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EXAFS and XANES structural characterization of bimetallic AuPd vapor derived catalysts.

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Abstract. Using an innovative procedure known as metal vapor synthesis (MVS) to prepare bimetallic catalysts, starting from Au and Pd vapors, [AuPd] co-evaporated and [Au][Pd] separately evaporated bimetallic catalysts were achieved. After being tested, the catalytic activity and selectivity of the [AuPd] catalyst turned out to be higher than the [Au][Pd] ones. Using EXAFS spectroscopy it was shown that, in the [AuPd] samples, small bimetallic AuPd nanoparticles were present, having an Au rich core surrounded by an AuPd alloyed shell while in the [Au][Pd] sample there was the presence of monometallic Au and Pd nanoparticles showing some alloying only in the boundary regions. The EXAFS results were also qualitatively confirmed by the XANES spectra.

1. Introduction

Bimetallic catalysts are of great interest due to their catalytic, electronic and optical properties that are different from the ones of their pure constituent metals. These catalysts are not only characterized by particles size and shape but also by the atomic ratios of the metals and their different electronic and chemical properties [1,2]. Among many metallic combinations, gold-palladium systems have been extensively studied due to their peculiar catalytic properties in many catalytic processes [3]. Au and Pd can form solid solutions at any ratio [4] and depending on the preparation method, AuPd bimetallic systems can contain different structural features including core-shell structure [5], segregated Au and Pd monometallic domains [6], uniform Au-Pd alloys [7] or a mixture of them [8]. In this paper, we report the XAFS (X-ray Absorption Fine Structure) structural characterization of AuPd bimetallic systems prepared by using Au and Pd vapors as reagents (metal vapor synthesis, MVS) [9] following two different synthetic procedures. In the first procedure, Au and Pd vapors are simultaneously co-condensed with acetone vapor in order to obtain a close interaction between the two metals, leading to a bimetallic AuPd/acetone solvated metal atoms (SMA) solution. Then, AuPd/acetone SMA is used as starting material to synthesize bimetallic [AuPd] catalysts supported on γ -Al₂O₃. In the second procedure, Au and Pd are evaporated separately in two different evaporation reactions; therefore, Pd/acetone and Au/acetone SMA are achieved. Afterwards, Pd and Au

SMA are mixed together and used as starting materials to obtain supported [Au][Pd] bimetallic systems. Since the bimetallic [AuPd] system shows higher catalytic activity and selectivity than the analogous [Au][Pd] system [9] their XAFS structural characterization becomes quite important. In order to have a further insight into their morphology and dimensions, all catalysts were also investigated by high resolution transmission electron microscopy (HRTEM)[9].

2. Results and Discussion

X-ray absorption spectra at the Au L₃ edge and at the Pd K-edge were taken at the GILDA beamline [10] of the European Synchrotron Radiation Facility (ESRF, Grenoble). Measurements were performed on two reference samples (Au and Pd foils) and on a complete set of two monometallic Au (1%) and Pd (0.5%) and two bimetallic [Au][Pd], [AuPd] samples supported on γ -Al₂O₃ [9]. Only the catalysts at the Pd K edge were measured in fluorescence mode while transmission mode was used for all the other XAFS spectra. To perform an accurate data analysis [11,12] data fitting was performed in both R-space and k-space with k² (Pd) and k³ (Au) weights; also an estimation of the accuracy of the obtained structural parameters, compatible with the data quality and k range used [13], was achieved. In Fig. 1 differences between the EXAFS spectra of the [Au][Pd] and the [AuPd] samples are clearly visible. The values of coordination numbers (N), nearest-neighbors distances (R) and DebyeWaller factors (σ^2) are reported in Table 1. Results achieved show a different environment for Au and Pd. In the monometallic Au/ γ -Al₂O₃ case, the reduction in the coordination numbers, N, was used to estimate the average nano-particle size [11]. The case of the monometallic Pd is more complicated because EXAFS data analysis indicates the presence of a Pd-O and a Pd-Pd coordination. As clearly visible in Table 1, small and comparable amounts of oxidized Pd are present in all the catalysts and this can probably exclude any significant effect on the different catalytic activities.

