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ARTICLE

In situ study of metal leaching from Pd/Al₂O₃ induced by K₂CO₃

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In situ time- and spatially-resolved Quick Extended X-ray Absorption Fine Structure Spectroscopy (QEXAFS) was deployed to study the leaching of Pd from a heterogeneous catalyst caused by K₂CO₃ temporally and spatially.

Introduction

The number of C-C, C-N and C-O bond-forming reactions that can be catalysed by palladium is truly astounding. The unique combination of selectivity and versatility had propelled Pd catalysis into one of the most important synthetic tools in the 21st Century, while also creating an impact in the fine chemicals and pharmaceutical industries, where Pd catalysis is routinely deployed in the discovery and production of several active ingredients of high value.¹⁻⁴ To date, the majority of palladium catalysts utilised for cross-coupling reactions is performed in a homogeneous phase, as discrete metal complexes dissolved in the reaction solvent. While the use of heterogeneous or immobilised Pd catalysts can, in principle, lead to more cost-effective and sustainable processes (as the precious metal can be recovered, simplifying the 'work up' procedure), in practice they are not used in any industrial processes due to their limited stability.⁵ Of all the possible catalyst deactivation pathways,⁶ the most pernicious is undoubtedly leaching, where the catalyst is irretrievably lost to the solution phase and causes contamination of the product – effectively negating the benefits of using a heterogeneous catalyst. Understanding what causes leaching of Pd from solid supports will allow us to propose and devise effective mitigation strategies.

Loss of Pd from a support can conceivably occur *via* two different pathways: (i) Interaction of surface Pd species with reaction components (solvent, reactants, additives, products) to form a solubilised species that can pass into the bulk solution;

and (ii) a weakened interaction between the metal and the support, leading to physical detachment of the nanoparticle.⁷

Metal oxides are often used to support Pd nanoparticles for Suzuki-Miyaura coupling reactions. Studies of metal leaching during these reactions have been summarised in a recent review:⁸

- Proven correlation between the extent of Pd leaching with catalytic activity, leading to the conclusion that catalysis (mainly) occurs in solution;
- Amorphous PdO on the surface of Pd/Al₂O₃ and Pd/SiO₂ leaches more easily than Pd(0), suggesting that the release of Pd²⁺ is the fundamental step in the generation of catalytically active species;
- In a batch reactor, leached Pd species can be recaptured by the metal oxide support at the end of a reaction;
- The presence of a base (such as K₂CO₃) is critical to generate catalytically active species.⁹

In most of these studies, catalyst leaching was identified largely by *ex situ* methods, such as determination of Pd species by atomic absorption spectroscopy (AAS) or inductively coupled plasma-mass spectrometry (ICP-MS), detection of catalytic activity in solution (hot filtration), or a visual inspection of the catalyst before and after a reaction using transmission electron microscopy (TEM).

In comparison, X-ray Absorption spectroscopy (XAS) is a powerful method of interrogating changes of surface and solution species *in situ*.⁹ Typically, the X-ray absorption near edge structure (XANES) is element-specific and affords information on the average oxidation state,¹⁰ while the extended X-ray absorption fine structure (EXAFS) provides details of the coordination environment. However, most attempts to employ XAS to examine catalyst leaching were either performed *ex situ* or in "batch" reactors.¹¹⁻¹⁴ Given that leached species may redeposit on the catalyst during the experiment, this can mask the true levels of solubilisation and speciation.

In an earlier publication, we first described the design of a custom-made plug flow reactor that can be employed with

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quick scanning EXAFS (QEXAFS) to examine changes in a catalyst bed while it is subjected to a continuous flow of liquid reagents. This allowed us to track the speciation and mobilisation of Pd species axially within a pack bed, and to correlate this with attendant changes in oxidation state and particle morphologies.¹⁵ More recently, we showed that the exposure of heterogeneous Pd catalysts to an aqueous alcoholic solution is enough to reduce PdO to Pd(0), and induce the restructuring of very small Pd into larger particles, even under relatively mild conditions (≤ 353 K).¹⁶ The evolution of gradients within the catalyst bed allowed us to establish relationships between the sizes of the nanoparticles¹⁷ and the effect of chloride anions,^{18,19} with their redox and agglomeration behaviour.

