

Electronic Supplementary Information for

**Anionic D-Valine-Palladium(II) Complex Supported on Hydroxy
Double Salt with Brønsted Basic Phosphate Anion: Application for
Heterogeneous Catalyst toward Aerobic Alcohol Oxidation**

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1. Experimental

General

^1H and ^{13}C NMR spectra were obtained on JNM-LA400 spectrometers at 400 MHz in CDCl_3 , D_2O , $\text{DMSO-}d_6$, CD_3OD , or toluene- d_8 . Powder X-ray diffraction patterns were recorded on a MAC Science MXP³V with Cu $K\alpha$ radiation. Infrared spectra were obtained with a HORIBA FT-720. Samples were diluted with KBr and compressed into thin disk shaped pellets. UV-visible spectra were recorded on a Shimadzu UV-2101PC. Optical rotations were recorded on a JASCO DIP-370 with a 10 cm cell (c given in g/100 mL). Analytical GC was performed by Shimadzu GC-14B with a flame ionization detector equipped with column RT- β DEXsa capillary column and Shimadzu GC-8A with a flame ionization detector equipped glass column with Silicone OV-17, Silicone OV-101 and Thermon 2000 packing. GC-MS was performed by Shimadzu GC-17A with a thermal conductivity detector equipped with an RT- β DEXsm capillary column. Products were confirmed by the comparison of their GC retention time, mass, ^1H and ^{13}C NMR spectroscopy with those of authentic samples. Pd K -edge X-ray absorption fine structure spectra were recorded at room temperature in transmission and fluorescence modes using Lytle detector with a Si(311) double crystal monochromator at the beam line NW-10A station with 6.5 GeV storage ring of the Photon Factory, Advanced Ring for Pulse X-rays, Tsukuba, Japan. (KEK-PF, proposal No. 2009G069). The resulting EXAFS spectra were analyzed with REX2000 (Rigaku Co.). Fourier transforms of k^3 -weighted EXAFS spectra were performed the $35 \text{ nm}^{-1} < k < 130 \text{ nm}^{-1}$ range for the analysis of catalyst, and the $30 \text{ nm}^{-1} < k < 150 \text{ nm}^{-1}$ range for the analysis of catalyst preparation solution. Curve-fitting analysis was performed with the inverse FT of the $0.104 \text{ nm} < R < 0.199 \text{ nm}$ range in case of analysis of catalysts, and the $0.104 \text{ nm} < R < 0.224 \text{ nm}$ range in that of preparation solution using PdO and K_2PdCl_4 as a standard material.

Materials

$\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OCOCH}_3)_2 \cdot 2\text{H}_2\text{O}$, and K_3PO_4 were obtained from Wako Pure Chemical Ind. Ltd. K_2PdCl_4 and D-Valine were purchased from Aldrich, used without further purification. Alcohols as a substrate and solvents were purchased from Wako Pure Chemical Ind. Co. Ltd., Tokyo Kasei, and Aldrich, and purified by the standard procedures¹ before use.

Synthesis of anion-exchanged Ni-Zn mixed basic salt (X/NiZn: X= CH_3COO^- and PO_4^{3-})

Acetate anion intercalated Ni-Zn mixed basic salt ($\text{CH}_3\text{COO}^-/\text{NiZn}$) was prepared according to the literature procedures.² $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (32.8 g, 132 mmol) and $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ (14.5 g, 66 mmol) were dissolved in deionized water (200 mL). The resulting aqueous solution was hydrolyzed by heating in a Teflon-linked pressure bottle at 200 °C for 24 h. The resulting green precipitates were filtered, washed with deionized water, and dried under vacuum, yielding *ca.* 5.0 g of $\text{Ni}_{0.78}\text{Zn}_{0.44}(\text{OH})_2(\text{OCOCH}_3)_{0.44} \cdot 0.86\text{H}_2\text{O}$ as a light green powder. Intercalation of PO_4^{3-} anion was carried out as follows: K_3PO_4 (10.6 g, 50 mmol) was dissolved into deionized water (50 mL), and then $\text{CH}_3\text{COO}^-/\text{NiZn}$ (1.0 g) was added. The resulting slurry was stirred at 60 °C for 24 h, followed by filtration, washed with deionized water, and dried under vacuum overnight, yielding *ca.* 1.0 g of $\text{PO}_4^{3-}/\text{NiZn}$ as a light green powder.

