Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting information

In situ study of metal leaching from Pd/Al_2O_3 induced by K_2CO_3

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1. X-ray diffraction

The XRD pattern of 5PdA demonstrates that the sample is likely a mixed phase of γ- and θ-Al_2O_3.

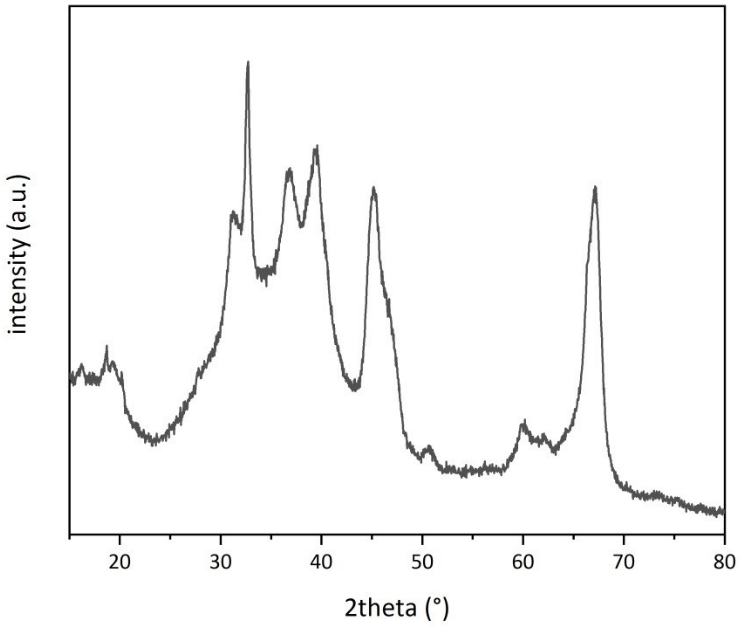

Figure S1. X-ray diffraction pattern of 5PdA.

2. EXAFS analysis of the pristine and calcined 5 wt% Pd/Al_2O_3 catalyst in dry and wet states at RT: k^3-weighted EXAFS and structural and statistical data

Figure S2 shows examples of the k^3-weighted QEXAFS (black) used to derive the Fourier transforms shown in Figure 1 of the main text, together with the fits (red) derived from analysis in EXCURV (ref. 31 main text). Table S1 summarises the structural and statistical data resulting from these analyses.