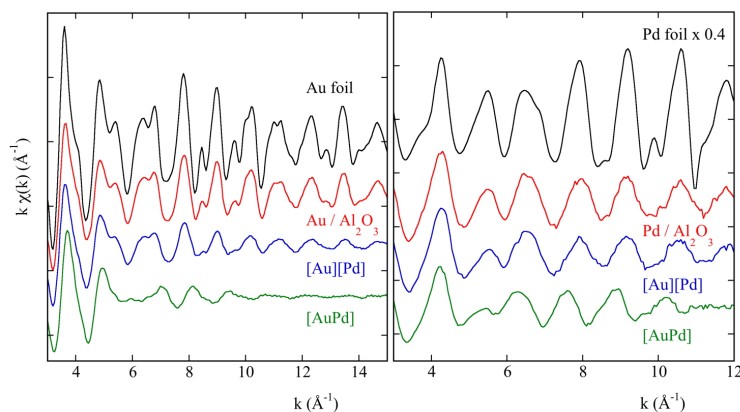


Figure 1. Experimental EXAFS spectra at the Au L₃ edge and at the Pd K edge.

In the bimetallic samples the presence of Au-Pd bonds was clearly observed (Tables 1). In the [Au][Pd] case, the number of Pd atoms among the Au neighbors (and the number of Au atoms among the Pd neighbors) is rather small (about 10% and about 20% respectively); on the other hand, in the [AuPd] case, the presence of Au-Pd bonds is much higher. The TEM analysis [9] showed that in the [Au][Pd] sample there is the presence of at least two families of nanoparticles: 70% of the nanoparticles exhibits a size distribution between 2 nm and 3 nm and a $D_m = 2.6$ nm but there is also a minor population of larger particles with sizes between 4 nm and 5.5 nm. In the [AuPd] case TEM analysis shows nanoparticles homogeneously and symmetrically distributed around a mean size of about 2.4 nm. Taking into account the TEM analysis and the

Table 1. Results of the EXAFS fitting procedure.

Sample	R-factor	Shell	N	R(\AA)	σ^2
<i>Au foil</i>	0.002	Au-Au	12(fixed)	2.875	0.0020
<i>Au</i> (1%)	0.006	Au-Au	10.9	2.867	0.0031
[<i>Au</i>][<i>Pd</i>]	0.006	Au-Au	10.2	2.854	0.0062
		Au-Pd	0.9	2.793	0.0063
[<i>AuPd</i>]	0.005	Au-Au	5.5	2.815	0.0087
		Au-Pd	3.6	2.794	0.0071
<i>Pd foil</i>	0.003	Pd-Pd	12(fixed)	2.745	0.0022
<i>Pd</i> (0.5%)	0.01	Pd-O	0.9	2.00	0.002
		Pd-Pd	5.2	2.74	0.007
[<i>Pd</i>][<i>Au</i>]	0.01	Pd-O	1.1	2.00	0.002
		Pd-Pd	4.3	2.74	0.008
		Pd-Au	1.2	2.79	0.012
[<i>PdAu</i>]	0.009	Pd-O	0.7	2.01	0.003
		Pd-Pd	2.5	2.80	0.005
		Pd-Au	3.6	2.79	0.006