Synthesis of $[\text{1-PdCl}_2]^-$ solution

K_2PdCl_4 (6.5 mg, 0.02 mmol) was dissolved in deionized water (3 mL), and pH was adjusted to 5.0 using a KOH aqueous solution (0.1 M). The color of solution was changed from yellow into dark brown. Then, D-Valine (2.2 mg, 0.02 mmol) was added to the above solution, and stirred for at 30 °C 30 min. it is noted that the color of solution was turned into orange after the addition of D-Valine.

^1H NMR (400 MHz, in D_2O): δ 3.42 (d, $J = 4.3$ Hz, 1H, $\text{CH-}i\text{Pr}$), 2.18 (m, 1H, $\text{CHCH}(\text{CH}_3)_2$), 1.10 (dd, $J = 7.2$ Hz, 6H, $\text{CHCH}(\text{CH}_3)_2$) Optical rotation: Pd-val solution $[\alpha]_{\text{D}} = 34.628$ ($c = 1.70$, H_2O), D-Val $[\alpha]_{\text{D}} = 41.97$ ($c = 0.44$, H_2O)

Synthesis of $[\mathbf{1}\text{-Pd}(\text{OH})_2]^-/\text{X}/\text{NiZn}$ catalyst ($\text{X}=\text{CH}_3\text{COO}^-$ and PO_4^{3-})

Ni-Zn mixed basic salt-supported anionic Pd(II) catalyst ($[\mathbf{1}\text{-Pd}(\text{OH})_2]^-/\text{X}/\text{NiZn}$) was prepared by intercalation of $[\mathbf{1}\text{-PdCl}_2]^-$ complex into interlayer space of X/NiZn. X/NiZn (1.0 g) was added into the $[\mathbf{1}\text{-PdCl}_2]^-$ aqueous solution, and stirred at 30 °C for 3 h. The obtained slurry was filtered, washed with deionized water, and dried under vacuum overnight, yielding $[\mathbf{1}\text{-Pd}(\text{OH})_2]^-/\text{X}/\text{NiZn}$ catalyst as a light green powder (Pd loading amount: 0.02 mmol/g).

Synthesis of $[\text{Pd}(\text{OH})_4]^{2-}/\text{X}/\text{NiZn}$ catalyst ($\text{X}=\text{CH}_3\text{COO}^-$ and PO_4^{3-})

$[\text{Pd}(\text{OH})_4]^{2-}/\text{X}/\text{NiZn}$ was synthesized according to the literature procedures.³ K_2PdCl_4 (6.5 mg, 0.02 mmol) was dissolved in deionized water (40 mL), and 0.1 M NaOH (10 mL) was added, adjusted to pH 12.6. Then, X/NiZn (1.0 g) was added to the resulting solution and stirred at room temperature for 3 h. The obtained slurry was filtered, washed with deionized water, and dried under vacuum overnight, yielding ca. 1.0 g of $[\text{Pd}(\text{OH})_4]^{2-}/\text{X}/\text{NiZn}$ as a light green powder.

Synthesis of $[\text{Pd}(\text{D-Val})_2] \cdot n\text{H}_2\text{O}$ Complex

$\text{Pd}(\text{D-Val})_2 \cdot n\text{H}_2\text{O}$ was synthesized according to the literature procedures.⁴ K_2PdCl_4 (6.5 mg, 0.02 mmol) was dissolved in deionized water (3 mL), and D-Valine (4.40 mg, 0.04 mmol) was added to solution, and stirred for 3 h at 30 °C. The yellow precipitates was filtered, washed with deionized water, and dried under vacuum overnight.