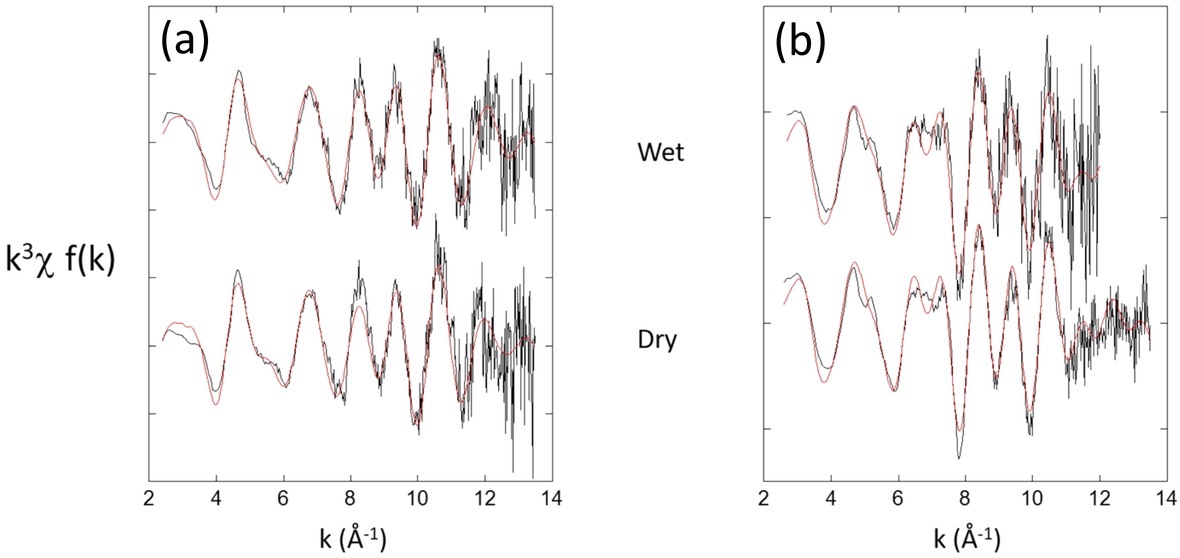

Figure S2. k^3-weighted Pd K-edge EXAFS of (a) 5PdA and (b) 5PdA^{500} at RT and in their dry and wet forms as indicated. The red lines are fits to the data derived from analysis using EXCURV.

3. Raw XANES spectra of PdA in water/ethanol and water/ethanol/K_2CO_3 flow

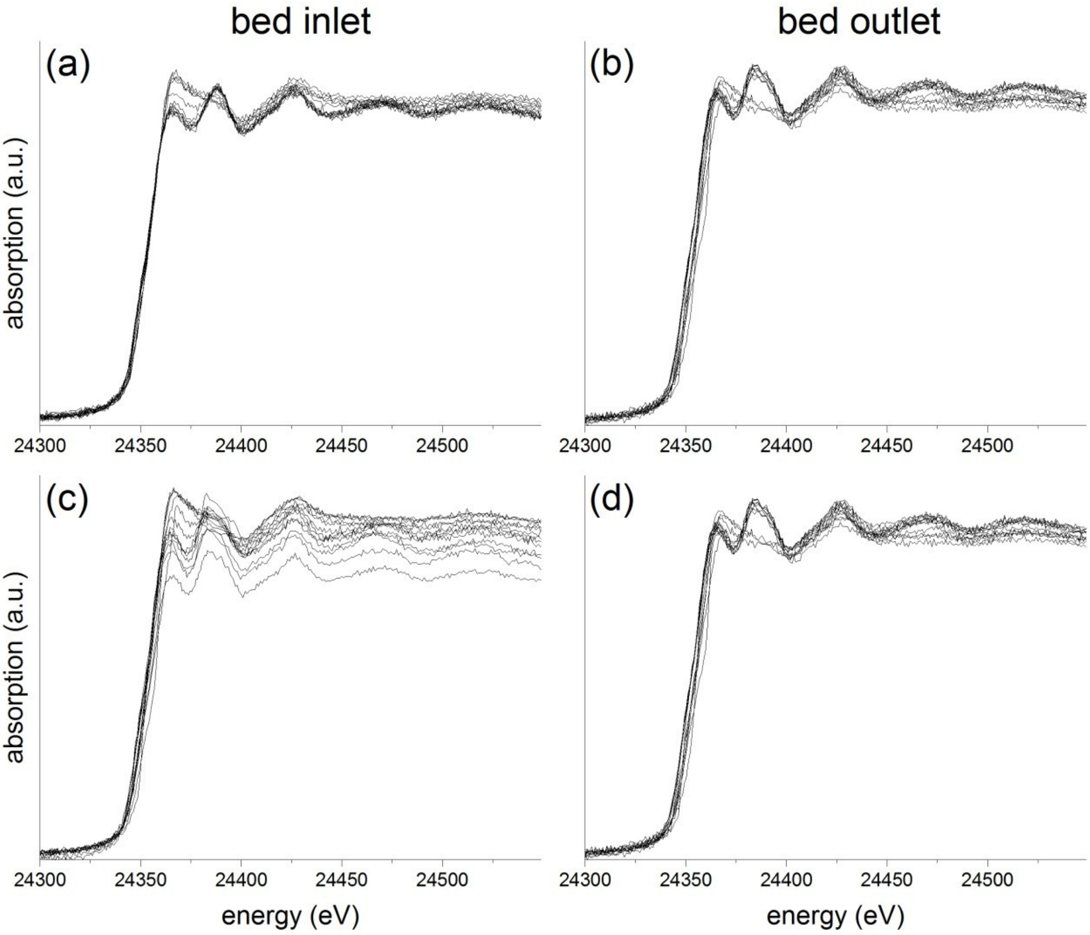

Figure S3. Pd K-edge XANES spectra collected while heating 5PdA in (a, b) water/ethanol and (c, d) in water/ethanol/K_2CO_3. The catalyst bed inlet is shown in (a) and (c), the catalyst bed outlet in (b) and (d). Spectra are not normalized in order to appreciate the levels of change of the edge jump in the spectra.

