

Electronic Supplementary Information

Carbon Supported Pd-Cu Nanoalloys: Support and Valence Band Structure Influence on the Reduction and Oxidation Reactions

Marcus V. Castegnaro^a, Andreia Gorgeski^a, Maria C. M. Alves^b and Jonder Morais^{a}*

^aInstituto de Física - UFRGS, 91501-970 Porto Alegre, RS, Brazil

^bInstituto de Química - UFRGS, 91501-970, Porto Alegre, RS, Brazil.

EXPERIMENTAL METHODS - XAS data analysis

The *in situ* XANES spectra were acquired at Cu-K edge (8979 eV) in the range between 8910 eV and 9040 eV with a 2 eV step and an acquisition time of 2 s/point. Considering the acquisition time and the delay due to monochromator movements, one scan was collected every

3.6 minutes. Thus, during the heating processes from RT to 450°C each spectrum covers a temperature range of about 27°C.

The XANES data obtained during the whole experiment were analyzed to extract information on the behavior of Pd_xCu_{1-x}/C samples during the reactions. Linear combinations (LC) of each spectrum were made using the ATHENA program of the IFEFFIT package¹, which was also used for the standard XAS reduction and normalization procedures. Different internal reference spectra were used for the LC of those data collected in each step. For the first step (heating under CO flow), the following equation was used for the LC of each Pd_xCu_{1-x}/C case: $\mu^{LC} = C_i\mu^i + C_f\mu^f$, where μ^i and μ^f are the as-prepared (first) and the reduced (last) spectra of each sample. The corresponding linear coefficients were normalized ($C_i + C_f = 1$) and their values were limited between 0 and 1. The μ^{LC} is the calculated absorption spectrum that best adjusts to the experimental data. All the spectra used as internal reference for the LC of the second step have been highlighted in Figure 3, while those for the steps (i) and (iii) are indicated in Figures SI1 and SI6.

For the second and third steps, slightly different data analysis approaches were used for the mono and bimetallic samples. Three internal references were used for the LC of sample Cu/C. Since μ^0 is the last spectrum collect before started the air flow, therefore it was used as the initial condition of the (reduced) sample before to its exposure to air and heating. The component μ^{2+} corresponds to the spectrum that presented the highest degree of oxidation. This is the one collected at 450°C and, by comparison to XANES spectra of some references and in view of the EXAFS analysis results, it is related to Cu⁺² in CuO. And for the component μ^+ , the last spectrum collected during the exposure to air was selected, which was confirmed to be related to Cu⁺¹ in Cu₂O. Hence, for the second and third steps of the experiment carried out with the

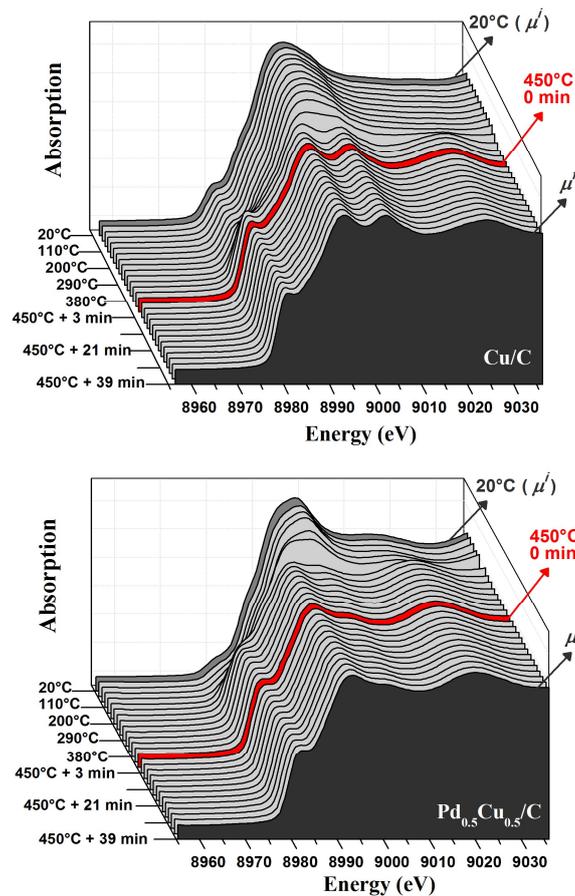
sample Cu/C, we used the following expression: $\mu^{LC} = C_0\mu^0 + C_+\mu^+ + C_{2+}\mu^{2+}$, where the linear coefficients were normalized and limited between 0 and 1. For the bimetallic cases, we just used two reference spectra: the last one collected before exposure to air, μ^m , and the spectra that present the highest degree of oxidation, μ^{ox} . The following expression was used for the LC of the XANES data collected for Pd_{0.5}Cu_{0.5}/C and Pd_{0.7}Cu_{0.3}/C during the two last steps of the experiment: $\mu^{LC} = C_m\mu^m + C_{ox}\mu^{ox}$, where the linear coefficients were subject to the same restrictions as in the previous cases.

