Electronic Supplementary Information for

Phosphoric acid-modified commercial kieselguhr supported palladium nanoparticles as efficient catalysts for low-temperature hydrodeoxygenation of lignin derivatives in water

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1. Supporting Figures

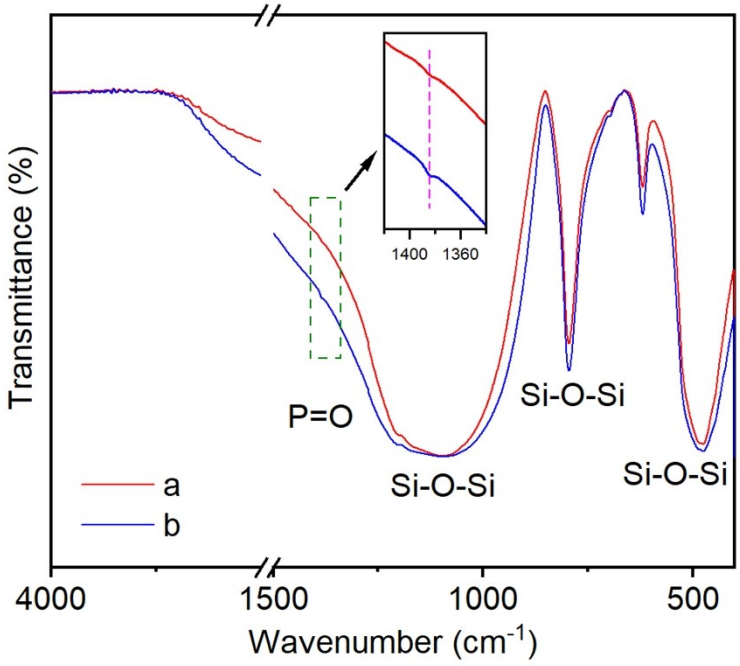

Fig. S1 FTIR spectra of (a) Pd/CE and (b) Pd/PCE.

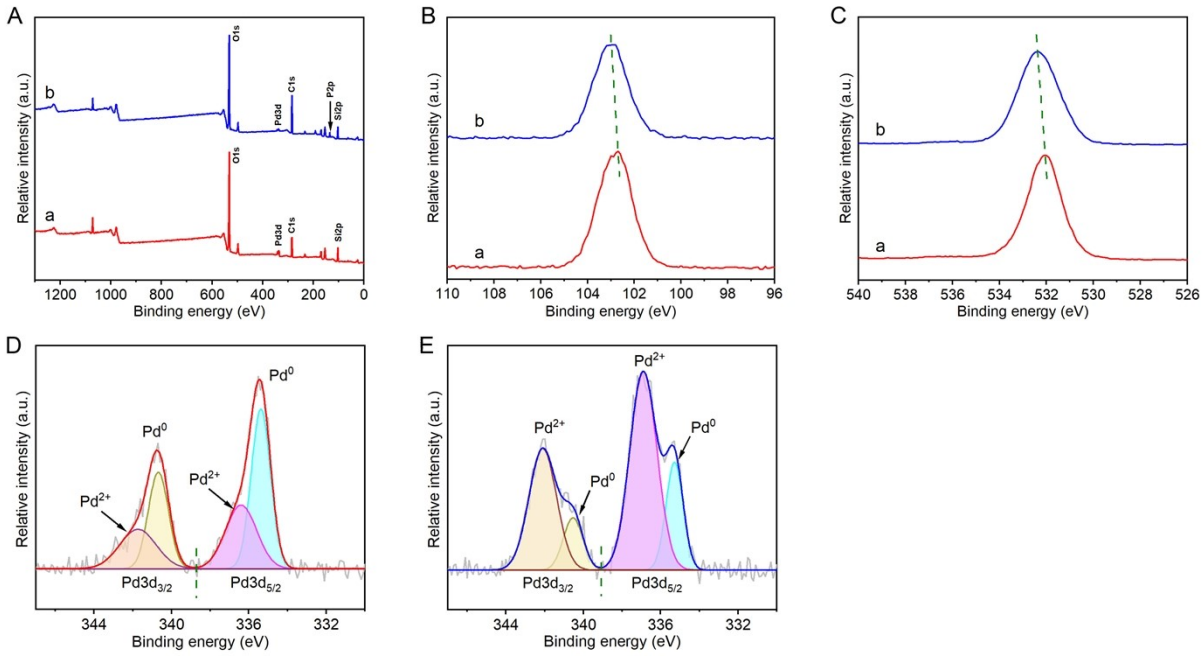

Fig. S2 (A) XPS surveys, (B) Si2p XPS spectra and (C) O1s XPS spectra of (a) Pd/CE and (b) Pd/PCE; Pd3d XPS spectra of (D) Pd/CE and (E) Pd/PCE.