In this work, the same approach was applied to examine the effect of K_2CO_3 , an inorganic base commonly employed in many Suzuki-Miyaura reactions, on the speciation of Pd(0) and Pd²⁺ (PdO) NPs supported on alumina. In this paper, we will demonstrate the effect of introducing an inorganic base (K_2CO_3) has on the leaching behaviour of reduced and oxidised forms of Pd/ Al_2O_3 .

Results and discussion

EXAFS analysis of reduced and oxidised forms of Pd/ Al_2O_3

Alumina is widely used as a support of Pd nanoparticles (NPs) for Suzuki-Miyaura cross-coupling reactions,²⁰⁻²³ where leaching was reported to occur under mild conditions (338 K).^{20,21,24,25} Catalyst activity is associated with the amount of Pd²⁺ present in alumina-based catalysts.²¹

To examine the effect of the Pd oxidation state on leaching, two forms of Pd/ Al_2O_3 were selected for this study: an as-received commercial catalyst in the reduced form (5PdA), which was calcined in air at 773 K for 5 h to produce an oxidised sample (5PdA⁵⁰⁰). Pd K-edge EXAFS were recorded of the dry powders, and after they have been wetted by water/ethanol. Fourier transforms of the k^3 -weighted EXAFS data are presented in Figure 1 while the results of the analysis are summarized in Table 1.

The pristine 5PdA sample is expected to compose predominantly of metallic Pd(0) entities, with a small amount of surface oxides due to prolonged contact with air. This was supported by the EXAFS data, showing the presence of a first oxygen shell at 2 Å (labelled as Pd-O in Figure 1a) and a first Pd shell at 2.74 Å (Pd-Pd^{fcc}), corresponding to Pd-O and Pd-Pd distances in the reduced form of this catalyst. The resultant EXAFS fitting (Table 1; Figure S2, Supporting info) returns evidence for aluminium neighbours (Pd-O-Al) at around 3.4 Å, overlapping with the second Pd shell at 3.86 Å (2nd Pd-Pd^{fcc}). The absence of a Pd-O-Pd scattering shell (expected at *ca.* 3 Å) rules out the presence of a significant amount of PdO in the sample. Coupled with the low first shell PdPd coordination number ($N_{1}^{PdPd} = 4$), and the absence of significant higher shell structure,²⁶ this suggests that 5PdA is comprised of *small and highly-dispersed Pd(0) NPs* consisting, on average, of less than ten atoms, *i.e.* less than one single shell of a fcc cluster.

In contrast, the FT spectrum of oxidised 5PdA⁵⁰⁰ contains two distinctive Pd shells at 3.05 and 3.42 Å (Pd-Pd^{fcc}), in addition to the first oxygen shell (2.01 Å; Pd-O, Figure 1b), suggesting that 5PdA⁵⁰⁰ consists mainly of PdO species.²⁶ In line with our previous studies, no significant differences can be seen between “dry” and “wet” catalysts, confirming that the Pd NPs are stable in water/ethanol at ambient temperature.¹⁶⁻¹⁸

Figure 1. Fourier transforms of k^3 -weighted Pd K-edge EXAFS of the two samples of 5wt% Pd/ Al_2O_3 employed in this work: (a) pristine material (5PdA), (b) calcined (5PdA⁵⁰⁰), under dry (red), and wetted (black) conditions (data are phase-shift corrected).

Table 1. Structural and statistical parameters used in the fit of the spectra of 5PdA and 5PdA⁵⁰⁰ in the k range 2.5–12.5 Å⁻¹.

5PdA: dry		N_1^a	R^b [Å]	DW ^c [2 σ^2]	
O		2	2.01	0.004	R% ^d =40.8
Pd		4.5	2.74	0.018	E_f^e =-0.48
Al		3.2	3.41	0.006	
Pd		1.3	3.86	0.014	
5PdA: wet		N_1	R [Å]	DW [2 σ^2]	
O		2.1	2.01	0.004	R%=41.1
Pd		4.7	2.74	0.018	E_f =0.076
Al		3.1	3.41	0.006	
Pd		1.1	3.88	0.014	
5PdA ⁵⁰⁰ : dry		N_1^{PdPd}	R [Å]	DW [2 σ^2]	
O		4.2	2.02	0.009	R%=37.43
Pd		4.1	3.05	0.018	E_f =2.714
Pd		5.8	3.42	0.014	
5PdA ⁵⁰⁰ : wet		N_1	R [Å]	DW [2 σ^2]	
O		4.5	2.01	0.009	R%=42.34
Pd		4	3.03	0.14	E_f =5.25
Pd		6.1	3.42	0.14	

