Supplementary Material (ESI) for Green Chemistry

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 Atomosphere

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1. Materials

$Ni(OAc)_2{\cdot}4H_2O$ and $Zn(OAc)_2{\cdot}2H_2O$ were obtained from Wako Pure Chemical Ind. Co. Ltd. K_2PdCl_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

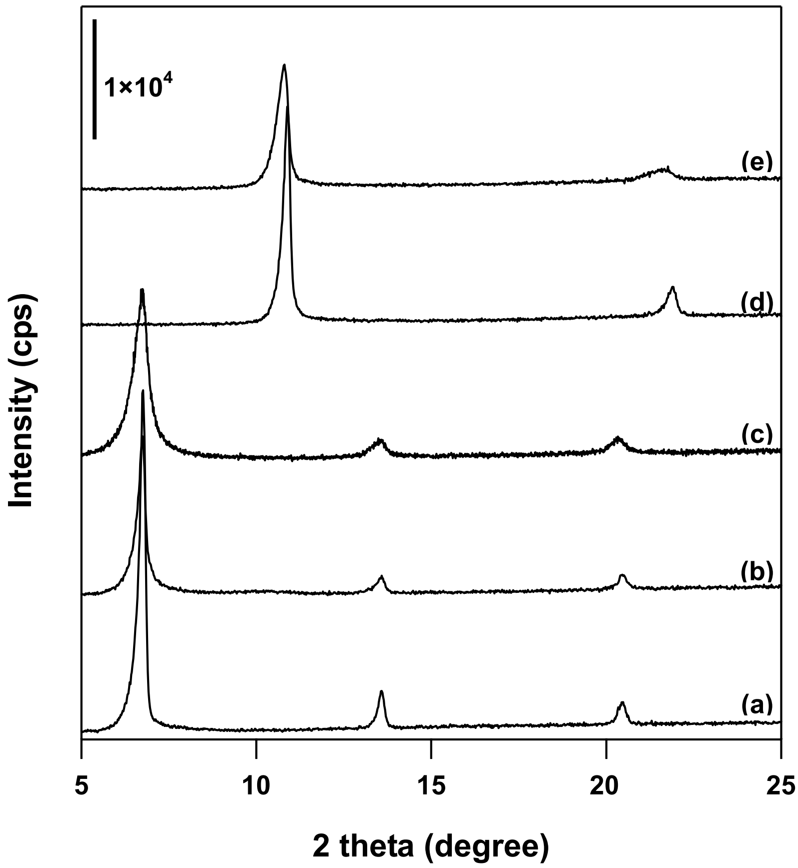


Figure 1S. XRD profiles for (a) NiZn, (b) fresh Pd/NiZn(0.02), (c) recovered Pd/NiZn(0.02), (d) fresh Pd/NiZn(1) and (e) NiZn treated with excess NaOH aq.

3. XRD profiles for the HT-supported Pd catalysts

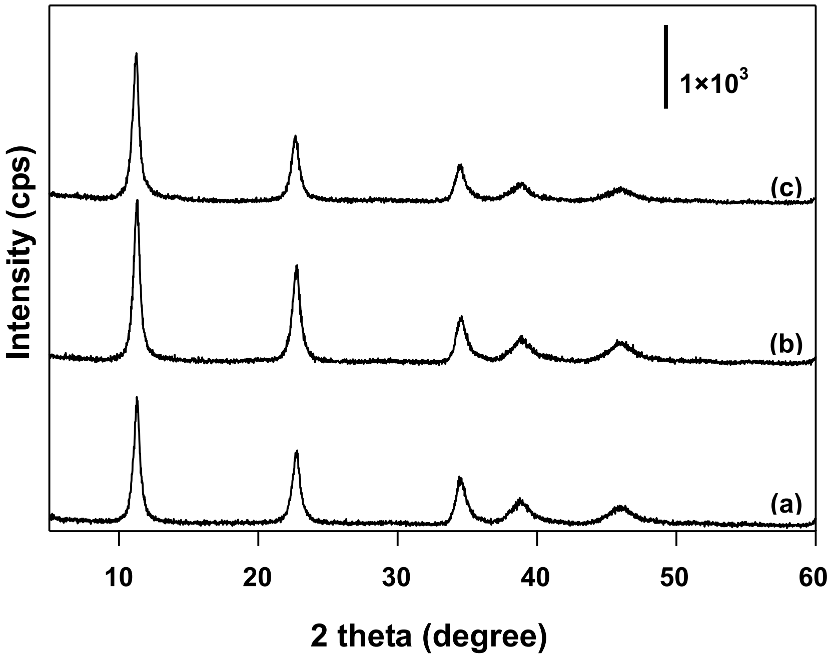


Figure 2S. XRD profiles for (a) fresh Pd/HT(0.02), (b) recovered Pd/HT(0.02) and (c) parent-HT.