XANES data at Pd-K edge (24350 eV) were collected for Pd/C sample during the first step of the reaction (heating under CO flow). The XANES spectra were collected in the range between 24320 eV and 24440 eV with a 2 eV step and an acquisition time of 2 s/point. Considering the acquisition time and the delay due to monochromator movements, one scan was collected every 3.4 minutes. Thus, during the heating processes from RT to 450°C each spectrum covers a temperature range of about 26°C. The XANES data were analyzed following the procedure described for Cu-K edge XANES data. Figure SI2 shows the XANES spectra evolution of Pd/C collected at the Pd-K edge during the first step of the experiment. Three spectra are highlighted in the graph: the initial and final ones, which were used in the linear combinations, and the spectra collected at 450°C.

Additionally, EXAFS data were collected before and after each experimental step. Each scan was acquired at the Cu-K edge (8979 eV) in the range of 8880 to 9970 eV with a 2 eV step and 2 s/point, and four scans were merged in order to improve the signal-to-noise ratio. The EXAFS signals $\chi(k)$ were extracted and then Fourier transformed (FT) using a Kaiser-Bessel window in a Δk range of 8.7 Å. The FEFF 9.6 code² was used to obtain the phase shift and scattering amplitudes. For the monometallic case, a Cu *fcc* (lattice parameter $a = 3.9239$ Å)

cluster with a radius of 10 Å was used in the FEFF calculations. For the bimetallic cases, a 10 Å cluster of Pd-Cu *fcc* alloy (lattice parameter $a = 3.75$ Å) was used. The S_0^2 (amplitude reduction term) was fixed for all samples at 0.8, which is the value obtained from the fitting of a standard Cu foil. During the EXAFS signal fitting, the number of free parameters was always maintained lower than the number of independent points in the fitted region. For the bimetallic samples, the distances and Debye-Waller factors for Cu-Cu and Cu-Pd pairs were adjusted independently, but they assumed similar values, as can be seen in Tables SI1-3.

FIGURES AND TABLES



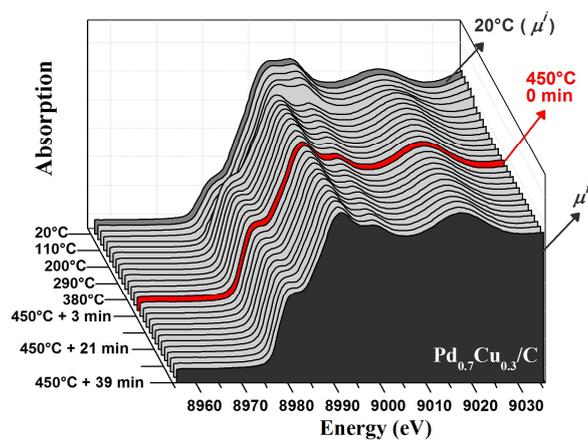


Figure SI1. XANES spectra evolution of each sample collected at the Cu-K edge during the first step of the experiment (heating under CO flow). Three spectra are highlighted in each graph: the initial and final ones, which were used in the linear combinations, and the spectra collected at 450°C.

