

XAFS Investigation of Palladium Interphase Catalyst

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The anchoring of transition metal complexes to an inert carrier matrix is regarded as an approach to combine the advantages of homogeneous and heterogeneous catalysis [1]. The sol-gel process offers a versatile and convenient route to generate such stationary phases under mild conditions, consisting of a polysiloxane matrix, spacer and reactive centre [2]. EXAFS (Extended X-ray absorption fine structure) and XANES (X-ray absorption near edge structure) spectroscopic methods were used to determine the local environment and oxidation state of palladium in such a system where the palladium complex is immobilized in silica substrate. The results of the analysis were compared with those obtained for the pure precursor complex in order to detect any change in the local environment that had taken place upon immobilization. The samples are X-ray amorphous and fluorescence mode XAFS detection method was employed to record the XAFS spectra due to the inherent low atomic weight percentage of the palladium in the samples.

The investigated palladium interphase catalyst (called **Sample 1**) was prepared using sol-gel process by introducing $\text{Pd}_2(\text{dba})_3$ (Tris(dibenzylideneacetone)dipalladium(0)) precursor (as solution in Tetrahydrofuran) into the silica matrix which was functionalized by the ligand system tri-*tert*-butylphosphine. The Fluorescent mode XAFS measurement of the sample was performed at the palladium K-edge (24350 eV), at the beam line X1 of HASYLAB using a 7-element liquid nitrogen cooled germanium detector and by using Si (311) double crystal monochromator. The data analysis of the measured XAFS spectra was performed using program packages IFEFFIT (Athena, AUTOBK) and EXCURV98. Data analysis in *k*-space was performed using the curved wave theory with XALPHA potentials and phase shifts and the resulting EXAFS function was weighted with k^3 . The amplitude reduction factor AFAC was fixed at 0.8, and the Fermi energy E_F was introduced to give a best fit to the data. The XANES region of Pd metal foil, $\text{Pd}_2(\text{dba})_3$ and **Sample 1** are compared in figure 1 and their edge positions are similar to each other. Therefore the oxidation state of Pd in **Sample 1** is similar to the oxidation state of Pd in $\text{Pd}_2(\text{dba})_3$.

EXAFS analysis of **Sample 1** was carried out to determine the local geometry around Pd in the synthesized sample. The experimental EXAFS spectra and the theoretical fit to the measured spectra for $\text{Pd}_2(\text{dba})_3$ and **Sample 1** are given in figure 2. Even though the crystal structure of $\text{Pd}_2(\text{dba})_3$ is available in literature, the EXAFS fitting for $\text{Pd}_2(\text{dba})_3$ was also carried out in order to use its structure as a model for the fitting of **Sample 1**. In the EXAFS fitting procedure for the $\text{Pd}_2(\text{dba})_3$, a two shell model was used, and the coordination number of neighboring atoms, the inter-atomic distance available from crystallographic data were used as initial guess [3]. Subsequently the coordination numbers interatomic distances and Debye-Waller factors were iterated in order to obtain a good fit. The structure parameters obtained by EXAFS for the $\text{Pd}_2(\text{dba})_3$ precursor is given in table 1.

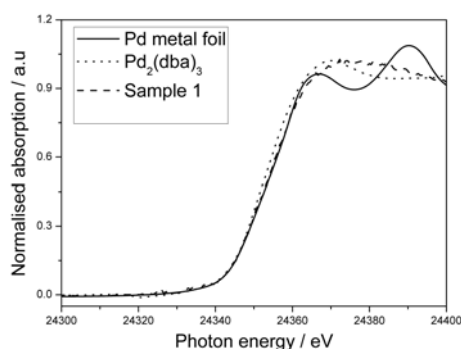


Figure 1: XANES spectra of Pd-metal foil, $\text{Pd}_2(\text{dba})_3$ and **Sample 1**

When the theoretical EXAFS function based upon $\text{Pd}_2(\text{dba})_3$ model was used for fitting the spectrum of **Sample 1**, it resulted in a statistically poor fit (not shown here). This observation indicates that the local structure around palladium in the samples might be different from that of the $\text{Pd}_2(\text{dba})_3$ precursor. In order to find out what could be the possible local geometry around palladium in **Sample 1**, different backscattering atoms were used in the fitting procedure. The low *k*-range of the EXAFS signal also made the task of determining the accurate local geometry around palladium difficult.