4. Calculation of average leaching rates from edge jumps variations observed in EXAFS

Figure S4 gives a schematic illustrating how the X-rays sample the catalyst bed. From this, and a knowledge of the bed volume, the weight of the sample loaded, the volume that the X-ray beam samples within the bed, and the EXAFS measurement itself being of a nature that conforms to a Beer-Lambert law, we may estimate the rate of Pd leaching (quoted for the entrance to the bed in the main text) as follows:

15 mg of sample is contained in a bed volume of 0.05 cm^3

The X-ray beam samples 0.016 cm^3

- mass of catalyst sampled by EXAFS = 4.8×10^{-4} g of which 2.5×10^{-5} g (@ 5 wt% loading) is Pd. i.e. 2.26×10^{-7} moles or 1.7×10^{17} Pd atoms.

As such (from Figure 3b and Figure 3c, main paper) a diminution of 10 % in the edge jump is seen on 5PdA in ca. 70 min and of 6% in $5PdA^{500}$ in ca. 35 min.

- the average rates of Pd loss induced by the presence of K_2CO_3 at the inlet of each bed are:

5PdA = 1.36×10^{16} / 70 min

$5PdA^{500}$ = 8×10^{15} / 35 min

i.e. 3.8×10^{12} and 3.2×10^{12} Pd atoms/s.

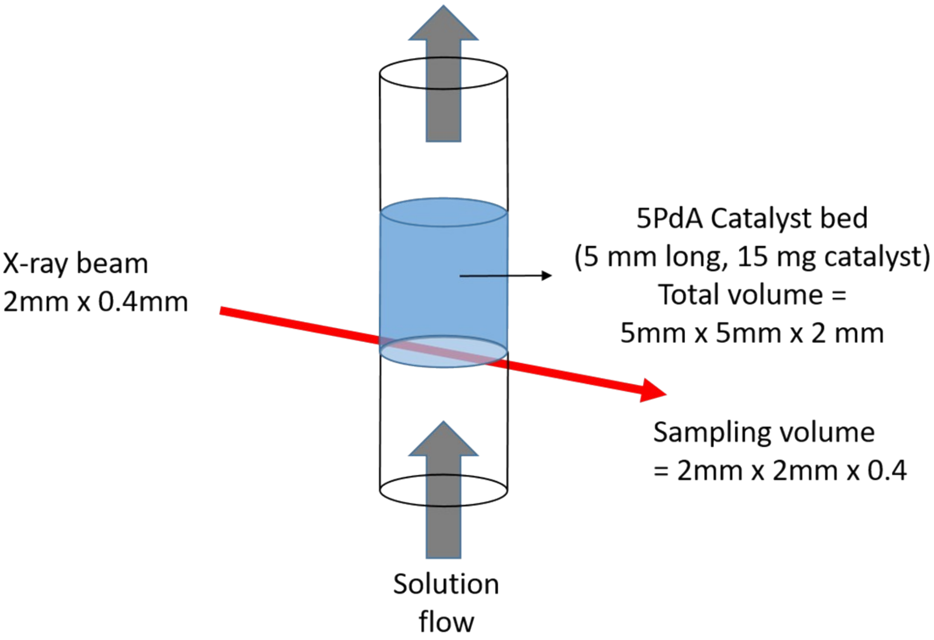

Figure S4. Schematic showing the relative dimensions and relationships of the X-ray beam used for the spatio-temporal QEXAFS measurements and the catalyst bed experiencing solvent flow. The estimation of the average rates of leaching of the Pd in the presence of K_2CO_3 at the inlets of the catalysts beds.