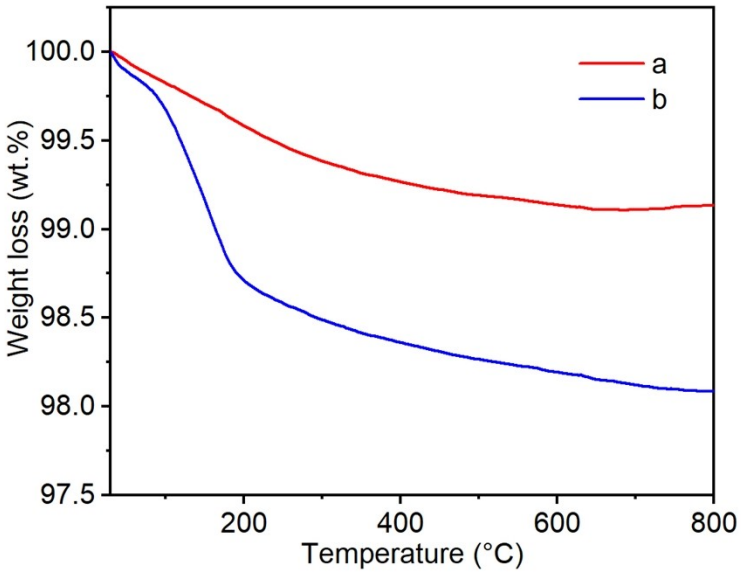

Fig. S3 TG curves of pyridine-adsorbed (a) Pd/CE and (b) Pd/PCE.

Notes: This experiment was performed as follows: Sample was put into a glass vial with a rubber stopper and degassed in vacuum at 100 °C for 2 h. After that, sample was cooled to room temperature and then two drops of pyridine were injected into the vial. After adsorption at room temperature for 30 min, sample was degassed in vacuum at room temperature for 2 h. Finally, sample in the vial was collected and tested by FTIR immediately.

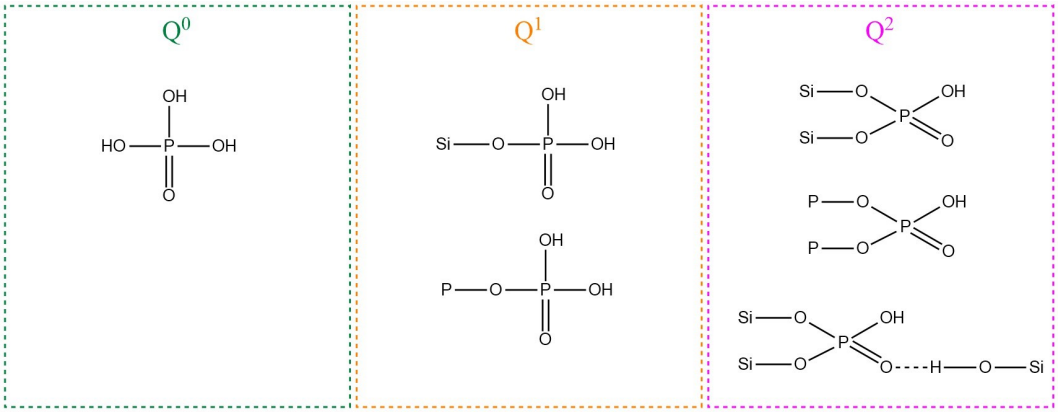

Fig. S4 Probable chemical environments of phosphorus.

