparison of the XANES region of pairs of Au and Au/Pd bimetallic nanoparticles; the inset magnifies the white line region of the Au L_{III} spectra

The situation becomes more complex when Pd comes into play. The intensity of the white line becomes even smaller with increasing Pd content and diminishes almost for the Au/Pd 1:9 system. Therefore the question arises, if the decrease in white line intensity is simply caused by the dilution of Au atoms in a Pd matrix (depending on the same effect discussed for size reduction of pure Au particles) or if an Au-Pd interaction is responsible for the change of the white line intensity. To distinguish the two possibilities two model systems were prepared. Each model system consisted of a pair of samples: a pure Au sample and an Au/Pd bimetallic one. The important point here is that the CN_{Au-Au} of the pair Au/Pd 1:1 and pure Au (a) (blue colored lines in Figure 2) as well as for the pair Au/Pd 1:9 and Au (b) (red colored lines in Figure 2) are almost equal. If the alloying had no influence on the electronic structure, the white line intensities for each pair should be similar due to the same Au-Au coordination number in both samples. But the spectra revealed the opposite. For both pairs the white line intensity of the alloy is smaller than for the pure Au sample. We assume here a strong interaction of the Pd 4d band with the Au $5d_{5/2}$ band resulting in an enhanced filling of the Au 5d band as indicated by XANES^[2,3].

In conclusion, we could show with the help of XAS that the electronic properties of gold are significantly altered by admixing of palladium. The d-hole count of gold reduces with increasing Pd content. This is not only an effect of the decreased number of like neighbors (size effect) but also dependent on the Pd concentration. The examined particles exhibit a core shell structure with an Au rich core and a Pd enriched shell. Both, the electronic configuration and structural properties have strong influence on the catalytic activity (for details, cf. ref. [4]) and are important to understand the superior behavior of bimetallic nanoparticles in catalysis.

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References

- [1] L. Vegard, Z. Phys. **5**, 17 (1921).
- [2] T. U. Nahm, R. Jung, J.U. Kim, W.G. Park, S. J. Oh, J. H. Park, J. W. Allen, S. M. Chung, Phys. Rev. B **58**, 9817 (1998).
- [3] F. Liu, D. Wechsler, P. Zhang, Chem. Phys. Lett. **461**, 245 (2008).
- [4] S. Marx, A. Baiker, J. Phys.Chem. C **113**, 6191 (2009).