4. IR spectra for the Pd/NiZn catalysts

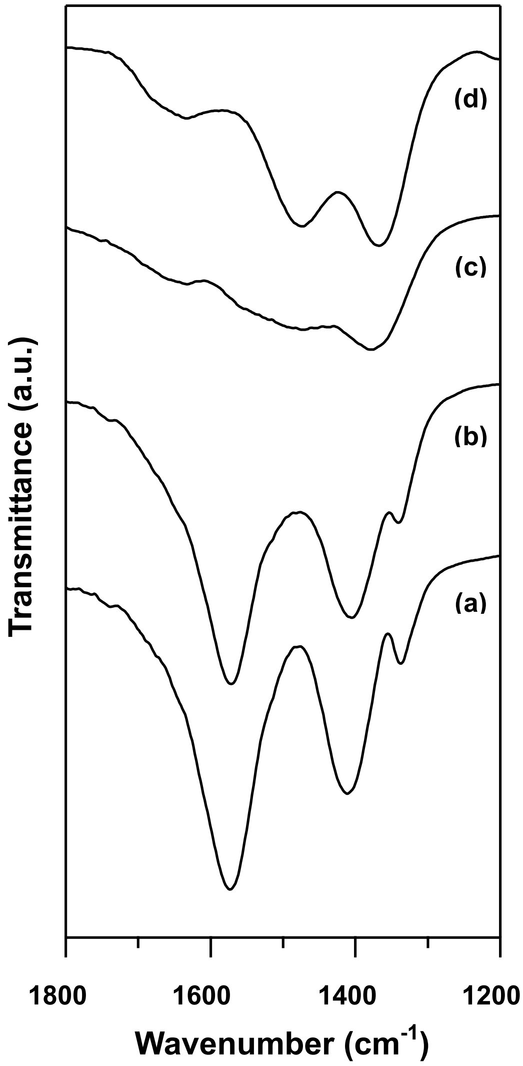


Figure 3S. IR spectra for (a) NiZn, (b) fresh Pd/NiZn(0.02), (c) fresh Pd/NiZn(1) and (d) NiZn treated with excess aqueous NaOH.

5. Curve-fitting result of the $[Pd(OH)_4]^{2-}$ species in the aqueous solution

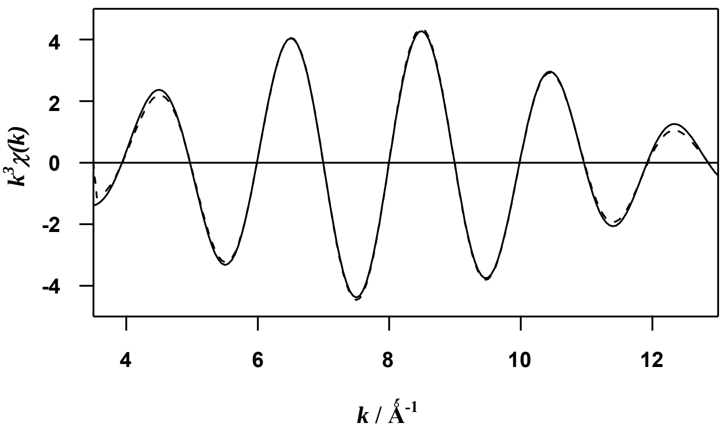


Figure 4S. Curve-fitting of Fourier-filtered EXAFS of aqueous $[Pd(OH)_4]^{2-}$ solution. The solid curve is obtained experimentally and the dashed curve is the calculated fit.