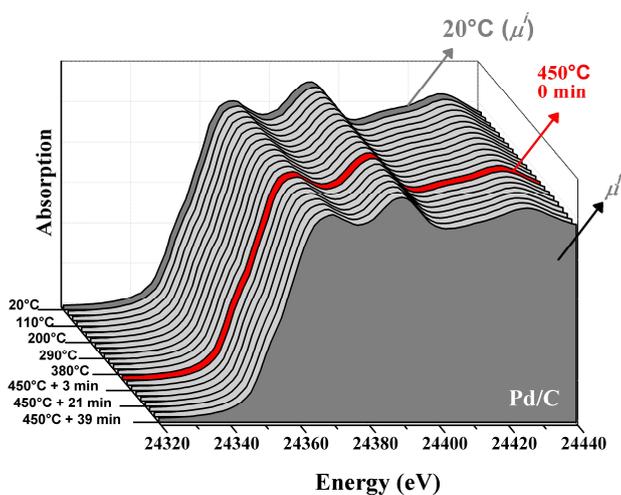


Figure SI2. XANES spectra evolution of Pd/C collected at the Pd-K edge during the first step of the experiment. Three spectra are highlighted in the graph: the initial and final ones, which were used in the linear combinations, and the spectra collected at 450°C.

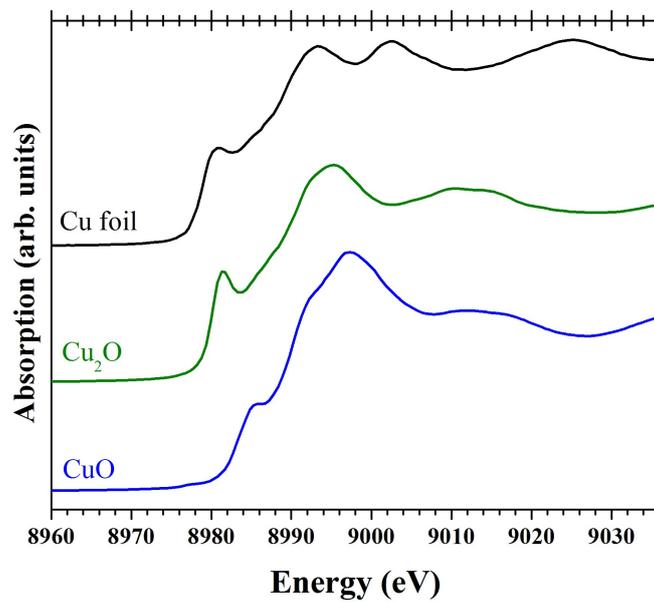


Figure SI3. XANES spectra at Cu-K edge of selected reference samples.

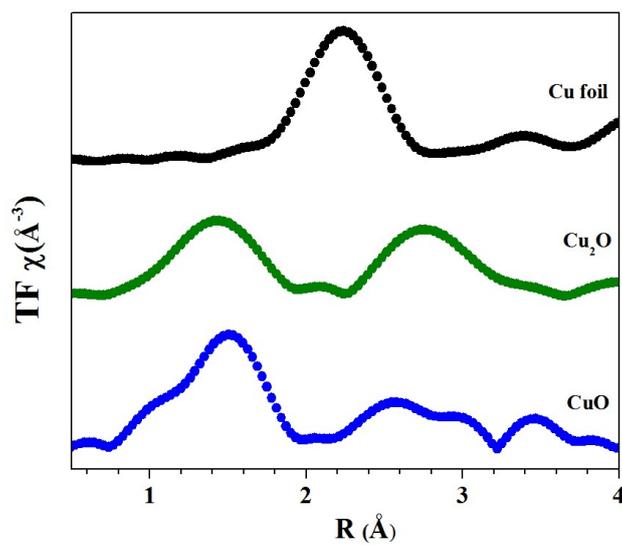


Figure SI4. Amplitudes of the FT of k^2 -weighted EXAFS signals at the Cu-K edge of the Cu foil, Cu_2O and CuO .

Table SII. Cu/C: Structural parameters obtained from the EXAFS analyses.

