

SUPPORTING INFORMATION

The effect of surface chemistry on the performances of Pd-based catalysts supported on activated carbons

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S1. Raman spectroscopy

The oxidation treatment is responsible for small changes in the micro-structure of the carbons, as revealed by Raman micro-spectrometry. Figure S1 shows the Raman spectra of samples of series **1**, while those of samples of series **2** are reported in Figure S2. The Raman spectrum of carbon **1** has been commented in detail in our previous work.¹ Two main bands are observed around 1605 cm⁻¹ (G band) and 1350 cm⁻¹ (D band), which are typical of carbon-based materials. The G band is assigned to in-plane $\nu(\text{C}=\text{C})$ vibrations of pairs of sp² carbon atoms, whether or not they belong to an aromatic ring structure. The D band is due to $\nu(\text{C}=\text{C})$ vibrations of sp² carbon atoms with structural imperfections (e.g. close to the edges of a graphene layer) and its intensity is proportional to the concentration of six-fold aromatic rings in the cluster.²⁻⁸ In addition, broad bands are observed around 1450 cm⁻¹ (D3 band) and 1150 cm⁻¹ (I band), both of them related to the presence of amorphous carbon phase,^{9,10} and around 1700 cm⁻¹, which is due to $\nu(\text{C}=\text{O})$ vibrational modes of surface functional groups.¹¹ This band is absent in the spectrum of carbon **2** (Figure S2), which has a smaller amount of functional groups.

In the Raman spectrum of sample **1a** band I disappears, while the band around 1700 cm⁻¹ slightly increases in intensity, testifying the occurrence of surface functionalization. The D band slightly increases in intensity with respect to the G band. The interpretation is not straightforward. Most of the times, an increase in the I(D)/I(G) ratio is taken as an indication of an increase in the structural disorder, according to the Tuinstra and Koenig (TK) correlation.¹² However, as discussed in our previous work,¹ carbon **1** is characterized by graphitic domains smaller than 2 nm, and in these conditions the TK correlation is no more valid.¹³ In contrast, an increase in the I(D)/I(G) value reflects an increase of the ordering of the sp² domains. Hence, our results seem in agreement with the recent work by Collins et al.,¹⁴ who showed that treatment in HNO₃ leads to a partial graphitization of activated carbons. It is worth noticing that the phenomenon is modest, but more pronounced for carbon **1** than for carbon **2** (see Figure S2), that was already characterized by more ordered sp² domains.

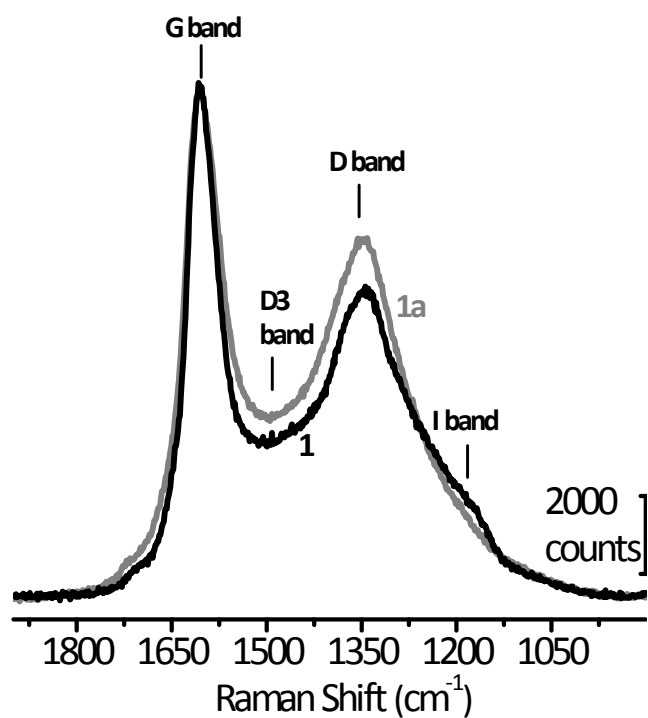


Figure S1. Raman spectra (excitation $\lambda = 514$ nm) of carbons **1** and **1a**. The spectra have been normalised to the intensity of the G band around 1600 cm^{-1} .