5. Divergence of EXAFS and TEM in their view of the 5PdA catalyst in its native state

The results of the Pd K-edge EXAFS and the TEM are significantly discrepant in the case of 5PdA as shown by EXAFS in Figure 1 of the main text in its dry and wet states (at ambient temperature). The former sees this catalysts as being comprised of Pd nanoparticles of very high dispersion and, on average, containing ca. 10 Pd atoms particle; the latter reports a catalysts comprised of Pd nanoparticles of average particle diameters of between 3 and 4 nm and therefore containing thousands of Pd atoms.

In our previous investigations of Pd catalysts experiencing flows of aqueous ethanol we have noted such a discrepancy in three other catalyst systems. From the EXAFS perspective, Pd was present as very highly dispersed Pd particles or rafts on Al_2O_3 and TiO_2 supports (ref. 16 and 17 main text) or as an Al_2O_3 supported PdO_xCl_y phase (ref. 18, main text). All these forms of Pd show significantly enhanced reducibility in water/ethanol compared to samples wherein Pd is present initially as supported PdO. In the latter case TEM and EXAFS in the dry states were found to be consistent from the point of view of the average Pd particle size indicated from each method. We have therefore concluded that, in cases where the Pd is present initially as a highly dispersed and non-PdO phase, the commonly employed use of alcohols to disperse the catalyst on a TEM grid, possibly combined with subsequent exposure to high energy electrons, provides sufficient impetus to grossly rearrange the Pd into much larger particles before they may be observed using TEM, as in the images derived from the dry and water/ethanol exposed 5PdA samples given in this report.

6. Ex situ XAFS at the Pd L_3-edge and K K-edge

In addition to the Pd K-edge EXAFS, ex situ measurement of the catalysts in their dry state and post-reaction with water/ethanol and water/ethanol/K_2CO_3 was undertaken at the Pd L_3- and K K-edges at the XMaS UK-CRG beamline at the ESRF.

These studies were aimed at uncovering any further evidence for the nature of the interaction of the base with the Pd and what effects these might have had on the Pd in the system that are not forthcoming from the higher energy K-edge studies. For instance, by using K K-edge XAFS we might obtain any evidence for the direct bonding of K to Pd. In this case, when the Pd is reduced, the Pd K-edge EXAFS is very much dominated by the Pd-Pd scattering. Hence, it is impossible to reliably extract any information pertaining to such possible interactions. Further, the Pd L_3-edge might provide more sensitive probe of the chemical state of the Pd resulting in each reactive case than the K-edge if only from the much reduced core-hole lifetime broadening in the former as compared to the latter.

Due to the much reduced core-hole lifetime broadening, the Pd L_3-edge is a more sensitive probe of the chemical state of the Pd [S1]. The normalized spectra of pristine $5PdA^{500}$ and $5PdA^{500}$ after reaction with water/ethanol in presence and in absence of K_2CO_3 are reported in Figure S5 together with their first derivatives. The much larger white line intensity of pristine $5PdA^{500}$ compared to the used samples is evident from the normalized XANES spectra of Figure S5a and confirms that Pd was initially in an oxidized state while it was reduced during the experiments with water/ethanol and water/ethanol/K_2CO_3. Small differences are found also between the two used samples: I_{WL} of the base-treated sample was slightly higher than in $5PdA^{500}$ reduced by water/ethanol only. These differences become more pronounced when the derivatives of the white line, dI_{wl}/dE, are compared as reported in Figure S5b. The Pd^0 signal at 3.175 keV is clearly strong only in the pristine sample but traces of metallic Pd might have survived also in the base-treated sample.