Experiment Step	Pair	N^a	R (Å)^b	σ^2 (10^{-2} Å²)^c
As-prepared (T _{acq} = RT) ^d	Cu-O	1.2 ± 0.2	1.91 ± 0.02	0.91 ± 0.07
	Cu-Cu	7.5 ± 0.2	2.52 ± 0.02	0.82 ± 0.05
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	10.4 ± 0.2	2.53 ± 0.02	1.65 ± 0.06
After Air (T _{acq} = 450°C)	Cu-O	2.6 ± 0.3	1.72 ± 0.02	1.95 ± 0.08
	Cu-Cu	5.5 ± 0.2	2.53 ± 0.02	2.01 ± 0.06
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	10.3 ± 0.2	2.53 ± 0.02	1.78 ± 0.04
After CO (T _{acq} = RT)	Cu-O	-	-	-
	Cu-Cu	10.3 ± 0.2	2.52 ± 0.02	1.02 ± 0.04

^a Coordination number or number of equivalent neighbors^b Bond distance^c Debye-Waller factor^d Sample temperature during measurement

Table SI2. Pd_{0.5}Cu_{0.5}/C: Structural parameters obtained from the EXAFS analyses.

Experiment step	Pair	N ^a	R (Å) ^b	σ ² (10 ⁻² Å ²) ^c
As-prepared (T _{acq} = RT) ^d	Cu-O	0.6 ± 0.1	1.92 ± 0.02	1.12 ± 0.02
	Cu-Cu	4.4 ± 0.1	2.68 ± 0.02	1.02 ± 0.02
	Cu-Pd	4.5 ± 0.1	2.68 ± 0.02	1.11 ± 0.05
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	4.8 ± 0.1	2.68 ± 0.03	1.94 ± 0.04
	Cu-Pd	4.9 ± 0.1	2.68 ± 0.03	1.96 ± 0.02
After Air (T _{acq} = 450°C)	Cu-O	0.2 ± 0.1	1.92 ± 0.03	1.95 ± 0.03
	Cu-Cu	4.5 ± 0.2	2.68 ± 0.02	2.01 ± 0.02
	Cu-Pd	4.6 ± 0.2	2.68 ± 0.02	2.00 ± 0.02
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	4.8 ± 0.2	2.68 ± 0.02	2.02 ± 0.03
	Cu-Pd	5.0 ± 0.2	2.68 ± 0.02	2.02 ± 0.02
After CO (T _{acq} = RT)	Cu-O	-	-	-
	Cu-Cu	4.9 ± 0.3	2.68 ± 0.02	1.24 ± 0.01
	Cu-Pd	5.0 ± 0.2	2.68 ± 0.02	1.29 ± 0.01

^a Coordination number or number of equivalent neighbors^b Bond distance^c Debye-Waller factor^d Sample temperature during measurement

Table SI3. Pd_{0.7}Cu_{0.3}/C: Structural parameters obtained from the EXAFS analyses.

Experiment step	Pair	N ^a	R (Å) ^b	σ^2 (10 ⁻² Å ²) ^c
As-prepared (T _{acq} = RT) ^d	Cu-O	0.4 ± 0.1	1.91 ± 0.02	1.13 ± 0.05
	Cu-Cu	2.6 ± 0.1	2.70 ± 0.03	0.92 ± 0.02
	Cu-Pd	6.4 ± 0.1	2.70 ± 0.02	0.94 ± 0.05
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	2.9 ± 0.1	2.69 ± 0.02	1.92 ± 0.03
	Cu-Pd	6.9 ± 0.1	2.69 ± 0.02	2.00 ± 0.05
After Air (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	2.9 ± 0.2	2.70 ± 0.03	2.00 ± 0.01
	Cu-Pd	7.0 ± 0.1	2.70 ± 0.03	2.02 ± 0.01
After CO (T _{acq} = 450°C)	Cu-O	-	-	-
	Cu-Cu	2.9 ± 0.2	2.70 ± 0.02	2.00 ± 0.04
	Cu-Pd	7.0 ± 0.2	2.70 ± 0.02	2.00 ± 0.05
After CO (T _{acq} = RT)	Cu-O	-	-	-
	Cu-Cu	2.9 ± 0.1	2.70 ± 0.02	1.11 ± 0.03
	Cu-Pd	6.9 ± 0.1	2.70 ± 0.02	1.18 ± 0.02

^a Coordination number or number of equivalent neighbors^b Bond distance^c Debye-Waller factor^d Sample temperature during measurement