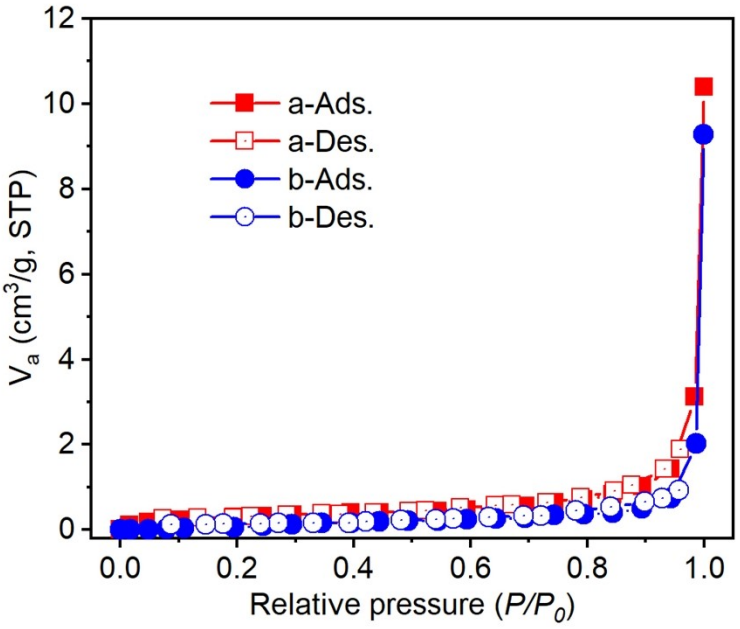

Fig. S5 Nitrogen isotherms of (a) Pd/CE and (b) Pd/PCE. The little amount of adsorbed N_2 showed that Pd/CE and Pd/PCE didn't have abundant micropores and no observation of hysteresis loop presented that Pd/CE and Pd/PCE didn't have mesopores either.

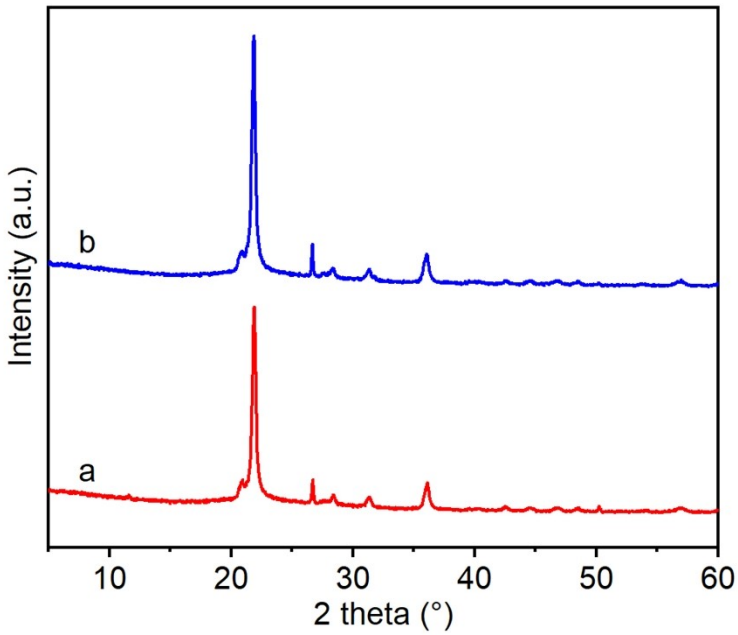

Fig. S6 XRD patterns of (a) Pd/CE and (b) Pd/PCE. These diffraction peaks were attributed to silica oxide.

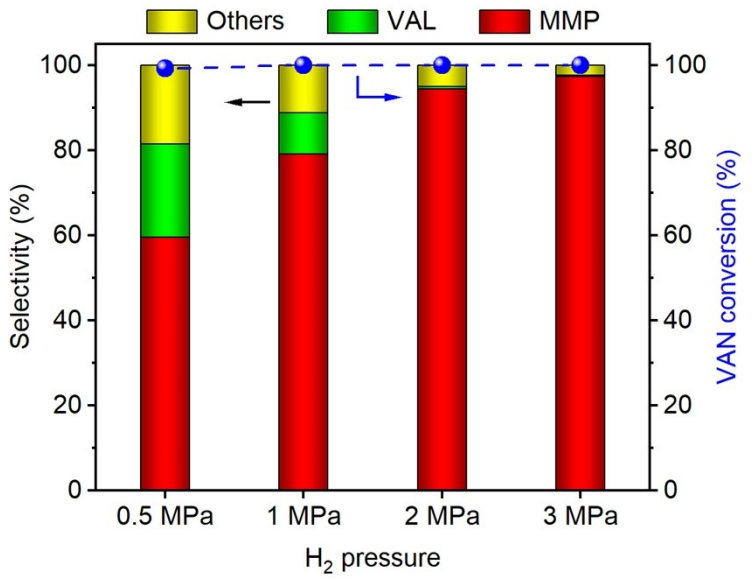

Fig. S7 Influence of H_2 pressure towards HDO performance of VAN over Pd/PCE. Reaction conditions: 1 mmol of VAN, catalyst (VAN/Pd = 240, mol/mol), 60 °C, 8 h, 10 mL of water.