^a Coordination number ($\pm 10\%$ of stated value). ^b Distance of the scattering atom from central atom ($\pm 1.5\%$). ^c Debye-Waller factor; σ is the root mean square inter-nuclear separation (Å). ^d R% = $\sum_i N_i 1/\sigma_i (\chi_i^e(k) - \chi_i^t(k))^2 \times 100$ where χ_i^e and χ_i^t are the experimental and theoretical EXAFS, respectively, and k is the photoelectron wave vector ($\text{\AA}^{-1}$). σ_i is the uncertainty in the data, with $1/\sigma_i = k_i^n / \sum_j N_j k_j^n (\chi_j^e(k_j))$. ^e Edge position relative to the vacuum zero (Fermi energy, eV).

Other parameters: AFAC = 1 (the proportion of electrons undergoing scattering post-adsorption that contribute to the EXAFS).

Evidence and extent of Pd leaching (ΔEdge)

In an earlier study by Köhler and co-workers,²⁴ Pd/Al₂O₃ was exposed to different components of a Suzuki-Miyaura coupling reaction, and the extent of leaching was established by the amount of Pd present in solution (determined using AAS). It was shown that the catalyst is largely stable in the solvent mixture of NMP/water (5:2), even after heating at 338 K for 1 h (8% Pd detected in solution). The addition of an inorganic base (Na₂CO₃), however, caused substantial dissolution of Pd from the support (38% Pd) under the same conditions.

With this in mind, the PdA and PdA⁵⁰⁰ samples were heated at 1 K·min⁻¹ under a flow of the water/ethanol mixture, with and without base (K₂CO₃), from 298 to 353 K (corresponding to the range of temperatures employed in Suzuki-Miyaura reactions), where it was maintained for an additional 25 min. During the heating process, the catalyst bed was mapped by QEXAFS: data were acquired in 5–7 min sequentially at nine distinct positions from the bottom to the top of the catalyst bed (along the liquid flow direction), before returning to the original position to restart the axial inspection. By comparing the XANES data collected at different positions within the bed (Figure S3), the extent of Pd leaching can be assessed simply by observing changes in the absolute levels of X-ray absorption (ΔEdge) over time (Figure 2).

A uniform ΔEdge was observed across all positions in the catalyst beds of 5PdA and 5PdA⁵⁰⁰ in a flow of water/ethanol even at elevated temperatures (indicated by the open symbols in Figures 2b and 2c). Hence, no significant Pd leaching occurs in the solvents, which supports the earlier study.²⁴

The presence of K₂CO₃ in the solvent mixture, however, clearly triggered a redistribution of Pd at the inlet, middle and outlet of the catalyst bed. For the 5PdA sample, a reduction of ΔEdge at the inlet of the cell was noticeable from the beginning of the experiment (Figure 2b, green line), continuing after the maximum temperature of 353 K had been reached (after 55 min). Simultaneously, a gradual increase of the Pd concentration at the outlet of the catalyst bed (blue line) was observed, while the centre of the bed (red line) exhibited a somewhat intermediate behaviour between the two other positions. These observations suggest that Pd is mobilized in the direction of the liquid flow, and at least some of the Pd appear to be redeposited in the latter part of the packed bed. In accordance with Beer-Lambert Law, ΔEdge in transmission XAS should be proportional to the amount of Pd present in the volume probed by the X-ray beam. Over the course of these experiments, Pd losses of up to about 10% could be observed at the inlet of the bed of 5PdA, with an estimated average leaching rate in the order of $3\text{--}4 \times 10^{12}$ Pdatoms·s⁻¹ (see page S5, supporting info).