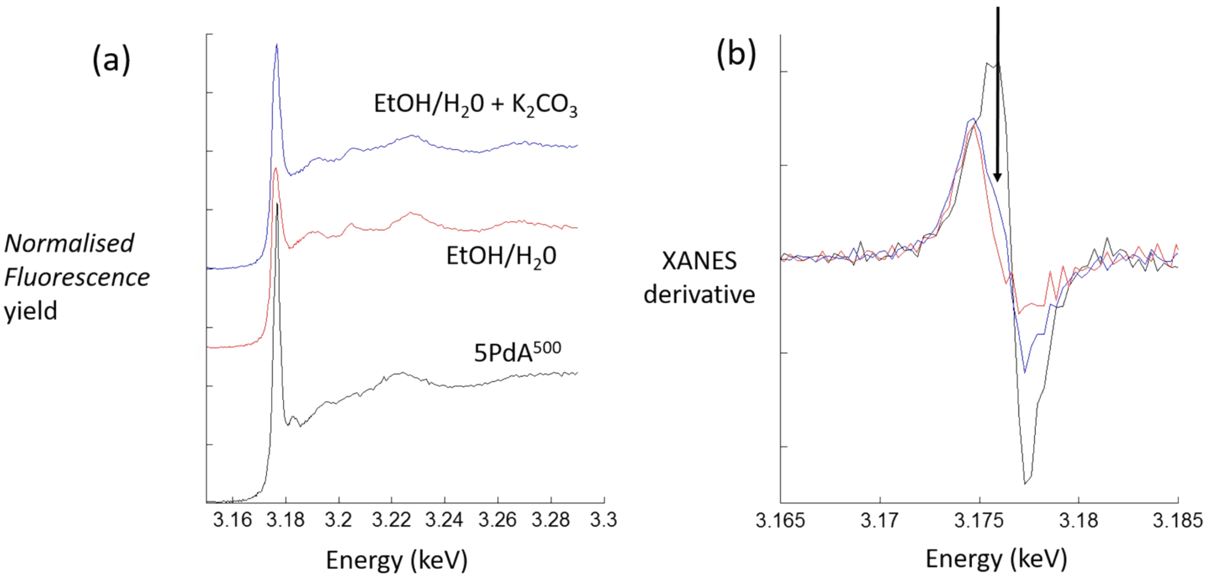

Figure S5. (a) Normalised Pd L_3-edge fluorescence XAFS obtained post factum for the fresh 5PdA^{500} sample (black) and after it has been reacted to 350 K in the presence of water/ethanol (red) and water/ethanol/K_2CO_3 (blue). (b) Corresponding first derivative of the Pd L_3-edge region.

The principal observations to be made from the Pd L_3-edge are that in both cases after exposure to the solvent mixtures the Pd is completely reduced as expected. The more pronounced nature of the two EXAFS features observable in water/ethanol compared to water/ethanol/K_2CO_3 would also be consistent with the Pd particles at the higher end of the particle size distribution having been eluted to some degree from the sample in the latter case leaving a rump of somewhat smaller Pd particles remaining attached to the Al_2O_3 support (TEM, main paper). We also note that in water/ethanol/K_2CO_3 the Pd L_3-edge white line is significantly larger than in the case where no K was added, and that a new state, indicative of an oxidised fraction of the Pd, is present in the derivative (Figure S5b blue curve, indicated by the black arrow) that is not present after reaction in the absence of the base.

These latter observations could also indicate that the net particle size of the Pd remaining in the catalyst after reaction in water/ethanol/K_2CO_3 is smaller than in the case where the base has not been used, and that, most likely at the surface of the remaining particles, adsorption of K and/or more extensive adsorption of ethoxy groups or carbonates has occurred than in the water/ethanol case.

Figure S6 shows K K-edge EXAFS obtained from used 5PdA^{500} with water/ethanol/K_2CO_3. The data range obtainable was limited by a Ca K-edge contamination (4.038 keV) most likely emanating from the pyrex mirrors used on XMaS at these energies. The resulting K-edge EXAFS, shown in Figure S6a k^3-weighted and Figure S6b Fourier transform representations, is rather complex and, similar to the K-edge XANES, is indicative of a multiplicity of K environments.

Supplementary references

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