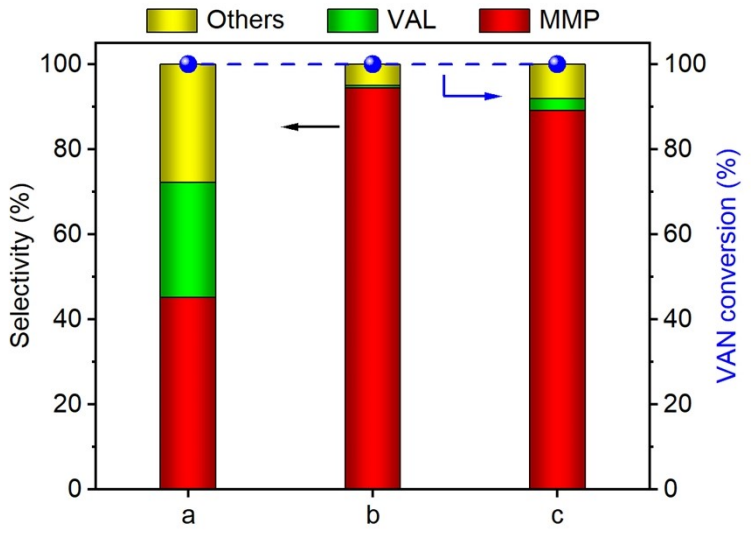

Fig. S8 Influence of Pd loading towards HDO performance of VAN over Pd/PCE: (a) 0.5 wt.%, (b) 1.0 wt.%, and (c) 2.0 wt.%. Reaction conditions: 1 mmol of VAN, 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

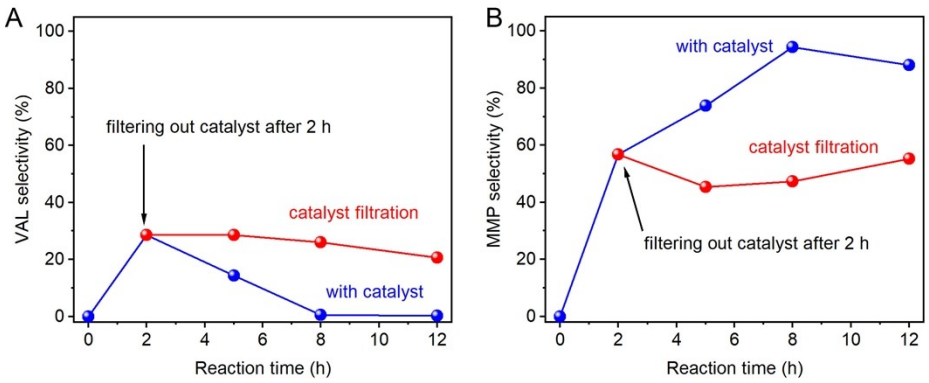

Fig. S9 (A) VAL selectivity and (B) MMP selectivity in hot-filtration test during HDO reaction. Catalyst was filtered out after reaction for 2 h.

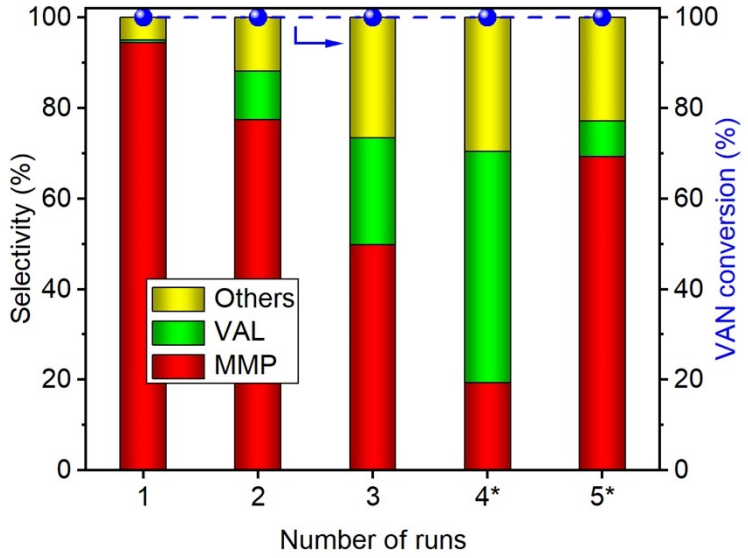

Fig. S10 Stability test of Pd/PCE in HDO of VAN to MMP. Reaction conditions: 1 mmol of VAN, catalyst (VAN/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

Notes: Recycled catalyst from Run 3th was calcined at 500 °C for 4 h in air, reduced at 200 °C for 4 h with H_2, and then used in Run 4th*. Recycled catalyst from Run 4th* was calcined at 500 °C for 4 h in air, re-impregnated with H_3PO_4, reduced at 200 °C for 4 h with H_2, and then used in Run 5th*