The effect of K₂CO₃ on leaching was also similarly observed in the XANES data collected for 5PdA⁵⁰⁰ (Figure 2c). In this case, decreases in ΔEdge at the inlet and the middle of the catalyst bed were only noticeable after 40 min from the start of heating (338 K). As a result of this delay in the onset of catalyst leaching, *ca.* 50% less Pd was lost by the end of the experiment, compared to that observed for PdA. In contrast to the

Figure 2. (a) Temperature profile, (b) evolution of the Pd concentration for 5PdA and (c) for 5PdA⁵⁰⁰ at inlet (green), centre (red) and outlet (blue) of catalyst bed under a constant flow of water/ethanol/K₂CO₃. Open symbols measured in absence of base. Coloured lines were hand drawn to guide the eye.

accumulative gradients observed at the middle and outlet of the 5PdA bed, there is little evidence for redeposition of Pd in 5PdA⁵⁰⁰. This implies that most of the leached Pd species is permanently lost to the mobile phase.

Even at this early stage of the investigation, important differences in catalyst leaching behaviour are uncovered, which are dependent upon the initial size and oxidation state of the nanoparticle. While the presence of the inorganic base causes Pd to leach in both cases, evidence for redeposition of Pd was only observed in the reduced form of the Pd (5PdA). It is also interesting to note that under these conditions, there is no evidence that PdO leaches more easily than Pd(0). In the next part of this study, we attempt to correlate this with the fundamental redox and agglomeration processes occurring in the samples under these conditions.

Reduction of Pd²⁺ to Pd in heated solutions: QEXAFS (I_{WL} , N_1^{PdPd})

White line intensities (I_{WL} , 24.367 keV), indicative of the oxidation state of Pd, and coordination numbers (N_1^{PdPd} , sensitive to the particle size^{27,28}), were extracted from the normalized XANES and EXAFS data, respectively. These data are presented in Figure 3 as a function of time (the original data are presented in Figure S3, supporting info).

At the beginning of the experiments ($t = 0$) the I_{wl} reflected the difference in Pd oxidation states in each sample as determined previously (Figure 1). After 20 min of heating (318 K), the onset of reduction of surface Pd^{2+} to $\text{Pd}(0)$ was indicated by a decrease in the I_{wl} of 5PdA (Figure 3b), which continued for the next 20 min. The reduction process was accompanied by an apparent increase in $N_{1^{\text{PdPd}}}$ from its initial value of 4 (Figure 3c), reaching the final value of between 8-10 after about 30 min (328 K). The observed change in oxidation state and attendant growth in particle size²⁹ is in accord with our earlier studies of similar $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts.^{16,17}

In the presence of K_2CO_3 , identical responses in I_{wl} and $N_{1^{\text{PdPd}}}$ were observed (overlap between red open and closed circles, Figure 3). Therefore, for the sample of reduced 5PdA, we can surmise that the reduction of the Pd and agglomeration processes are independent of the base and are unlikely to be involved in the leaching process.

As 5PdA^{500} consisted mainly of PdO phases at the beginning of the experiment, the initial white line I_{wl} (Figure 3b) was higher than that of 5PdA, and $N_{1^{\text{PdPd}}} = 0$ (Figure 3c). In the absence of K_2CO_3 (open black symbols), the onset of Pd reduction was observed at $t = 35$ min (333 K). Correspondingly, a sharp increase in $N_{1^{\text{PdPd}}}$ from 0 to between 8-10 was observed, indicating that the reduction of PdO to metallic Pd occurs rapidly, without leaching taking place.

Figure 3. Reduction of Pd NPs in 5PdA (red) and 5PdA^{500} (black) in water/ethanol (open symbols) and water/ethanol/ K_2CO_3 (filled symbols): (a) Temperature profile, (b) white line intensity and (c) number of nearest neighbours, $N_{1^{\text{PdPd}}}$. Black lines in (b) have been hand drawn to guide the eye.

Figure 4. Normalized fluorescence K K-edge XANES spectra of (a) PdA, (b) PdA^{500} after exposure to water/ethanol/ K_2CO_3 , and standard K compounds: (c) potassium tert-butoxide, (d) K_2CO_3 and (e) KOH.

