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EXAFS analysis of Pd atomic clusters

Alojz Kodre,[ab]* Iztok Arčon,[bc] Jurka Batista[d] and Albin Pintar[d]

[a]Faculty of Mathematics and Physics, University of Ljubljana, Ljubljana, Slovenia; [b]Institute Jozef Stefan, Jamova 39, 1000 Ljubljana, Slovenia; [c]School of Environmental Sciences, Vipavska 13, Nova Gorica, Slovenia; [d]National Institute of Chemistry, Ljubljana, Slovenia. E-mail:alojz.f.kodre@ijs.si

The structure of Pd/Cu catalysts on γ-alumina for nitrate/nitrite ion removal from drinking water is investigated. EXAFS spectra at the K edge of both elements show that small clusters with the basic crystal structure of bulk palladium metal are formed. The size of the clusters is estimated from the range of photoelectron scattering paths, and from the average number of first neighbors. Both estimates indicate clusters of about 12 atoms, ie two neighbor shells.

Keywords: Pd/Cu catalysts, Pd atomic clusters, Pd EXAFS

Palladium metal is one of the most promising catalysts for removing nitrate and nitrite ion from drinking water (Hörold *et al.*, 1993, Pintar *et al.*, 1996). For kinetic studies, monometallic Pd and bimetallic Pd-Cu catalysts were prepared by impregnation of γ-Al_2O_3 powder with Pd and Cu nitrate salts (5 and 1.5 at.% respectively) and subsequent calcination/reduction in hydrogen atmosphere.

EXAFS spectra of the samples at the K edge of Pd and Cu were measured at the ROEMO II and EXAFS II beamlines of HASYLAB at DESY, Hamburg, with resolution of 3 eV and 1.5 eV, respectively. Higher harmonics of the beam were eliminated by a slight detuning of the monochromator crystals. Due to low metal content and low density the optimum absorption samples were prepared by pressing the powder into 3 mm layers between the windows of a liquid-absorption cell.

The measured EXAFS spectra (Fig. 1) were analysed by the UWXAFS code (Stern *et al.*, 1995, Rehr *et al.*, 1992) in the k-range 3.5 – 12 $Å^{-1}$, using k^2 weight and Hanning window. The shape of the Pd K absorption edge, identical with that of bulk Pd, suggests a model based on the fcc crystal structure of Pd metal. When applied to the spectrum of the monometallic catalyst, excellent fit for the FT region from 2 Å to 5.5 Å, is found using the 8 shortest scattering paths of the lattice. For the lower part of the FT spectrum in the range 1 - 2 Å, a shell of oxygen atom neighbors at 1.9 Å, presumably from the contact layer with the substrate, is introduced into the model. The agreement (Fig. 2) indicates that clusters with fcc structure of Pd metal are formed. An estimate of their size is given by the cutoff in the FT spectrum at approx. 6.0 Å. Specifically, the absence of a prominent peak at 7 Å in FT spectra of bulk Pd provides a definite upper limit. A better estimate of the average cluster size is obtained from the number of first neighbors (5.9) which is considerably lower than the coordination number 12 of an infinite lattice. A calculation (Table 1) shows that the observed value is reached in a cluster of about 12 atoms in a tentative shape of an octahedron with a diameter of 5.5 Å formed by a layer of nearest neighbors around a central atom.

Table 1
Average number of first Pd neighbors in clusters with maximum mnp site indices.

mnp	number of atoms in the cluster	average number of 1st neighbors	mnp-shell radius [Å]
000	1	0	-
011	12	6.0	2.69
200	18	6.3	3.80
112	42	7.4	4.65
022	54	8.0	5.37
031	78	8.6	6.01

Since the Pd EXAFS spectrum of the bimetallic Pd-Cu catalyst retains the characteristic fcc shape, the same cluster model with addition of a shell of Cu atoms at the contact Pd-Cu distance (2.65Å) is applied. Again, the agreement is very good, as shown in Fig. 3. Apart from a slight but significant change in the Pd-Pd distance, the best fit values of the corresponding model parameters for the bimetallic and monometallic clusters are essentially the same (Table 2).

The FEFF model for the Cu EXAFS spectrum of the bimetallic sample is constructed from the bimetallic Pd fcc model by substitution of the central atom, retaining the four shortest scattering paths to fit the r-range 1.2Å - 3.5Å. The fit (Fig. 4) shows that the Cu neighborhood is less populated by metal atoms than that of Pd (Table 3). Together with the stronger Cu-O correlation this indicates that the Cu atoms are attached to the Pd cluster. The description of Pd-Cu bonds, as seen from both atoms, agrees well in distance parameter, and satisfactorily in the coordination number. The σ^2 parameters, however, cannot be reconciled.