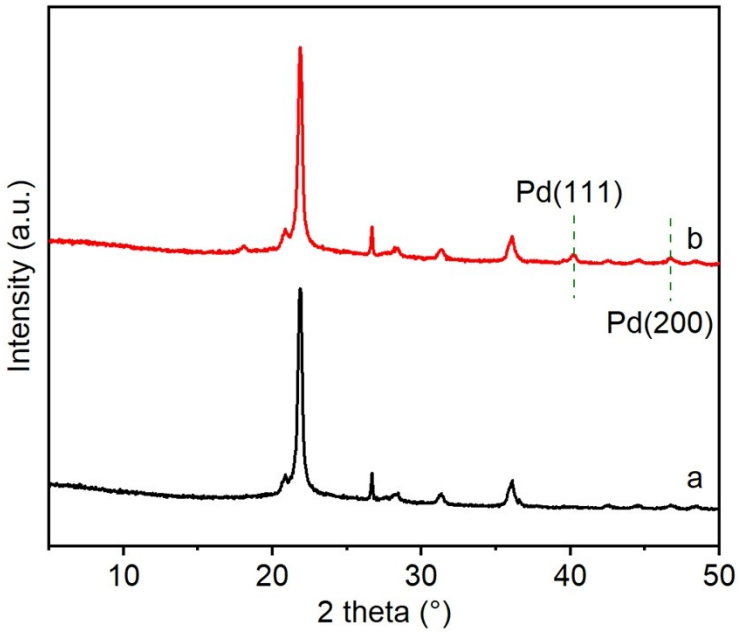

Fig. S11 XRD patterns of (a) fresh and (b) recycled Pd/PCE.

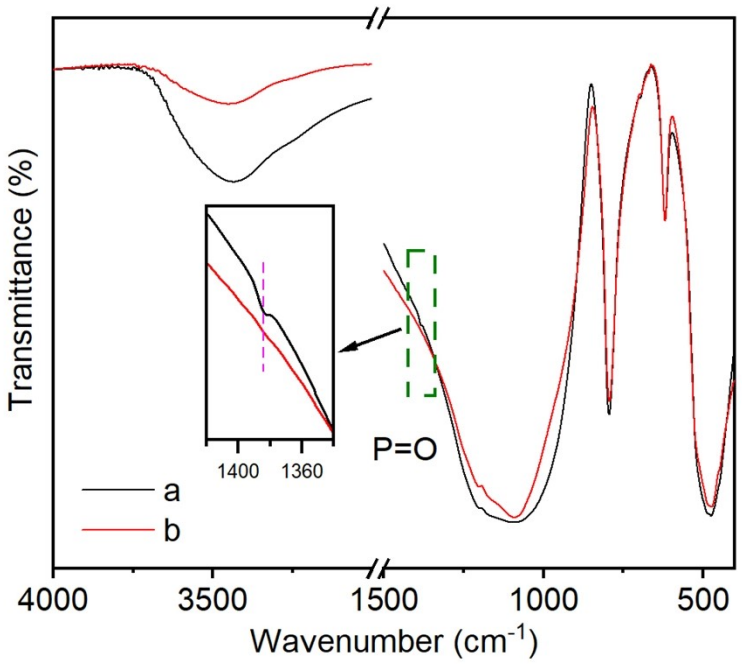

Fig. S12 FTIR spectra of (a) fresh and (b) recycled Pd/PCE.

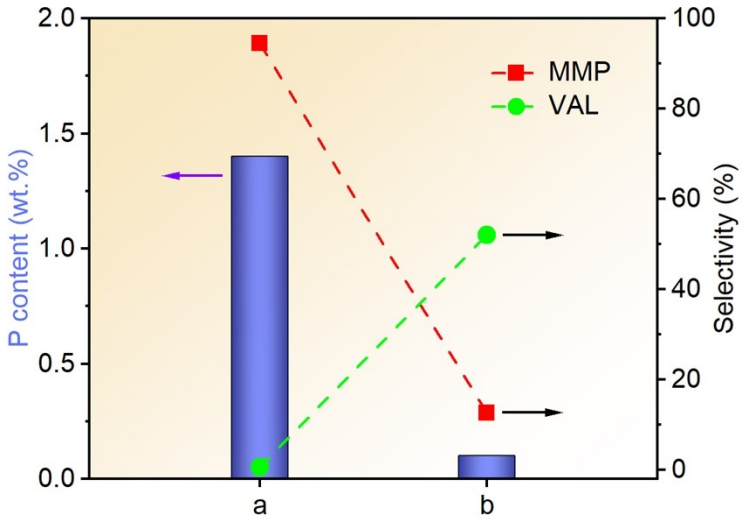

Fig. S13 Correlation of catalytic performance with the actual content of P in (a) Pd/PCE and (b) Pd/CE. Reaction conditions: 1 mmol of VAN, catalyst (VAN/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