In the presence of K_2CO_3 , the only discernible difference between this and the above is a slight delay in the reduction process by *ca.* 10 min, occurring at $t = 45$ min/343 K in the basic solution (Figure 3b, black open and filled symbols). This coincides with the beginning of the leaching process at 40 min (Figure 2c), suggesting the introduction of K_2CO_3 has a retarding effect on the reduction process. The observation echoes the result of an independent study, where the presence of K_2CO_3 was also found to delay the PdO reduction in Pd NP deposited on $\text{SiO}_2\text{-Al}_2\text{O}_3$.³⁰

Within the error afforded by intensity measurements in EXAFS ($\pm 10\%$ at best), identical final values of I_{wl} and $N_{1^{\text{PdPd}}}$ were observed for both 5PdA and 5PdA^{500} at the end of these experiments.

Interaction of potassium with the catalyst & support (K K-edge)

The result above showed that the leaching of Pd occurs only in the presence of K_2CO_3 . This can be attributed to the elevated pH of the solution (12.9), which exceeds the point of zero charge (PZC) of alumina (between 8-10), which can interrupt the metal-support interaction.³¹ However, additional interactions between the inorganic base and the support may also further contribute to leaching.

Potassium salts are known to interact with different metal surfaces to form highly dispersed K_2O to stabilise certain facets.³² The adsorption of K^+ ion on $\text{Pd}(100)$ and $\text{Pd}(111)$ surfaces alters their electronic properties,^{33,34} and is known to enhance the catalytic performance of $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts.³⁵⁻³⁷ On $\text{Pd}(100)$ and silica-supported Pd NPs, adsorption of K^+ was also reported to promote the dissociation of methanol to form surface-bound potassium methoxide.^{38,39} Similarly, the first step of ethanol decomposition on $\text{Pd}(110)$ is the cleavage of the O-H bond to form surface-bound ethoxide species,⁴⁰ prior to C-H and C-C cleavages at elevated temperatures.^{41,42}

In order to determine the nature of interaction between K^+ with the catalytic material, *ex situ* fluorescence K K-edge XANES data were recorded of the samples exposed to

water/ethanol/ K_2CO_3 (Figure 4). The normalized spectra of 5PdA and 5PdA⁵⁰⁰ were practically identical (Figures 4a and 4b), exhibiting distinctive features at 3615 and 3619 eV.

Compared to selected potassium standards (potassium *tert*-butoxide, K_2CO_3 and KOH, Figures 4c-e), it is evident that the intensity of the white-line features in the two recovered catalysts is more than a simple summation of components from the standards. Specifically, the spectrum of the K_2CO_3 (Figure 4d) contains a distinctive peak at 3622 eV, which is notably absent from the other samples. This led us to propose that the residual potassium in the catalyst is likely to exist in more than one form, which may include K-Pd and K-O interactions.

The existence of multiple K environments is further supported by fitting of the K K-edge EXAFS spectra (Figure 5).⁴³ A list of the fit parameters is given in Table 2, along with the effect of the sequential addition of the shells on the R factor returned from analysis. It is important to note that the shells presented are required to produce satisfactory fittings to the k-weighted EXAFS (k_1 , k_2 or k_3 weightings). At this juncture, the fitting can only be treated as "indicative" in nature, given that there are very few reports on the adsorption of K directly to metal or oxide surfaces. Casanova and co-workers utilised K K-edge SEXAFS to study the nature of bonding between alkali metals and metal oxides. K-O bond distances of 2.62 Å and 2.70 Å were reported of potassium adsorbed on rutile TiO_2 ⁴⁴ and ZnO surfaces,⁴⁵ respectively. Subsequently, Burchhardt *et al* employed low energy electron diffraction (LEED) to measure the adsorption of K on the Pd(100) surface, found a Pd-K distance of 2.13 Å,⁴⁶ which was supported later by DFT calculations.⁴⁷

The data provided by these studies agree well with two of the fitted shells (O at 2.71 Å, and Pd at 2.30 Å), suggesting that K is adsorbed all over the catalyst (on both the Al_2O_3 and Pd). The nature of the remaining two shells (Pd at 3.25 Å, and C at 1.82 Å) is difficult to identify at this juncture.

Figure 5. (a) Top: k^3 -weighted K K-edge EXAFS derived from the recovered 5PdA catalysts following treatment in water/ethanol/ K_2CO_3 at 350K. (b) Bottom: The corresponding Fourier transform of the k^3 -weighted data. Fits obtained by EXCURV analysis are given in red.