6. Curve-fitting result for the synthesized Pd/NiZn catalysts

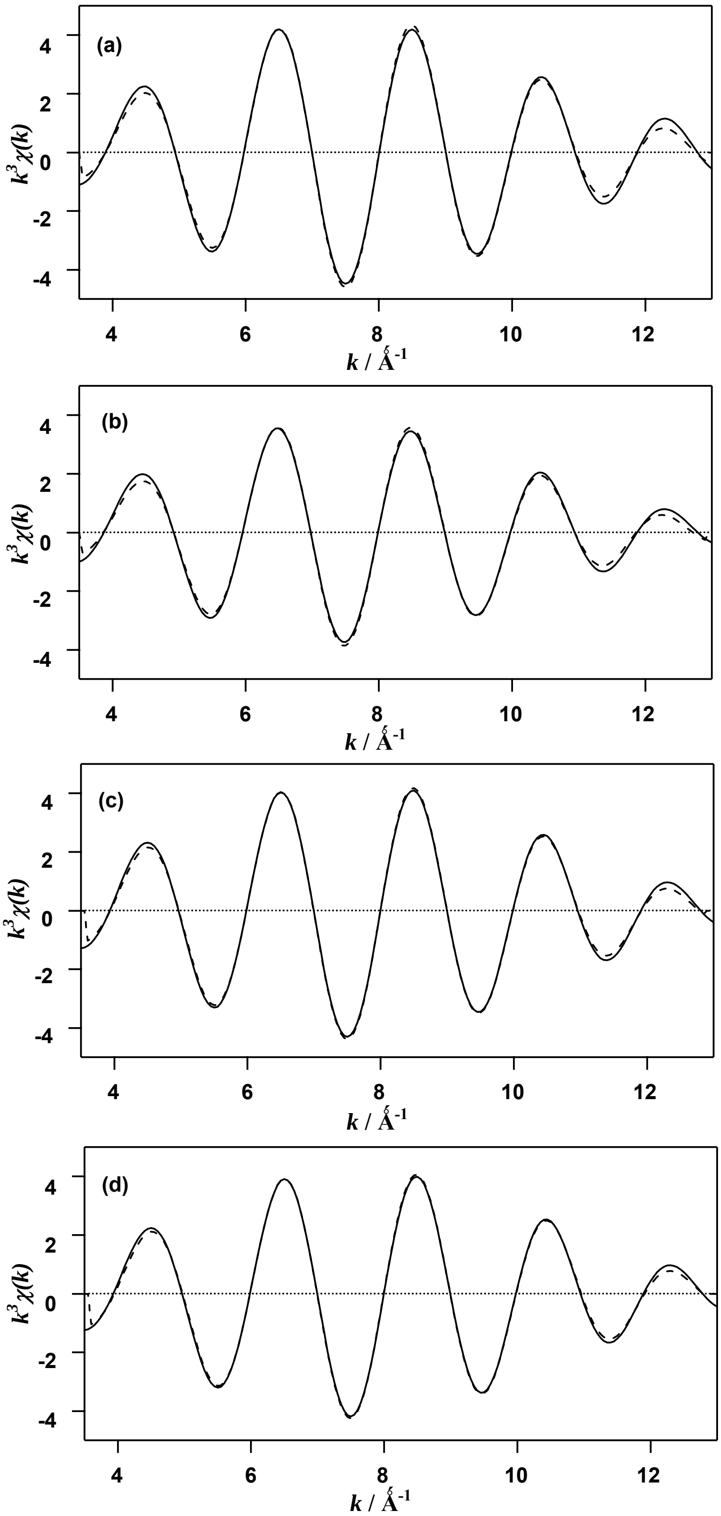
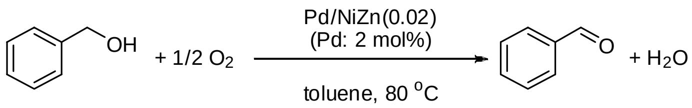


Figure 5S. Curve-fitting of Fourier-filtered EXAFS of (a) fresh Pd/NiZn(0.02) and (b) recovered Pd/NiZn(0.02), (c) fresh Pd/NiZn(1) and (d) Pd/NiZn(1). The solid curve is obtained experimentally, and the dashed curve is the calculated fit.

7. Hot filtration experiment



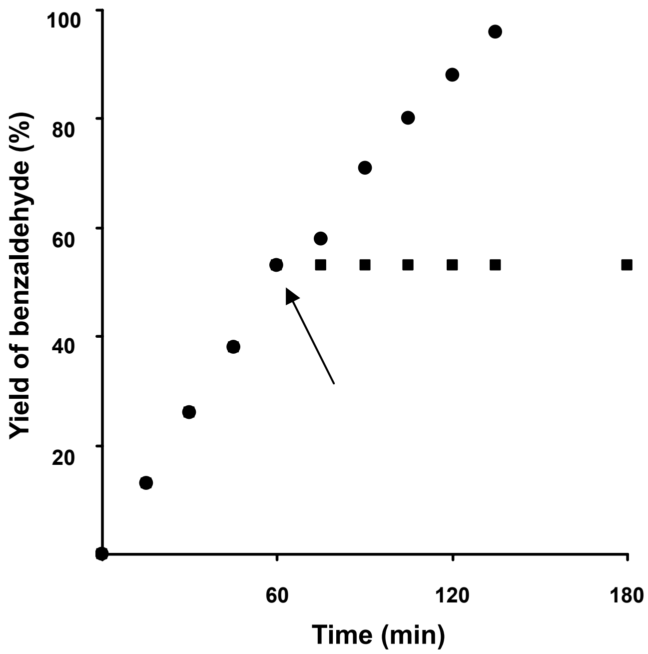
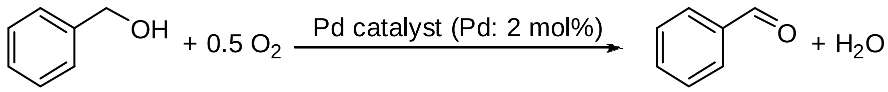