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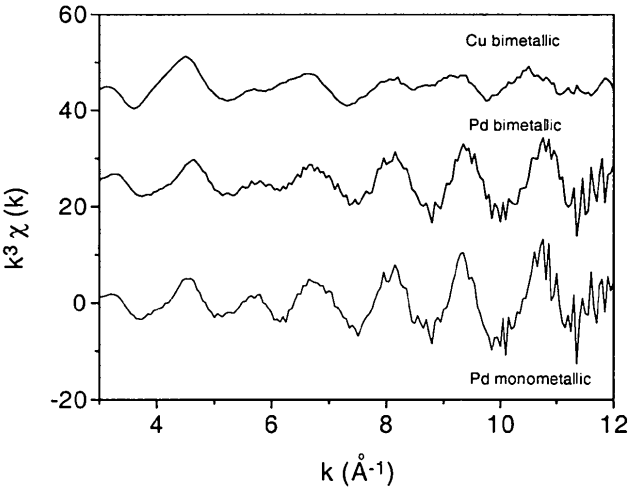

Figure 1
Pd and Cu K edge EXAFS spectra of the monometallic and bimetallic catalysts.

Table 2
Model parameters of the EXAFS at the Pd K edge.

	Monometallic Pd			bimetallic Pd-Cu		
Neig.	r[Å]	N	σ^2 [Å^2]	r[Å]	N	σ^2 [Å^2]
O	1.984(9)	1.0(1)	0.002(1)	2.00(2)	0.9(5)	0.005(2)
Cu				2.64(1)	1.6(3)	0.005(1)
Pd	2.727(2)	5.9(4)	0.0067(2)	2.693(6)	5.9(4)	0.0067(4)

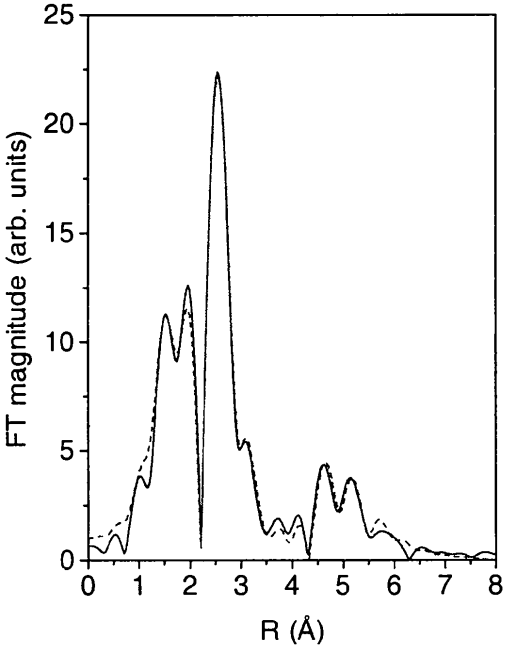

Figure 2
Fourier transform magnitude of Pd K-edge EXAFS spectra measured on monometallic Pd catalysts: experiment - solid line, fit - dashed line.

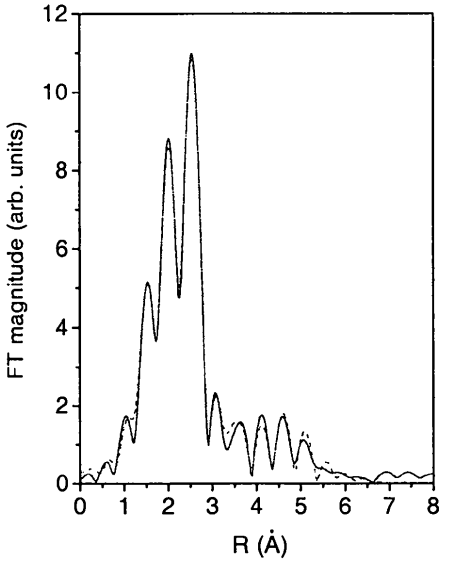

Figure 3
Fourier transform magnitude of Pd K-edge EXAFS spectra measured on bimetallic Pd-Cu catalysts: experiment - solid line, fit - dashed line.

Table 3
Model parameters of the EXAFS at the Cu K edge for Pd-Cu sample.

Neighbor	r [Å]	N	σ^2 [Å^2]
O	1.917(4)	1.9(1)	0.005(1)
Cu	2.59(1)	1.3(5)	0.012(1)
Pd	2.647(4)	4.5(9)	0.013(1)

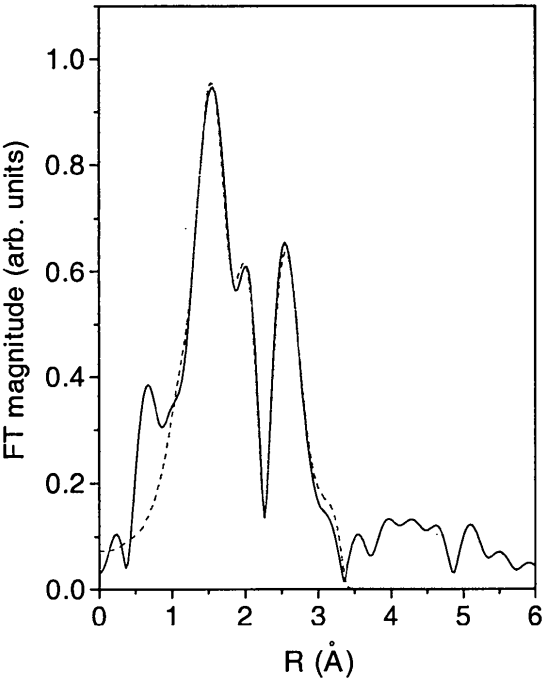

Figure 4
Fourier transform magnitude of Cu K-edge EXAFS spectra measured on bimetallic Pd-Cu catalysts: experiment - solid line, fit - dashed line.

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