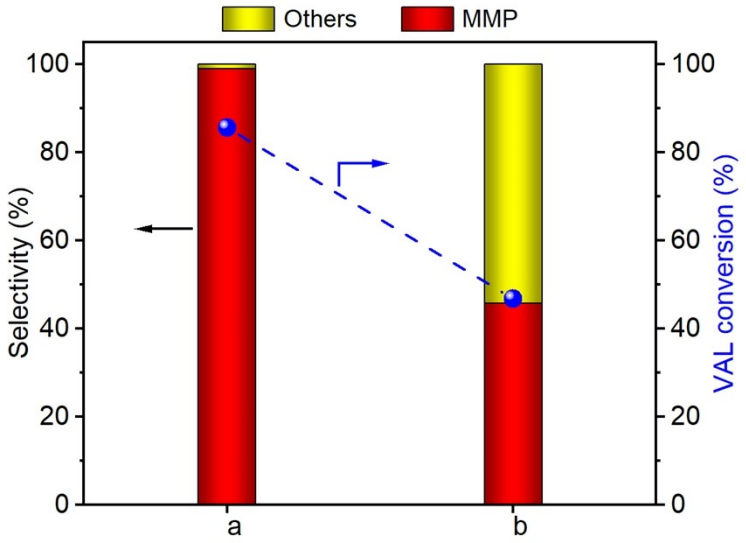

Fig. S14 Catalytic HDO performances of (a) Pd/PCE and (b) Pd/CE in HDO of VAL. Reaction conditions: 1 mmol of VAL, catalyst (VAL/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

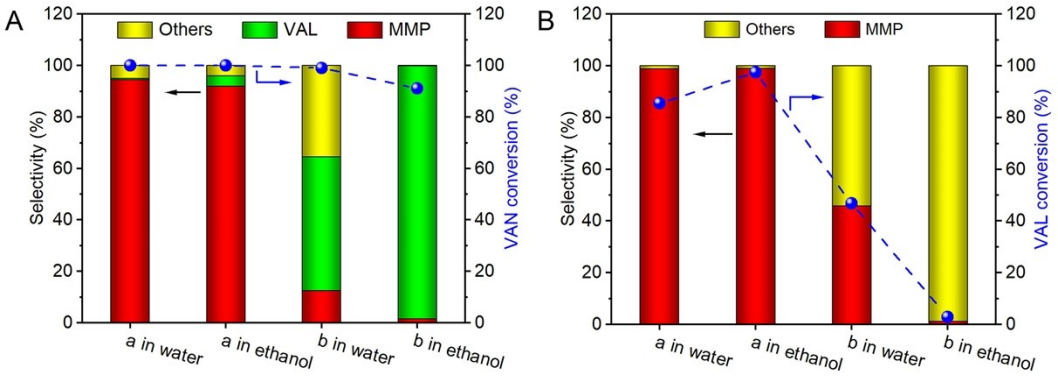

Fig. S15 Catalytic HDO performances of (a) Pd/PCE and (b) Pd/CE in HDO of (A) VAN and (B) VAL using water or ethanol as reaction solvent. Reaction conditions: 1 mmol of reactant, catalyst (reactant/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of reaction solvent.