IR (KBr): 1660 ($\nu_{\text{as}}(\text{COO}^-)$), 1631 ($\nu(\text{NH}_3^+)$), 1604 ($\nu(\text{NH}_3^+)$), 1461 ($\nu_{\text{s}}(\text{COO}^-)$)

General procedures for the aerobic 2-adamantanol oxidation using Various Pd Catalysts

Into a Schlenk tube with a reflux condenser was placed 2-adamantanol (0.5 mmol), Pd catalyst (Pd: 1 mol%), and trifluorotoluene (5 mL). The resulting mixture was stirred at 80 °C under air flow condition (20 mL/min). After 3 h, conversion of 2-adamantanol and yield of 2-adamantanone were determined by GC analysis using *n*-tetradecane as an internal standard.

Procedure for reuse experiment

First run of the aerobic oxidation of 1-phenylethanol catalyzed by [1-Pd(OH)₂]/PO₄³⁻/NiZn was performed by the above described procedure. After catalytic reaction, the heterogeneous catalyst was separated by centrifugation and filtration. Recovered catalyst was washed with acetone (20 mL×4) and dried under vacuum at room temperature before recycling for the next run.

Oxygen uptake measurement

The uptake of molecular oxygen was measured by the following experiment. [1-Pd(OH)₂]/PO₄³⁻/NiZn catalyst (Pd: 1 mol%) was placed in a side-armed flask with a reflux condenser attached to a gas burette. The system was evacuated and filled with molecular oxygen, followed by the addition of trifluorotoluene (5 mL) and 1-phenylethanol (0.5 mmol), and then reacted for 1 h at 80 °C. The molar ratio of O₂ gas uptake to acetophenone was *ca.* 1:2.

Intramolecular competitive aerobic oxidation reaction of 4-(1'-hydroxyethyl)benzyl alcohol

The intramolecular competitive aerobic oxidation of 4-(1'-hydroxyethyl)benzyl alcohol was carried under the standard conditions. The reaction mixture was analyzed by GC

and identified by GC-MS and were identical to literature values.

4-(Hydroxymethyl)acetophenone: m/z 150 (M^+ , 31), 135 (100), 107 (23), 89 (37), 77 (29).

4-(1'-Hydroxyethyl)benzaldehyde: m/z 150 (M^+ , 5), 149 (5), 107 (100), 79 (74), 77 (50), 51 (21).

4-Acetylbenzaldehyde: m/z 148 (M^+ , 41), 134 (17), 133 (100), 105 (49), 77 (33), 51(24), 50 (15).

Intermolecular competitive aerobic oxidation reaction between benzylalcohol and 1-phenylethanol

The intermolecular competitive aerobic oxidation between benzyl alcohol and 1-phenylethanol was carried out under the standard conditions. The products were identified the comparison of their GC retention time by Shimadzu GC-8A with a flame ionization detector equipped with Thermon3000.

Kinetic isotope effect for competitive aerobic oxidation of α -deuterio-*p*-methyl-benzylalcohol

α -Deuterio-*p*-methylbenzyl alcohol (0.25 mmol) and [1-Pd(OH)₂]/PO₄³⁻/NiZn (0.125 g, Pd: 1 mol%) were dissolved in toluene-*d*₈ (2.5 mL) at 80 °C under air flow (20 mL/min). The reaction mixture was stirred for 0.5 h. The yield of *p*-Methylbenzaldehyde was determined by GC analysis. Kinetic isotope effect values (k_H/k_D) was determined by ¹H-NMR estimating ratio of α -deuterio-*p*-methyl-benzaldehyde and *p*-methylbenzaldehyde yield.

Synthesis of 4-(1'-hydroxyethyl)benzyl alcohol⁵

4-(1'-Hydroxyethyl)benzyl alcohol was synthesized by the reduction of 4-acetylbenzoic acid using lithium aluminum hydride (LiAlH₄) according to literature procedures. A

solution of 4-acetylbenzoic acid (5 g, 34.5 mmol) in dry THF (20 mL) was added slowly to a suspension of LiAlH₄ (4 g, 132 mmol) in dry THF (30 mL) at room temperature, and the resulting mixture was refluxed overnight under N₂ atmosphere. The mixture was cooled to room temperature and unreacted LiAlH₄ was destroyed by the addition of water, and aqueous solution of NaOH (50 mL, 0.1 M) was added slowly to the mixture. The resulting solid was removed by filtration and washed with THF. The combined filtrate dried and evaporated to give 4-(1'-Hydroxy-ethyl)benzyl alcohol as a white powder. *m/z* 152 (M⁺, 19), 137 (M⁺ -Me, 96), 134 (M⁺ -H₂O, 19), 121 (22), 107 (31), 105 (28), 91 (60), 79 (100), 77 (58), 63 (16), 51 (35).