small amount of heteroatomic Au-Pd bonds present in the [Au][Pd] sample a possible explanation of the achieved results could be that probably some smaller Pd nanoparticles sit on the surface of the larger Au ones giving rise to alloying only in the boundary regions and to the two families of nanoparticles sizes observed. In the case of the [AuPd] sample, at the Pd K-edge the Pd-Pd coordination number is smaller than the Pd-Au one while the interatomic distances are comparable. The presence of a Pd-Pd distance comparable to the Pd-Au one suggests the presence of a well-defined Pd-Au phase. Since the Pd:Au molar ratio is equal to 1 in the presence of a homogenous Pd-Au alloy, the Pd-Pd and Pd-Au coordination numbers should be the same but this is not the case because the number of Pd and Au atoms around the Pd absorber is different. At the Au L₃ edge the Au-Au distance of about 2.82 Å is different from the Au-Pd and the Pd-Pd ones and is contracted with respect to the Au bulk value. This, together with the value of the Au-Au coordination number rather higher than the Au-Pd one, indicates the presence of small Au-rich cores. From the value of the Au-Au distance [14], we quote a dimension of about 11 Å corresponding to a nanoparticle of about 55 atoms. From all these considerations, we conclude that in our [AuPd] sample, bimetallic Au-Pd nanoparticles, composed of an Au rich core surrounded by an AuPd alloyed shell, are present. A physical reason of such a structure could be attributed to kinetically more favorable nucleation steps of Au atoms in acetone solution during the melting of the acetone solid matrix, followed from a slower aggregation of Au and Pd atoms on preformed Au seeds but also by the high thermodynamic stability at low temperatures (<500 K) of Au-Pd bimetallic particles having a Au rich shell [15,16]. This can be related to the different stabilization properties of acetone towards Pd and Au atoms, as observed in the [Au][Pd] sample. The different structural results achieved by the EXAFS data analysis for the [AuPd] and [Au][Pd] samples can be also qualitatively observed in the normalized experimental X-ray Absorption Near Edge Structure (XANES) spectra reported in Fig. 2. In Fig. 2, the peak indicated by the arrow at the Au L₃ edge is known as white line and its intensity is related to the presence of unoccupied 5d states (d-holes) [17]. In the nanoparticles, the reduced number of Au-Au bonds results in an increase in the 5d level occupancy and hence in a decrease in its

intensity. As shown by Liu et al. [16] in Au-Pd clusters, a further reduction in the intensity of the white line can be due to a charge transfer from Pd to Au. Therefore, the strong electronic effect observed in Fig. 2 comparing the [Au][Pd] sample to the [AuPd] one can be related to the increased Au-Pd coordination, which causes a further filling of the Au d band.

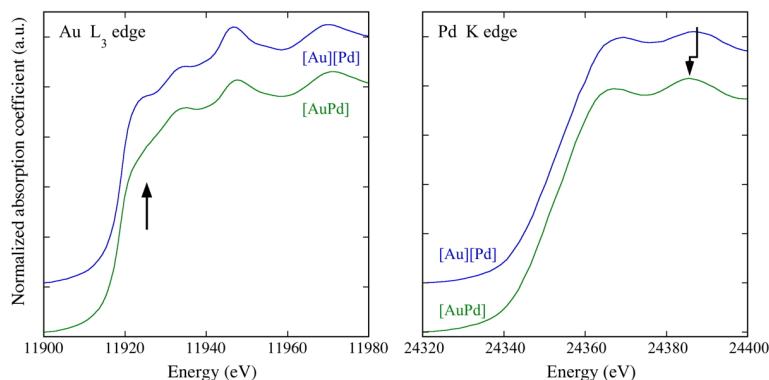


Figure 2. XANES spectra at the Au L_3 edge and at the Pd K edge.

In the Pd XANES the small shifts to higher energies observed in the [Au][Pd] spectra come from lattice contraction. The opposite shift observed in the [AuPd] sample is associated to the large amount of Au atoms present around Pd, which, as given by EXAFS data analysis, results in an increase in the interatomic distances, in agreement with Ref. [5].

3. Conclusions

Investigations on bimetallic Au-Pd catalysts prepared using different procedures have shown different structural features. Simultaneous evaporation of the two metals produces nanoparticles having an Au rich core surrounded by an Au-Pd alloyed shell. Separate evaporation produces monometallic Au and Pd nanoparticles and a small presence of hetero-atomic Au-Pd bonds could be given by the sitting of the smaller Pd nanoparticles on the surface of the larger Au ones giving rise to some alloying only in the boundary regions.

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