Table 2. Shells fitted to the k^3 -weighted K K-edge EXAFS derived from the 5PdA catalysts (Figure 5). The sequential change in R factor as shell are added and refined is also given.

shell	N^a	$R \text{ (Å)}^b$	$DW (2\sigma^2\text{Å}^{-1})^c$	R% per shell added
O	3.7	2.71	0.013	86.6
Pd	1.2	2.30	0.014	67
C	0.6	1.82	0.011	61
Pd	0.7	3.25	0.008	56.8

Parameters: $K_{\min} = 2$; $K_{\max} = 10.5$; AFAC = 1; EF = 1; R% = 56.8. R% and AFAC are defined in the main text (Table 1). ^a Coordination number; ^b distance of the scattering atom from central atom; ^c Debye-Waller factor; σ is the root mean square inter-nuclear separation (Å).

Figure 6. TEM micrographs of PdA (a) pristine and (b) exposed to water/ethanol/ K_2CO_3 (recovered from the experiment shown in Figure 2b).

Detachment of Pd nanoparticles from support (TEM)

Transmission electron microscopy (TEM) is frequently employed to inspect catalysts visually before and after reactions, and had been previously employed to study fresh and recovered Pd/ Al_2O_3 catalysts used in the Suzuki-Miyaura reaction.²⁴ However, in a previous study, we had reported that the process of dispersing the catalyst on the TEM grid, combined with subsequent exposure to high energy electron beam, is sufficient to cause significant rearrangement of Pd(0) particles on Al_2O_3 and TiO_2 supports.¹⁶ Thus, a great deal of caution must be exercised in using the technique to determine particle shapes and sizes. It is also important to note that metallic NPs of <1 nm can be difficult to detect by TEM.

K_2CO_3 can also interact strongly with Al_2O_3 to form AlOK groups,⁴⁸ and the porous structure of Al_2O_3 can be destroyed by an excess of the base.⁴⁹ Thus, detachment of the NPs from the damaged support is a possible mechanism for leaching. With

this in mind, TEM was deployed to assess the effect of K_2CO_3 on the alumina support (Figure 6). Initially, a mixture of Al_2O_3 crystallites can be observed in the pristine sample of 5PdA, consistent with the heterogeneous phase composition of the starting material (confirmed by XRD, Figure S1, supporting info), including a typical needle with straight and regular edges (Figure 6a). Following the exposure to K_2CO_3 (Figure 6b), however, corrugated needles and large portions of grooves (not shown) were detected in the recovered catalyst, indicative of an aggressive chemical attack by the basic solution (pH = 12.9).

In contrast, pristine 5PdA⁵⁰⁰ consisted of loose Al_2O_3 aggregates covered with oxidised Pd NPs (Figure 7a). Following exposure to water/ethanol, the reduced Pd NPs show a higher contrast in the micrographs, compared to the PdO particles in the pristine sample (Figure 7b). The Pd particle size distributions are rather similar in these two samples, found to be mostly in the range of 3–4 nm (histograms in Figures 7d and 7e). Additionally and somewhat unexpectedly, the micrographs recorded of the base-treated 5PdA⁵⁰⁰ sample were found to contain numerous Pd NPs *adsorbed directly on the lacey carbon film*, along with those remaining on the alumina support (figure 7c).⁵⁰ The substantial number of free-standing particles observed in the recovered 5PdA⁵⁰⁰ sample is particularly noticeable, considering that none can be found in the equivalent sample of 5PdA. The size distributions of Pd particles observed on the carbon grid (98 particles counted in 6 micrographs) were compared to particles that remained attached to the oxide support (76 particles from 5 micrographs). The result revealed not only a significant number of detached particles, but that they also appear to be larger, on average, compared to those remained attached to the support (Figure 7f).

The empirical observation suggests that the initial oxidation state of Pd on an alumina support can not only delay the onset of the reduction process (Figure 3), it can also cause the wholesale physical detachment of the Pd NP from the metal oxide during treatment with a basic solution. Analogies can be drawn between this and a recent study,⁹ where the leaching of Pd NP and molecular Pd^{2+} from a strongly acidic support (Lewatit K2629) was attributed to K_2CO_3 causing an interruption of electrostatic interaction between the NP and the support.

