Supporting Information

Advances in the Sol-immobilisation Preparation of Supported Metal Nanoparticles with Tailored Catalytic Properties: Applications for the Hydrogenation of Nitrophenols.

Scott M. Rogers\textsuperscript{a,b}, C. Richard. A. Catlow\textsuperscript{a,b,c}, Diego Gianolio\textsuperscript{d}, Peter P. Wells\textsuperscript{a,d,e} and Nikolaos Dimitratos\textsuperscript{c}

\textsuperscript{a}. UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Harwell Oxon, Didcot OX11 0FA, U.K.
\textsuperscript{b}. Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, U.K.
\textsuperscript{c}. Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Cardiff CF10 3AT, U.K.
\textsuperscript{d}. Diamond Light Source, Harwell Science and Innovation Campus, Chilton, Didcot OX11 0DE, U.K.
\textsuperscript{e}. School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, U.K.

Table S1. MP-AES results of the sol-immobilised prepared 0.2 wt. % Pd/TiO\textsubscript{2} catalysts.

The metal loadings for the 1 wt. % Pd/TiO\textsubscript{2} catalysts was 0.72 wt. % Pd, with this value taken from the previous work.

<table>
<thead>
<tr>
<th></th>
<th>Concentrations (ppm) at different Pd wavelengths (nm) 1\textsuperscript{st} repetition</th>
<th>Concentrations (ppm) at different Pd wavelengths (nm) 2\textsuperscript{nd} repetition</th>
<th>Average Pd wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2 PdA1</td>
<td>1.45</td>
<td>1.45</td>
<td>0.14</td>
</tr>
<tr>
<td>0.2 PdA2</td>
<td>1.80</td>
<td>1.73</td>
<td>0.18</td>
</tr>
<tr>
<td>0.2 PdA3</td>
<td>1.47</td>
<td>1.49</td>
<td>0.15</td>
</tr>
<tr>
<td>0.2 PdA4</td>
<td>1.65</td>
<td>1.65</td>
<td>0.17</td>
</tr>
</tbody>
</table>
Figure S1. UV-Vis spectra of the K$_2$PdCl$_4$ precursor and the subsequent Pd sol generated after reduction of K$_2$PdCl$_4$ by NaBH$_4$, in the presence of PVA; A) prepared in a H$_2$O solvent at 50°C and B) prepared in a H$_2$O solvent at 75°C.

Figure S2. Selected TEM images of 0.2 wt. % Pd/TiO$_2$ catalysts prepared at different temperatures, in H$_2$O solvent environment; A) 1°C (0.2 PdA1), B) 25°C (0.2 PdA2), C) 50°C (0.2 PdA3) and D) 75°C (0.2 PdA4).
**Figure S3.** Pd particle size distribution histograms of 0.2 wt. % Pd/TiO$_2$ catalysts prepared at different temperatures, in H$_2$O solvent environment; A) 1°C (0.2 PdA1), B) 25°C (0.2 PdA2), C) 50°C (0.2 PdA3) and D) 75°C (0.2 PdA4).
Figure S4. Linear combination fits for the different 0.2 wt. % Pd/TiO$_2$ catalysts using PdO and Pd foil as reference materials; A) 1°C (0.2 PdA1), B) 25°C (0.2 PdA2), C) 50°C (0.2 PdA3) and D) 75°C (0.2 PdA4).
Figure S5. FTIR spectra from CO-adsorption studies onto different 0.2 wt. % Pd/TiO₂ catalysts: (B) 0.2 Pd30, (C) 0.2 Pd50.
Figure S6. Conversion profiles of Pd catalysts for the hydrogenation of (A) \textit{m}-nitrophenol and (C) \textit{o}-nitrophenol. \(\ln(C/C_0)\) versus time plots for Pd catalysts tested for (B) \textit{m}-nitrophenol and (D) \textit{o}-nitrophenol hydrogenation. Reaction conditions: \textit{m}-nitrophenol:Pd molar ratio = 36, \textit{o}-nitrophenol:Pd molar ratio = 14 \(\text{NaBH}_4\):nitrophenol molar ratio = 24.