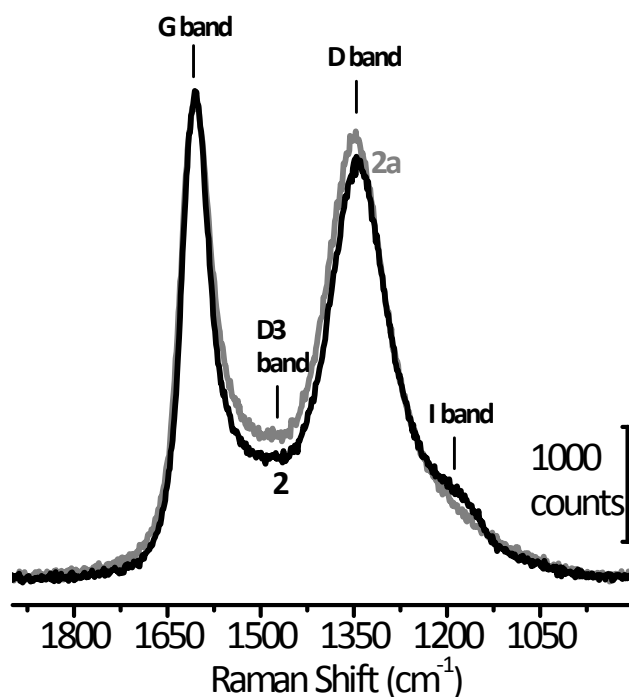


Figure S2. Raman spectra (excitation $\lambda = 514$ nm) of carbons **2** and **2a**. The spectra have been normalised to the intensity of the G band around 1600 cm^{-1} .

S2. ^{13}C SSNMR measurements

The presence of oxygen functionalities in carbon **1a** is well evident by looking to the ^{13}C CPMAS NMR spectrum in comparison to that of the parent **1** (Figure S3). The two spectra are dominated by a broad peak around 125 ppm, which is characteristic of sp^2 carbons belonging to condensed aromatic rings. However, the spectrum of **1a** distinctly shows a peak around 180 ppm, which indicates the presence of $\text{C}=\text{O}$ functional groups, most likely carboxylic rather than carbonyl groups. Similar spectra have been collected for carbons of series **2** (Figure S4), but less intense and with a worst signal-to-noise ratio (as a consequence of the smaller H content). Unfortunately, in both cases the resonance associated with $\text{C}=\text{O}$ groups is too broad to allow a quantitative evaluation of the oxygen species. We just observe here that the $\text{C}=\text{O}$ signal in the spectrum of carbons **1a** and **2a** are slightly different, suggesting a different population of the functional groups, with **1a** being more populated than **2a**.

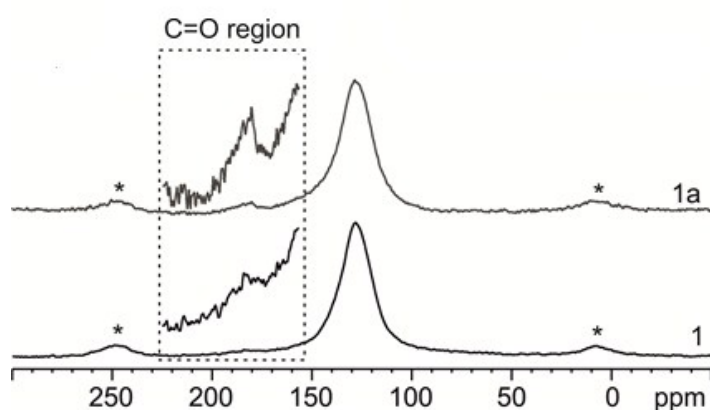


Figure S3. ^{13}C CPMAS NMR spectra of carbons **1** and **1a**, recorded at 12 kHz. Asterisks indicate spinning sidebands.

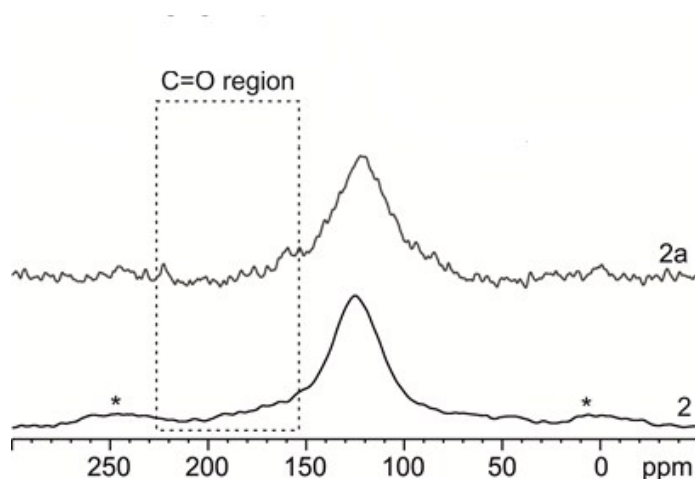


Figure S4. ^{13}C CPMAS NMR spectra of carbons **2** and **2a**, recorded at 12 kHz. Asterisks indicate spinning sidebands.

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