¹H NMR (400 MHz, CDCl₃, TMS): δ 7.28 (d, *J* = 8.4 Hz, 2H, 2*H*_{meta}), 7.24 (d, *J* = 8.4 Hz, 2H, 2*H*_{ortho}), 4.81 (q, *J* = 6.6 Hz, 1H, CHCH₃), 4.60 (s, 2H, CH₂-OH), 2.72 (s, 2H, CH₂OH and CH(CH₃)OH), 1.43 (d, *J* = 6.6 Hz, 3H, CH₃). ¹³C NMR (400 MHz, CDCl₃, TMS): δ 145.1 (C_{ipso}), 140.0 (C_{para}), 127.1 (2C_{meta}), 125.6 (2C_{ortho}), 70.0 (CHOH), 64.7 (CH₂OH), 25.1 (CH₃).

Synthesis of α -deuterio-*p*-methylbenzyl alcohol⁶

α -Deuterio-*p*-methylbenzyl alcohol was synthesized by the reduction of *p*-methylbenzaldehyde using LiAlD₄ by a modification of the procedure reported for the synthesis of deuterium-labeled toluene. A solution of *p*-methylbenzaldehyde (3.2 g, 26.7 mmol) in dry THF (20 mL) was added slowly to a suspension of LiAlD₄ (0.33 g, 7.9 mmol) in dry THF (20 mL) at room temperature, and the resulting mixture was refluxed under N₂ atmosphere for 8 h. The mixture was cooled to room temperature and unreacted LiAlD₄ was destroyed by the addition of water, and aqueous solution of NaOH (50 mL, 0.1 M) was added slowly to the mixture. The resulting solid was removed by filtration and washed with THF. The combined filtrate dried and evaporated to give α -deuterio-*p*-methylbenzyl alcohol as a white powder.

m/z: 124 (17), 123 (M⁺, 92), 122 (25), 108 (100), 106 (33), 94 (50), 93 (31), 92 (32), 91

(48), 80 (71), 78 (52), 77 (36), 65 (28).

^1H NMR (400 MHz, CDCl_3 , TMS): δ 7.25 (d, $J = 8.0$ Hz, 2H, $2H_{\text{ortho}}$), 7.16 (d, $J = 7.8$ Hz, 2H, $2H_{\text{meta}}$), 4.60 (s, 1H, CHDOH), 2.35 (s, 3H, CH_3). ^{13}C NMR (400 MHz, CDCl_3 , TMS): δ 137.8 (C_{ipso}), 137.4 (C_{para}), 129.2 (2C_{meta}), 127.2 (2C_{ortho}), 64.9 (CH_2OH), 21.2 (CH_3).