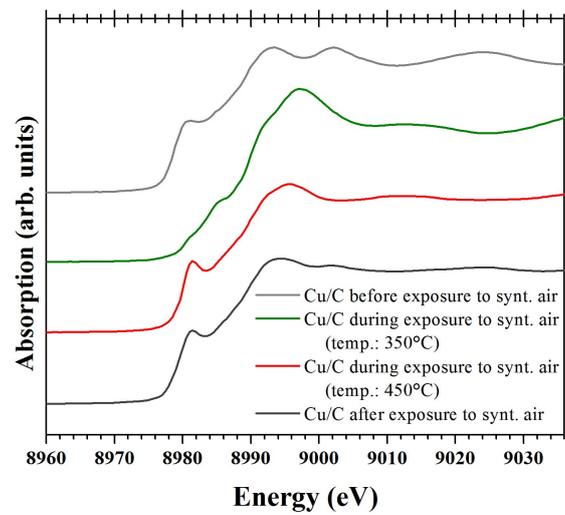


Figure SI5. Cu/C: XANES spectra at the Cu-K edge collected for selected steps during the exposure to synthetic air.

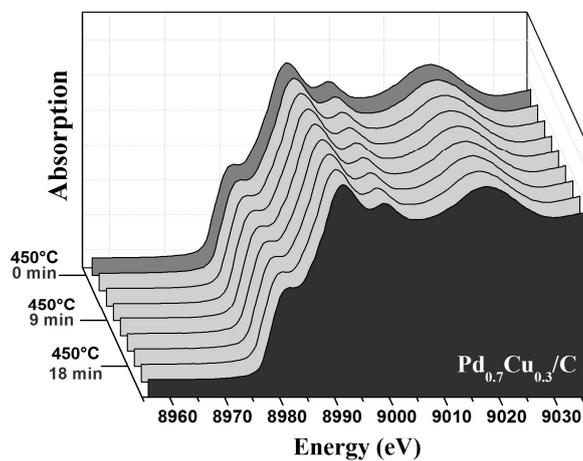
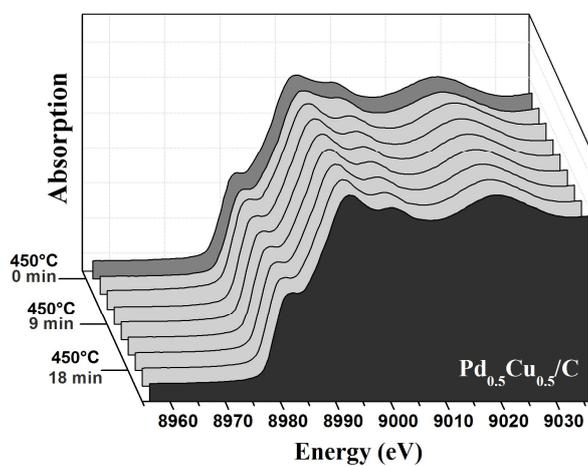
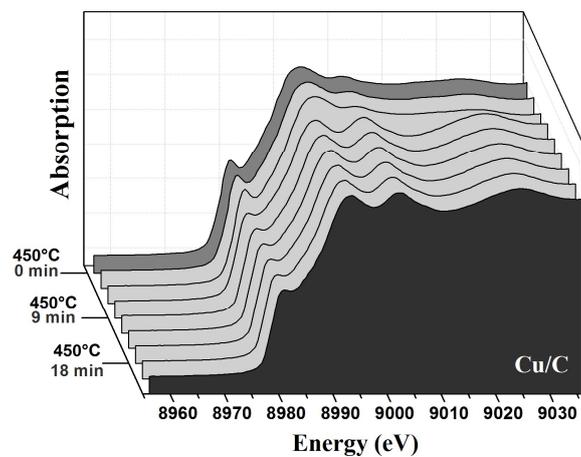


Figure SI6. XANES spectra evolution of each sample collected at the Cu-K edge during the third step of the experiment (exposure to CO at 450°C).

REFERENCES

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- 2 Rehr, J. J.; Kas, J. J.; Vila, F. D.; Prange, M. P.; Jorissen, K. Parameter-free calculations of X-ray spectra with FEFF9. *Phys. Chem. Chem. Phys.* **2010**, *12* (21), 5503-5513.