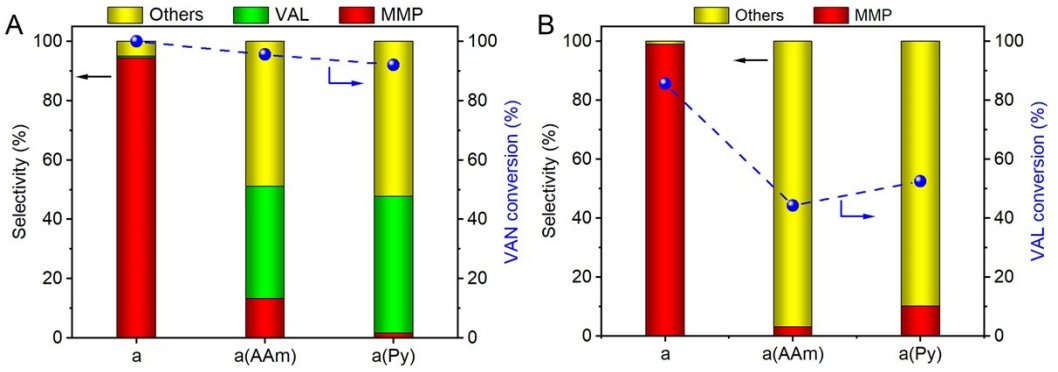

Fig. S16 HDO of (A) VAN and (B) VAL over different catalysts: (a) fresh Pd/PCE catalyst, (a(AAm)) Pd/PCE catalyst poisoned by aqueous ammonia, and (a(Py)) Pd/PCE catalyst poisoned by pyridine. Reaction conditions: 1 mmol of reactant, catalyst (reactant/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

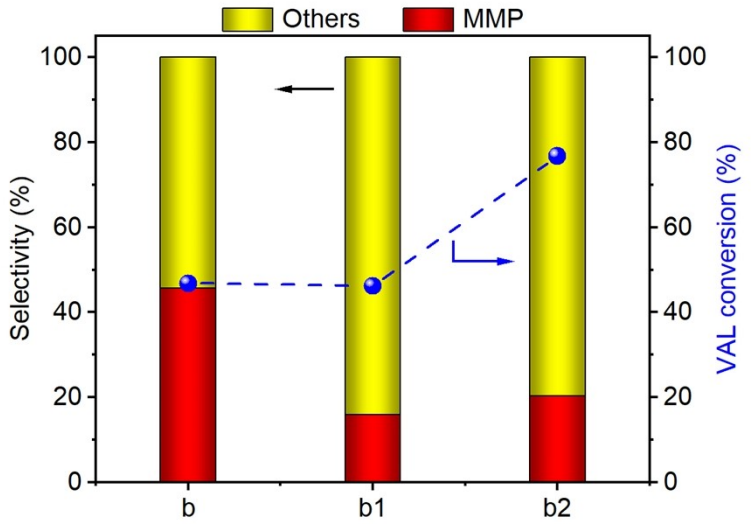

Fig. S17 HDO of VAL over (b) 45 mg of Pd/CE, (b1) 45 mg of Pd/CE with 45 mg of PCE, and (b2) 45 mg of Pd/CE with 225 mg of PCE. Reaction conditions: 1 mmol of VAL, catalyst (VAL/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

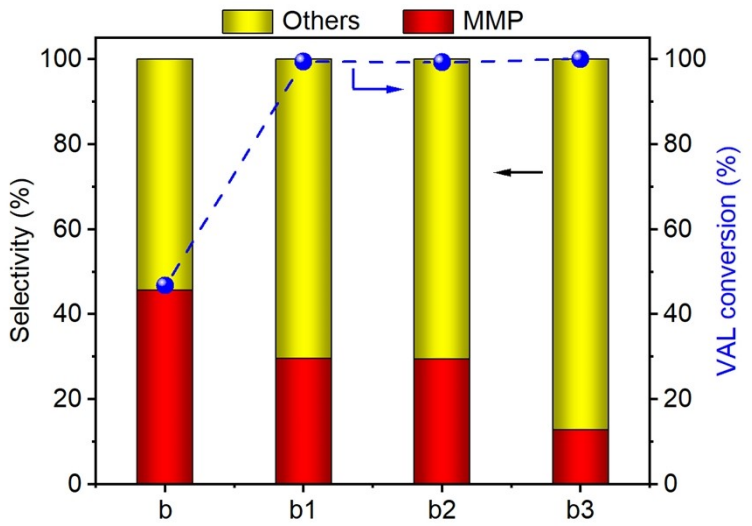

Fig. S18 HDO of VAL over Pd/CE mixed with phosphoric acid: (b) 45 mg of Pd/CE, (b1) 45 mg of Pd/CE with 1 μL of phosphoric acid, (b2) 45 mg of Pd/CE with 5 μL of phosphoric acid, and (b3) 45 mg of Pd/CE with 1 mL of phosphoric acid. Reaction conditions: 1 mmol of VAL, catalyst (VAL/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