2. ^1H NMR Spectrum of $[\text{1-PdCl}_2]^-$ Complex in D_2O

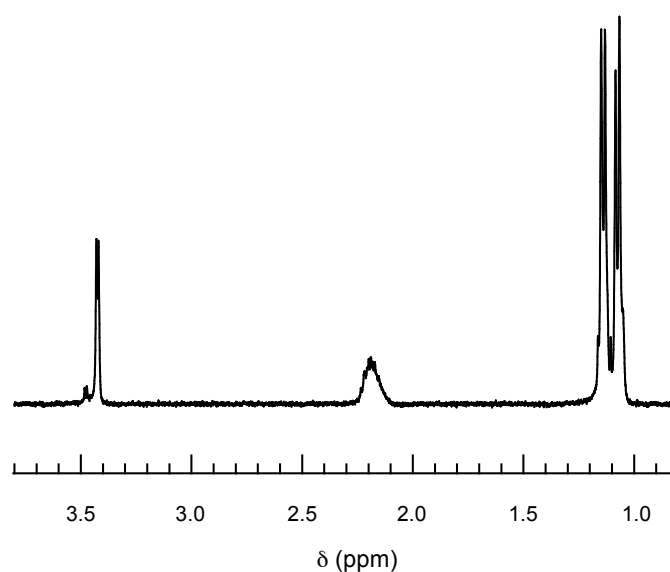


Figure S1 ^1H NMR Spectrum of $[\text{1-PdCl}_2]^-$ complex in D_2O

3. XRD Profiles for Various NiZn Catalysts

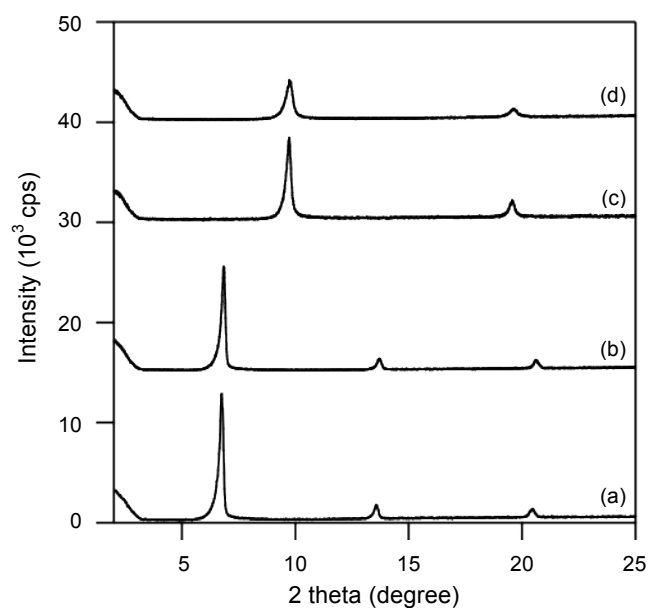


Figure S2 XRD profiles for (a) $\text{CH}_3\text{COO}^-/\text{NiZn}$, (b) $[\text{1-Pd}(\text{OH})_2]^-/\text{CH}_3\text{COO}^-/\text{NiZn}$, (c) $\text{PO}_4^{3-}/\text{NiZn}$, and (d) $[\text{1-Pd}(\text{OH})_2]^-/\text{PO}_4^{3-}/\text{NiZn}$.

4. Hot Filtration Experiment

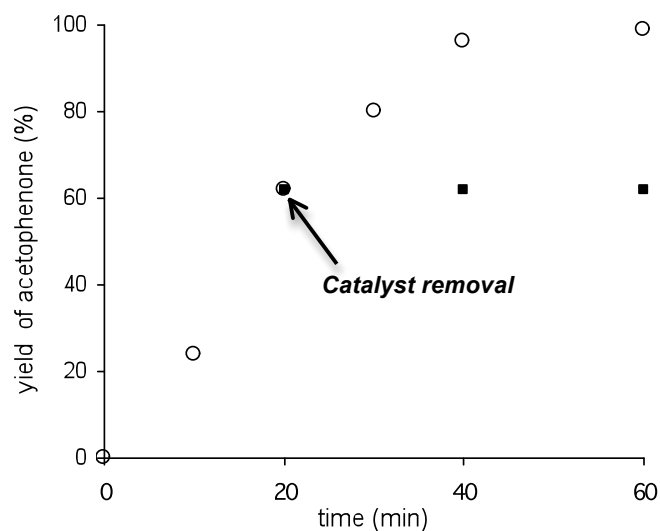


Figure S3 Effect of removal of the $[\text{1-Pd}(\text{OH})_2]^-/\text{PO}_4^{3-}/\text{NiZn}$ catalyst on the aerobic 1-phenylethanol oxidation: without removal of catalyst (○); an arrow indicates the removal of the catalyst (▲). Reaction conditions: 1-phenylethanol (0.5 mmol), $[\text{1-Pd}(\text{OH})_2]^-/\text{PO}_4^{3-}/\text{NiZn}$ (Pd: 2 mol%), PhCF_3 (2.5 mL), 353 K, air flow (1 atm, 20 mL/min).