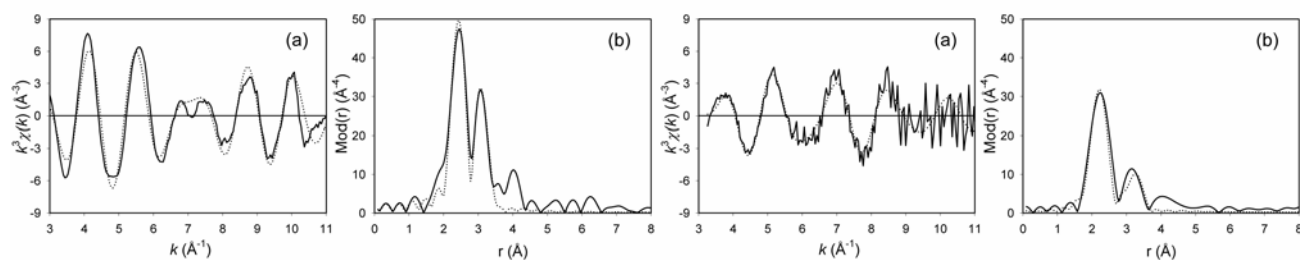


Figure 2. Experimental (solid line) and calculated (dotted line) EXAFS functions and Fourier Transform plots of $\text{Pd}_2(\text{dba})_3$ (left) and **Sample 1** (right)

The use of Pd-P, Pd-C amplitude and phase functions resulted in a good fit to the experimental EXAFS function of **Sample 1**. The structure parameters obtained by EXAFS for **Sample 1** are given in table 1. The Pd-P distance of 2.2 Å and Pd-C distance of 3.3 Å obtained from EXAFS are in agreement with the distances reported for similar atomic pairs in literature [4]. Moreover, evidence for similar local geometry of palladium in the presence of a phosphine ligand has also been reported for Bis(dibenzylideneacetone)palladium (0) complex [5]. From the structure parameters obtained for **Sample 1**, it could be hypothesized that a local structure similar to that depicted in figure 3 could possibly exist. For comparison, the simplified local geometry around palladium observed in $\text{Pd}_2(\text{dba})_3$ is given as well. From the comparative structural investigation of the $\text{Pd}_2(\text{dba})_3$ precursor and the palladium interphase catalyst, it is observed that there is a change in the local geometry around palladium upon immobilization and the possible local geometry is obtained from EXAFS analysis.

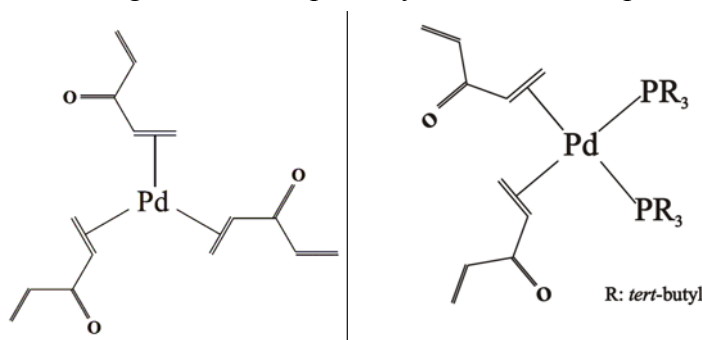


Figure 3: Local geometry around palladium in $\text{Pd}_2(\text{dba})_3$ and **Sample 1**

Table 1. Parameters for the local structure determined from EXAFS

Case	A-Bs ^a	N ^b	r ^c [Å]	σ ^d [Å]	E _F ^e [eV]	k-range [Å ⁻¹]	R-factor
$\text{Pd}_2(\text{dba})_3$ precursor	Pd – C	7.6 ± 0.7	2.46 ± 0.02	0.059 ± 0.006	-1.171	2.99 – 11.05	33.22
	Pd – C	10.0 ± 1.0	3.13 ± 0.03	0.071 ± 0.010			
Sample 1	Pd – P	2.2 ± 0.2	2.27 ± 0.02	0.084 ± 0.008	10.69	3.20 – 11.00	40.39
	Pd – C	5.8 ± 0.5	3.33 ± 0.03	0.097 ± 0.013			

^a absorber (A) – backscatters (Bs), ^b coordination number N, ^c interatomic distance r,

^d Debye-Waller factor σ with its calculated deviation and ^e Fermi energy E_F.

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