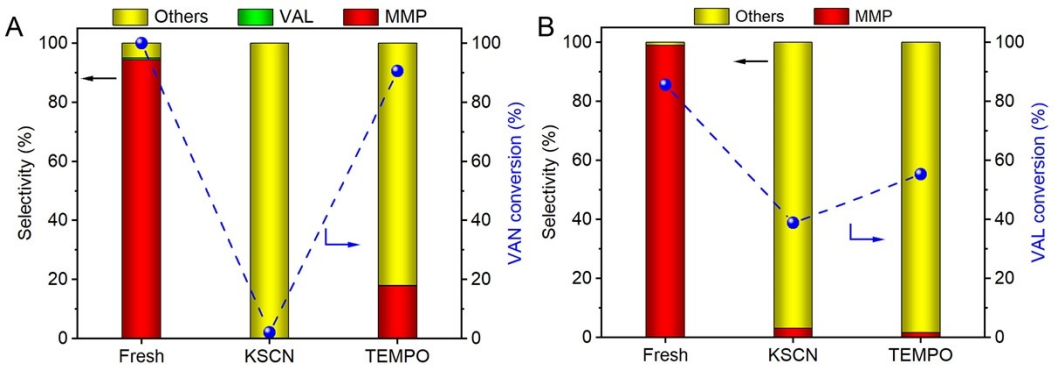

Fig. S19 Catalytic performance over Pd/PCE catalyst with addition of KSCN (KSCN/reactant = 0.5, mol/mol) and TEMPO (TEMPO/reactant = 2, mol/mol) in HDO of (A) VAN and (B) VAL. Reaction conditions: 1 mmol of reactant, catalyst (reactant/Pd = 240, mol/mol), 2 MPa of H_2, 60 °C, 8 h, 10 mL of water.

2. Supporting Tables

Table S1 Physical properties of Pd/CE and Pd/PCE.

Entry	Samples	BSA (m^2/g)[a]	TPV (cm^3/g)[b]	Pd loading (wt.%)[c]	Pd dispersion (%)[d]	P content (wt.%)[c]	Weak acid (mmol/g)[e]	Medium acid (mmol/g)[f]
1	Pd/CE	<10	<0.1	1.0	1.8	0.1	-	0.22
2	Pd/PCE	<10	<0.1	0.9	<1	1.4	0.21	1.68
3	Recycled Pd/PCE	<10[g]	<0.1[g]	1.0	-	0.2	-	-

[a] BET surface area (BSA) calculated in the P/P_0 range of 0.01 to 0.2. [b] Total pore volume (TPV) collected at P/P_0 = 0.95. [c] Measured by ICP-OES. [d] Calculated based on CO uptake. [e] Calculated below 200 °C. [f] Calculated from 200 °C to 350 °C. [g] The isotherm of recycled Pd/PCE was similar to that of Pd/PCE and not shown in the paper.

Table S2 HDO of VAN over different catalysts.

Entry	Catalyst	Reaction conditions	VAN Con. (%)[a]	MMP sel. (%)[b]	VAL sel. (%)[c]
1	Blank	60 °C/8 h	7.0	0.1	1.7
2	CE	60 °C/8 h	34.8	1.4	18.4
3	PCE	60 °C/8 h	38.5	1.9	21.9
4	Pd/C	60 °C/8 h	96.8	26.3	58.1
5	Pd/CE	60 °C/8 h	> 99	12.6	52.0
6	Pd/PCE	60 °C/8 h	> 99	94.4	0.6

[a] Conversion of VAN. [b] Selectivity of MMP. [c] Selectivity of VAL.

Table S3 HDO of VAN over Pd/PCE compared to that reported in literature.

Entry	Catalyst	T/t/RS[a]	Pd (wt.%)[b]	VAN Con. (%)[c]	MMP Sel. (%)[d]	Reference
1	Pd/PCE	60 °C/8 h/water	0.9	>99	94.4	This work
2	ClMPA@Pd/Al_2O_3	50 °C/1 h/ethanol	1.0	>99	87.0	[1]
3	Pd/MSMF	110 °C/2 h/water	4.5	>99	>99	[2]
4	Pd/biochar	100 °C/3 h/water	2.0	>99	92.0	[3, 4]
5	Pd/CFR	70 °C/1 h/ *n*-butanol	0.5	>99	>99	[5]
6	Pd/NH_2-UiO-66	100 °C/1 h/water	2.0	>99	>99	[6]
7	Pd@UiO-66(Hf)	90 °C/2 h/water	5.2	>99	>99	[7]
8	$Pd_1@WO_{2.72}$	40 °C/15 min/ethanol	0.58	>99	>99	[8]
9	Pd_{SA+C}/SAPO-31	80 °C/30 min/ethanol	0.38	>99	>99	[9]

[a] Reaction temperature (T), time (t) and reaction solvent (RS). [b] Pd loading. [c] Conversion of VAN. [d] Selectivity of MMP.

3. References

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