SUPPORTING INFORMATION

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


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. 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 ν(C=C) vibrations of pairs of sp\(^2\) carbon atoms, whether or not they belong to an aromatic ring structure. The D band is due to ν(C=C) vibrations of sp\(^2\) 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. 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, and around 1700 cm\(^{-1}\), which is due to ν(C=O) vibrational modes of surface functional groups. This band is absent in the spectrum of carbon 2, 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. However, as discussed in our previous work, carbon 1 is characterized by graphitic domains smaller than 2 nm, and in these conditions the TK correlation is no more valid. In contrast, an increase in the I(D)/I(G) value reflects an increase of the ordering of the sp\(^2\) domains. Hence, our results seem in agreement with the recent work by Collins et al., who showed that treatment in HNO\(_3\) 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 sp\(^2\) 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 C=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 C=O groups is too broad to allow a quantitative evaluation of the oxygen species. We just observe here that the C=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.