Figure 7. Transmission electron micrographs of (a) pristine and (b, c) recovered 5PdA⁵⁰⁰ and (d-f) corresponding Pd particle size distributions.

Proposed mechanisms for leaching

We have shown that the addition of K_2CO_3 to an ethanol/water mixture can cause significant leaching of Pd from the alumina support (Figure 2). In each sample, leaching by dissolution of Pd^{2+} species by the basic solution cannot be entirely ruled out.²⁴ However, this is unlikely to be the dominant mechanism, as this would be expected to lead to a reduction of particle size, reflected by N_1^{PdPd} , which is not the case in these experiments (Figures 3b and 3c).

In 5PdA, the majority of the palladium was initially present as highly dispersed metal clusters of <10 atoms. Contact with heated water/ethanol removes residual surface oxides from these metal clusters, causing them to agglomerate on the surface to form larger NPs, or, leaches into the bulk solution in the direction of the mobile phase. The small nanoclusters (not visible by TEM) can be retained by the support relatively easily at the middle/outlet of the catalyst bed, where they can be assimilated into larger agglomerates.¹⁷

In contrast, 5PdA⁵⁰⁰ contained PdO NPs of between 3–4 nm at the beginning of these experiments (Figure 7a). The higher oxidation state of PdO enables a stronger electrostatic interaction with the Al_2O_3 support, ensuring greater resistance against reduction by water/ethanol (Figure 2), which is further delayed by the adsorption of K^+ . Once the reduction process commences, the interaction between the particle and the support is disrupted, causing the NP to detach. In this case, the

(larger) NPs released into the mobile phase are less likely to be retained by the metal oxide support, while also being more visible in the TEM micrographs.

A simple mechanistic picture is proposed, to explain the underlying processes of leaching observed in 5PdA⁵⁰⁰ in the presence of K₂CO₃ (Figure 8). While there is evidence to suggest that the alumina support does suffer from chemical attack by the basic solution, this alone is insufficient to cause the physical detachment of the Pd nanoparticles, at least within the

Figure 8. Pictorial representation of the proposed mechanism responsible for the detachment of Pd particles observed in 5 wt% Pd/Al₂O₃ during heating in water/ethanol and water/ethanol/K₂CO₃.

timescale of these experiments. In line with earlier proposals, we believe that the primary mode of attachment between the Pd nanoparticles and the alumina support is largely electrostatic in nature, which is disrupted as the PdO is reduced to Pd(0). This is exacerbated by adsorption of the different charged species (K⁺, EtO⁻) onto the support and the Pd, further interfering with the electrostatic interactions during the reduction process. Eventually, the interaction of the catalyst particles with the support is reduced to such an extent that detachment can occur (Figure 8).

Experimental section

Materials

Pd/Al₂O₃ (Johnson Matthey, type 324; 5 wt% Pd; received in reduced form) was used both in its pristine state (denoted as 5PdA) and after calcination in air at 773 K for 5 h (5PdA⁵⁰⁰). Prior to use the material was sieved to a 100–150 μm fraction. The X-ray diffraction pattern of the pristine catalyst (5PdA; Figure S1) was recorded on a Bruker D8 Advance diffractometer (Cu K_α source).

XAS Experiments

Spatially-resolved quick extended X-ray absorption fine structure spectroscopy (QEXAFS) measurements were performed at the Swiss-Norwegian Beamline (SNBL) of the