5. Hammett Plot

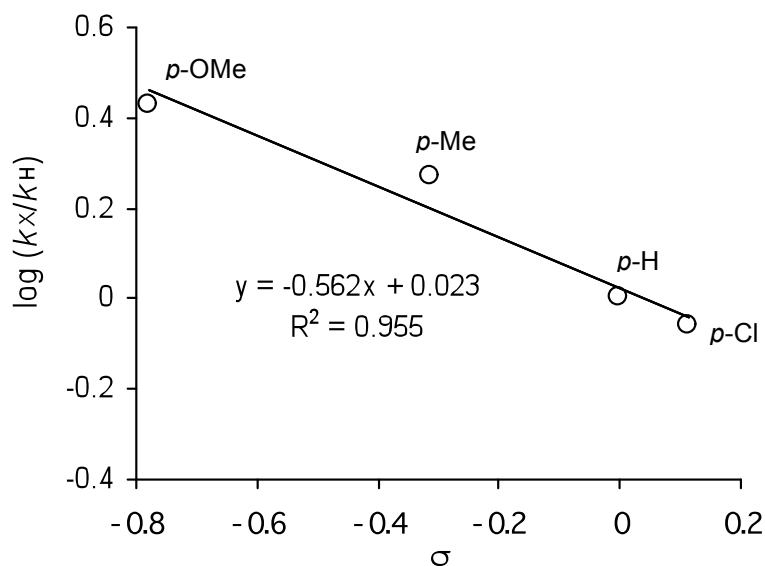


Figure S4 Hammett plots for competitive oxidation of benzyl alcohol and *p*-substituted benzyl alcohols. $\log(k_x/k_H)$ versus Brown-Okamoto σ^+ (H. C. Brown and Y. Okamoto, *J. Am. Chem. Soc.* **1958**, *80*, 4979). Reaction conditions: benzyl alcohol (0.5 mmol), *p*-substituted benzyl alcohol (0.5 mmol), $[1\text{-Pd}(\text{OH})_2]/\text{PO}_4^{3-}/\text{NiZn}$ (Pd: 2 mol%), PhCF_3 (2.5 mL), 353 K, air flow (1 atm, 20 mL/min).