Figure 6S. Effect of removal of the Pd/NiZn(0.02) catalyst on the aerobic benzyl alcohol oxidation: without removal of Pd/iZn(0.02) (●); an arrow indicates the removal of the Pd/NiZn(0.02) (■). Reaction conditions: benzyl alcohol (0.5 mmol), Pd/NiZn(0.02) (Pd: 2 mol%), toluene (2.5 mmol), 353 K, O_2 atmosphere..

8. Screening of reaction conditions

Table 1S Screening of reaction conditions for benzylalcohol oxidation[a]



Entry	Pd catalyst	Solvent	Convn[b] (%)	Yield[b] (%)
1	Pd/NiZn(0.02)	$PhCF_3$	>99	97
2	Pd/NiZn(0.02)	toluene	81	79
3	Pd/NiZn(0.02)	$ClCH_2CH_2Cl$	79	71
4	Pd/NiZn(0.02)	n-heptane	58	50
5	Pd/NiZn(0.02)	ethyl acetate	47	42
6	Pd/NiZn(0.02)	acetonitrile	trace	trace
7	Pd/NiZn(0.02)	DMF	trace	trace
8	Pd/NiZn(0.02)	DMSO	trace	trace
9	Pd/NiZn(0.02)	ethanol	47	41
10	Pd/NiZn(0.02)	water	trace	trace
11	$Pd(OAc)_2$	toluene	8	8
12	K_2PdCl_4	toluene	0	0
13	$PdCl_2(PhCN)_2$	toluene	trace	trace
14	NiZn	$PhCF_3$	trace	trace
15	none	$PhCF_3$	0	0

[a] Reaction conditions: benzylalcohol (0.5 mmol), Pd catalyst (Pd: 2 mol%), solvent (2.5 mL), 353 K, 1 h, O_2 balloon. [b] Determined by GC analysis using an internal standard technique.

9. Hammet plot

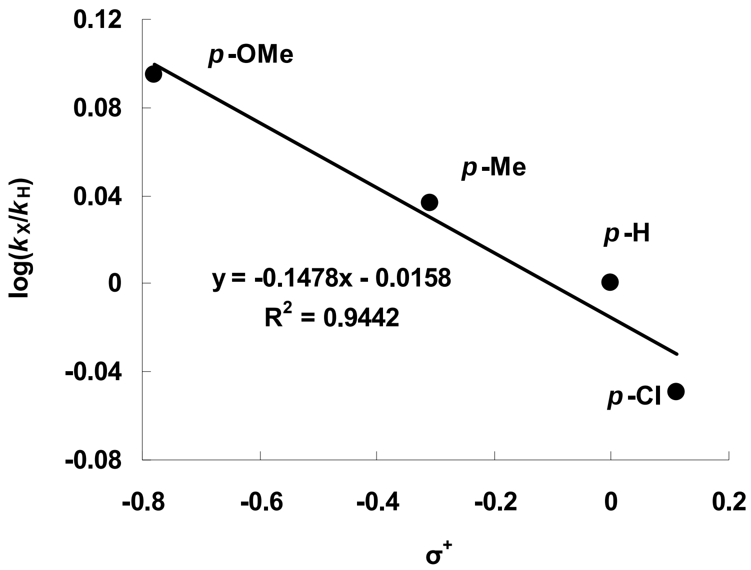


Figure 7S. Hammett plots for competitive oxidation of benzyl alcohol and *p*-substituted benzyl alcohols. $\log(k_X/k_H)$ versus Brown-Okamoto σ^+.[1] Reaction conditions: benzyl alcohol (0.5 mmol), *p*-substituted benzyl alcohol (0.5 mmol), Pd/NiZn(0.02) (Pd: 2 mol%), $PhCF_3$ (2.5 mL), 353 K, air flow (1 atm, 20 mL/min).

[1] H. C. Brown, Y. Okamoto, *J. Am. Chem. Soc.*, 1958, **80**, 4979.