European Synchrotron Radiation Facility (ESRF) using a Si (111) double crystal monochromator and ion chambers for detection of the transmitted X-rays. A Pd foil was mounted between the second and the third ionization chambers for calibration of the energy scale. The continuous flow reactor used in this study has been described previously for experiments with gases.^{51,52} For use with flowing liquids it was sealed using 0.1 mm thick Teflon disks on either side of the catalyst bed. The catalyst (*ca.* 15 mg) was loaded into this cell to form a *ca.* 5 mm long bed with a cross section of 5×2 mm². The latter dimension provides the sample thickness probed by the transmission QEXAFS experiment. The bed was secured on either end using quartz wool. In this arrangement, the sample is mounted between the two heat cartridges, thus ensuring homogeneous temperature distribution along the bed. The reactor was mounted on the xyz motor stage of the beamline. The overall experimental protocol followed in this study has been described previously.^{15–19} Solvent components were individually degassed by bubbling nitrogen gas through the liquids followed by sonication after mixing. Once loaded into the reactor the sample was measured in the dry state before pumping of the solvent (50% v/v ethanol in water; pH = 6.3) was initiated at a flow rate of 0.1 mL·min⁻¹ using a syringe pump. The bed was mapped again “wet” at ambient temperature. All tubing was Teflon (1/16” inner diameter). The sample was then heated under solvent flow to 353 K at 1 K·min⁻¹ and held at this temperature for 25 min. The same measurement was repeated on a fresh sample bed in presence of flowing water/ethanol/K₂CO₃ 0.1 M solution (pH = 12.9). The catalyst bed was probed by the X-ray beam (3×0.4 mm², 1×h) every 0.5 mm between inlet and outlet while moving the cell downwards during the experiment to complete a full bed scan. Individual, unidirectional Pd K-edge QEXAFS spectra (24–25.5 keV) were recorded in about 30–40 s while a complete axial scan of the bed was completed in 5–7 min. Data reduction was performed using the Prestopronto XAFS software⁵³ or PAXAS30 prior to EXAFS analysis using EXCURV.⁵⁴

Ex situ measurements at the K K-edge were carried out at the XMaS UK-CRG beamline of the ESRF (Grenoble, France) on samples previously used in the Pd K-edge measurements (above), recovered from the cell. Equipment and methods utilized in the measurement are outlined in detail elsewhere.⁵⁵ The data range obtainable at the K K-edge was limited by a Ca K-edge contamination at 4.038 keV; the likely source of this contamination being the pyrex mirror then used on XMaS at these energies. Powder samples were mounted on carbon tape and placed inside a vacuum chamber at 318 K to both the X-ray source and a single element silicon fluorescence detector (Ketek). Spectra were collected sequentially overnight under vacuum.

Transmission Electron Spectroscopy (TEM)

Specimens for transmission electron microscopic analysis of the materials before and after use in the QEXAFS experiments were prepared on lacey carbon copper grids from sonicated dispersions in isopropanol. Micrographs were collected with a JEOL JEM 2010 transmission electron microscope equipped with a LaB6 cathode and operated at 200 keV. Images were

recorded by a slow scan CCD camera (4008×2672 pixels, Orius Gatan Inc.). Particle size distributions were obtained from the electron micrographs by manually measuring the diameter of particles from at least five different regions of the grid. Binning of the data was performed by NumPy's np.histogram(bins='auto') method.⁵⁶ This method selects an optimum bin width based on the statistical characteristics of the data set. In the case of the sample treated with the base ca. 100 particles were counted on carbon and ca. 80 particles on Al₂O₃.

Conclusions

Pd leaching from two Pd/Al₂O₃ samples (reduced and oxidised) was found to occur under basic conditions in flowing water/ethanol, proposed to be driven by the reduction process combined with actions of the base and elements of the solvent (e.g. ethoxides) to reduce the electrostatic forces between the metal and the support. For the reduced form of the catalyst (5PdA), leaching of small metal clusters occurs in a facile manner, which can be redeposited later in the catalyst bed. In contrast, the oxidised form of the catalyst (5PdA⁵⁰⁰) consists of larger PdO NPs (>3 nm diameter), which are more resistant to leaching, but eventually detaches as whole particles. In both cases, the basic solution is also corrosive to the supporting Al₂O₃ phase, which can further contribute to the loss of Pd.

The implications of these findings are highly significant for catalysis, as K₂CO₃ are widely used in Pd catalyzed C-C coupling reactions, and often in quantities far exceeding those used in this study. Alcoholic solvents such as the water/ethanol mixture are also desirable as they are consistently highly rated in 'green' solvent selection guides. The results of our study indicate that the combined use of these reagents could significantly promote the leaching of Pd, at least for Pd/Al₂O₃, even in the absence of reactants.

Conflicts of interest

There are no conflicts to declare.

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‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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In situ Quick Extended X-ray Absorption Fine Structure Spectroscopy (QEXAFS) was deployed to study the leaching of Pd from a heterogeneous catalyst caused by K₂CO₃ temporally and spatially.