Electronic Supplementary Information for

Creation of Highly Stable Monomeric Pd(II) Species in an Anion-exchangeable Hydroxy Double Salt Interlayer: Application to Aerobic Alcohol Oxidation under an Air Atmosphere

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1. Materials

Ni(OAc)$_2$·4H$_2$O and Zn(OAc)$_2$·2H$_2$O were obtained from Wako Pure Chemical Ind. Co. Ltd. K$_2$PdCl$_4$ purchased from Aldrich was used without further purification. Alcohols as a substrate and solvents were purchased from Wako Pure Chemical Ind. Co. Ltd., Tokyo Kasei, and Aldrich.

2. XRD profiles of the synthesized Pd/NiZn catalysts

![XRD profiles](image)

*Figure 1S.* XRD profiles for (a) NiZn, (b) fresh Pd/NiZn(0.02), (c) recovered Pd/NiZn(0.02), (d) fresh Pd/NiZn(1) and (e) NiZn treated with excess NaOH aq.
3. XRD profiles for the HT-supported Pd catalysts

![XRD profiles](image)

**Figure 2S.** XRD profiles for (a) fresh Pd/HT(0.02), (b) recovered Pd/HT(0.02) and (c) parent-HT.
4. IR spectra for the Pd/NiZn catalysts

Figure 3S. IR spectra for (a) NiZn, (b) fresh Pd/NiZn(0.02), (c) fresh Pd/NiZn(1) and (d) NiZn treated with excess aqueous NaOH.
5. Curve-fitting result of the $[\text{Pd}(\text{OH})_4]^{2-}$ species in the aqueous solution

Figure 4S. Curve-fitting of Fourier-filtered EXAFS of aqueous $[\text{Pd}(\text{OH})_4]^{2-}$ solution. The solid curve is obtained experimentally and the dashed curve is the calculated fit.
6. Curve-fitting result for the synthesized Pd/NiZn catalysts

Figure 5S. Curve-fitting of Fourier-filtered EXAFS of (a) fresh Pd/NiZn(0.02) and (b) recovered Pd/NiZn(0.02), (c) fresh Pd/NiZn(1) and (d) Pd/NiZn(1). The solid curve is obtained experimentally, and the dashed curve is the calculated fit.
7. Hot filtration experiment

\[
\begin{align*}
\text{C}_6\text{H}_5\text{OH} + \frac{1}{2}\text{O}_2 & \xrightarrow{\text{Pd/NiZn(0.02) (Pd: 2 mol%)}} \text{C}_6\text{H}_5\text{CHO} + \text{H}_2\text{O} \\
\text{toluene, 80 }^\circ\text{C} & 
\end{align*}
\]

![Graph showing yield of benzaldehyde over time](image)

**Figure 6S.** Effect of removal of the Pd/NiZn(0.02) catalyst on the aerobic benzyl alcohol oxidation: without removal of Pd/iZn(0.02) (●); an arrow indicates the removal of the Pd/NiZn(0.02) (■). Reaction conditions: benzyl alcohol (0.5 mmol), Pd/NiZn(0.02) (Pd: 2 mol%), toluene (2.5 mmol), 353 K, O\textsubscript{2} atmosphere..
8. Screening of reaction conditions

Table 1S  Screening of reaction conditions for benzylalcohol oxidation

<table>
<thead>
<tr>
<th>Entry</th>
<th>Pd catalyst</th>
<th>Solvent</th>
<th>Convn&lt;sup&gt;b&lt;/sup&gt; (%)</th>
<th>Yield&lt;sup&gt;b&lt;/sup&gt; (%)</th>
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<tbody>
<tr>
<td>1</td>
<td>Pd/NiZn(0.02)</td>
<td>PhCF&lt;sub&gt;3&lt;/sub&gt;</td>
<td>&gt;99</td>
<td>97</td>
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<td>2</td>
<td>Pd/NiZn(0.02)</td>
<td>toluene</td>
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<td>79</td>
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<tr>
<td>3</td>
<td>Pd/NiZn(0.02)</td>
<td>ClCH&lt;sub&gt;2&lt;/sub&gt;CH&lt;sub&gt;2&lt;/sub&gt;Cl</td>
<td>79</td>
<td>71</td>
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<tr>
<td>4</td>
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<td>58</td>
<td>50</td>
</tr>
<tr>
<td>5</td>
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<td>42</td>
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<td>PhCF&lt;sub&gt;3&lt;/sub&gt;</td>
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<td>0</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction conditions: benzylalcohol (0.5 mmol), Pd catalyst (Pd: 2 mol%), solvent (2.5 mL), 353 K, 1 h, O<sub>2</sub> balloon. <sup>b</sup> Determined by GC analysis using an internal standard technique.
Figure 7S. Hammett plots for competitive oxidation of benzyl alcohol and $p$-substituted benzyl alcohols. $\log(k_X/k_H)$ versus Brown-Okamoto $\sigma^+$.  
Reaction conditions: benzyl alcohol (0.5 mmol), $p$-substituted benzyl alcohol (0.5 mmol), Pd/NiZn(0.02) (Pd: 2 mol%), PhCF$_3$ (2.5 mL), 353 K, air flow (1 atm, 20 mL/min).