6. Curve-fitting Results

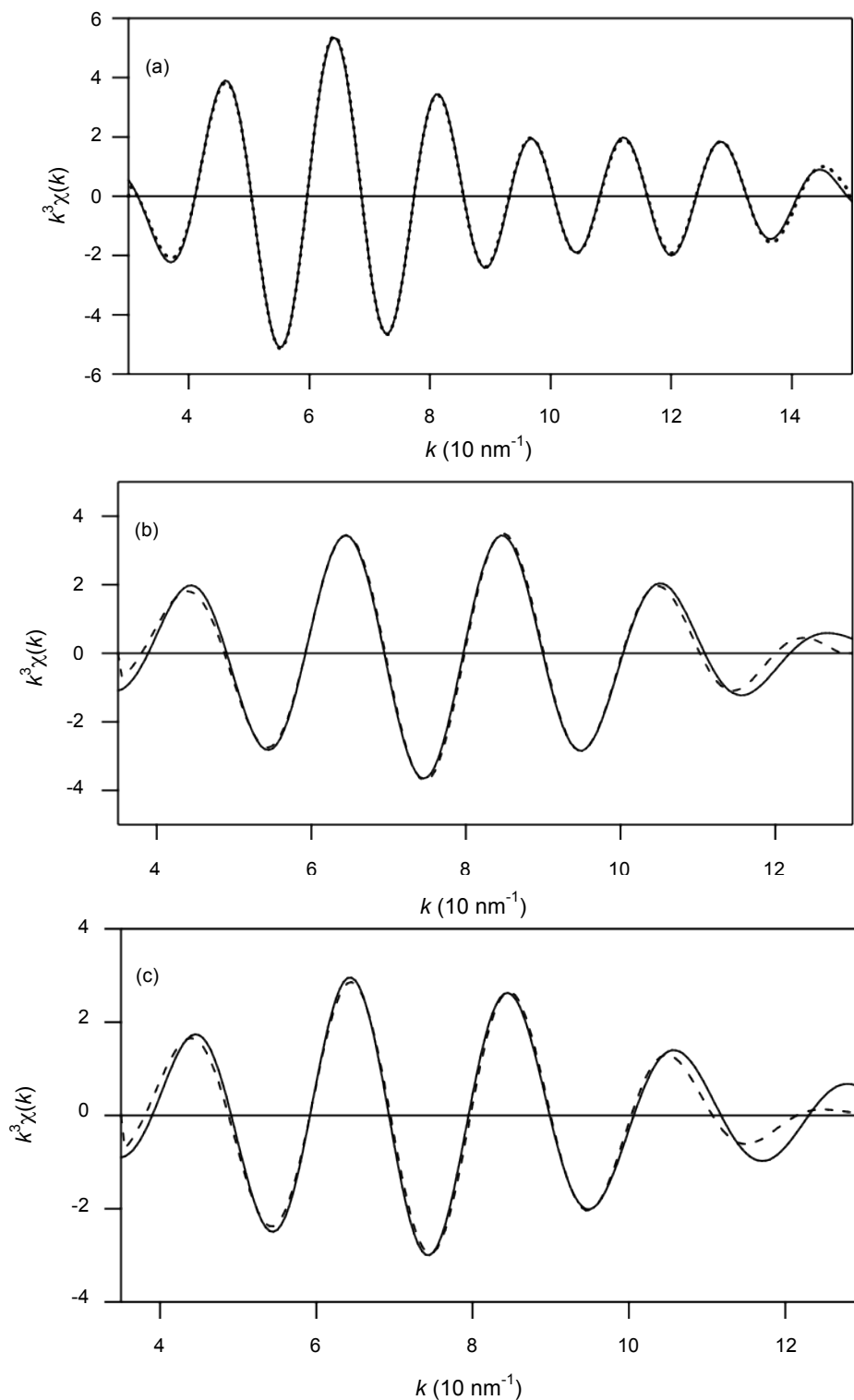


Figure S5 Curve-fitting of Fourier-filtered EXAFS of (a) K_2PdCl_4 + Val solution, (b) fresh $[1-Pd(OH)_2]/PO_4^{3-}/NiZn$, and (c) recovered $[1-Pd(OH)_2]/PO_4^{3-}/NiZn$. The solid curve is obtained experimentally and the dashed curve is the calculated

7. FT-IR Spectrum of $\text{PO}_4^{3-}/\text{NiZn}$ Catalyst

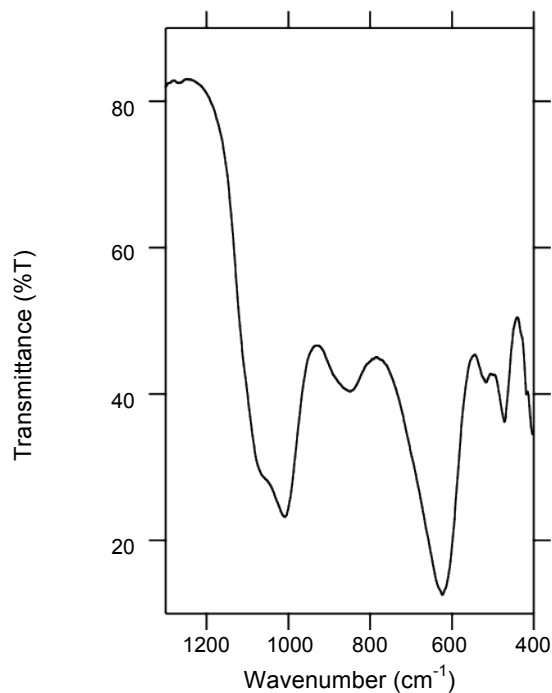


Figure S6 FT-IR spectrum of $\text{PO}_4^{3-}/\text{NiZn}$ catalyst

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