Supplementary Material

Construction of Pd-TiO_x interfaces for selective hydrodeoxygenation of C=O bands in vanillin by supporting Pd nanoparticles on ETS-10 zeolite

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Supplementary Figures

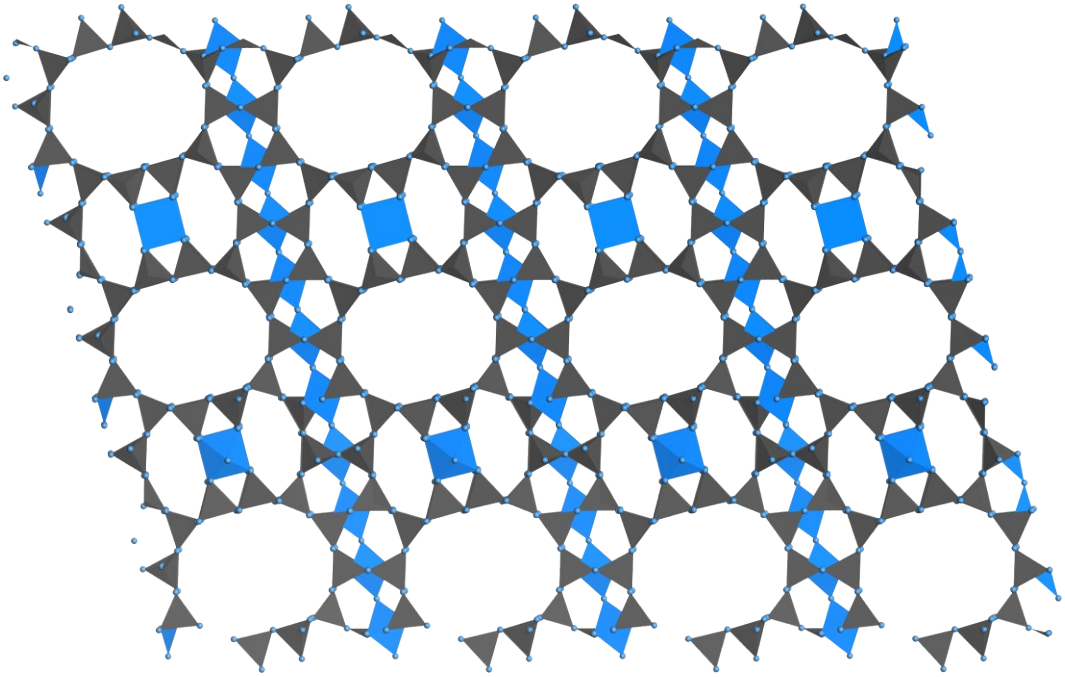

Fig. S1 Framework structure of ETS-10. TiO_x nanowires and SiO_2 framework are shown in blue and gray, respectively. The counter cations (H^+, Na^+ and K^+) are not shown for clarity.

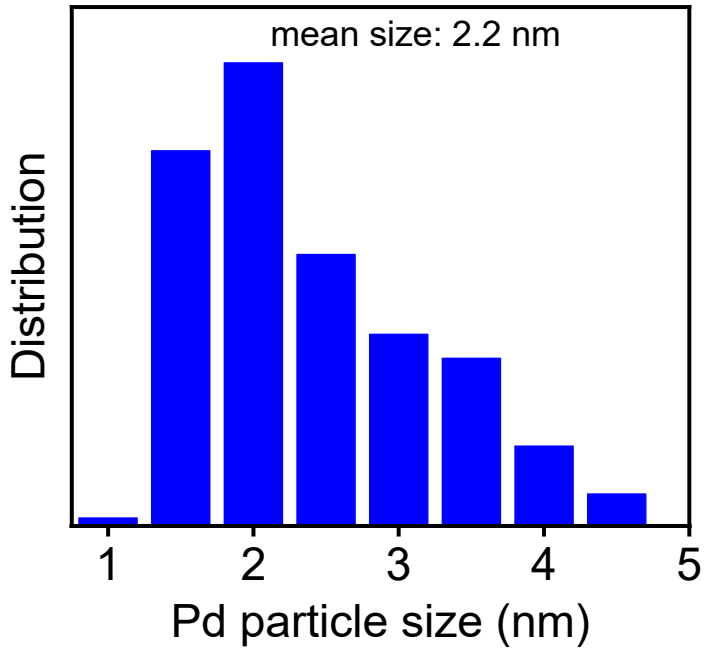

Fig. S2 Pd nanoparticle size distribution of the Pd/ETS-10 sample.

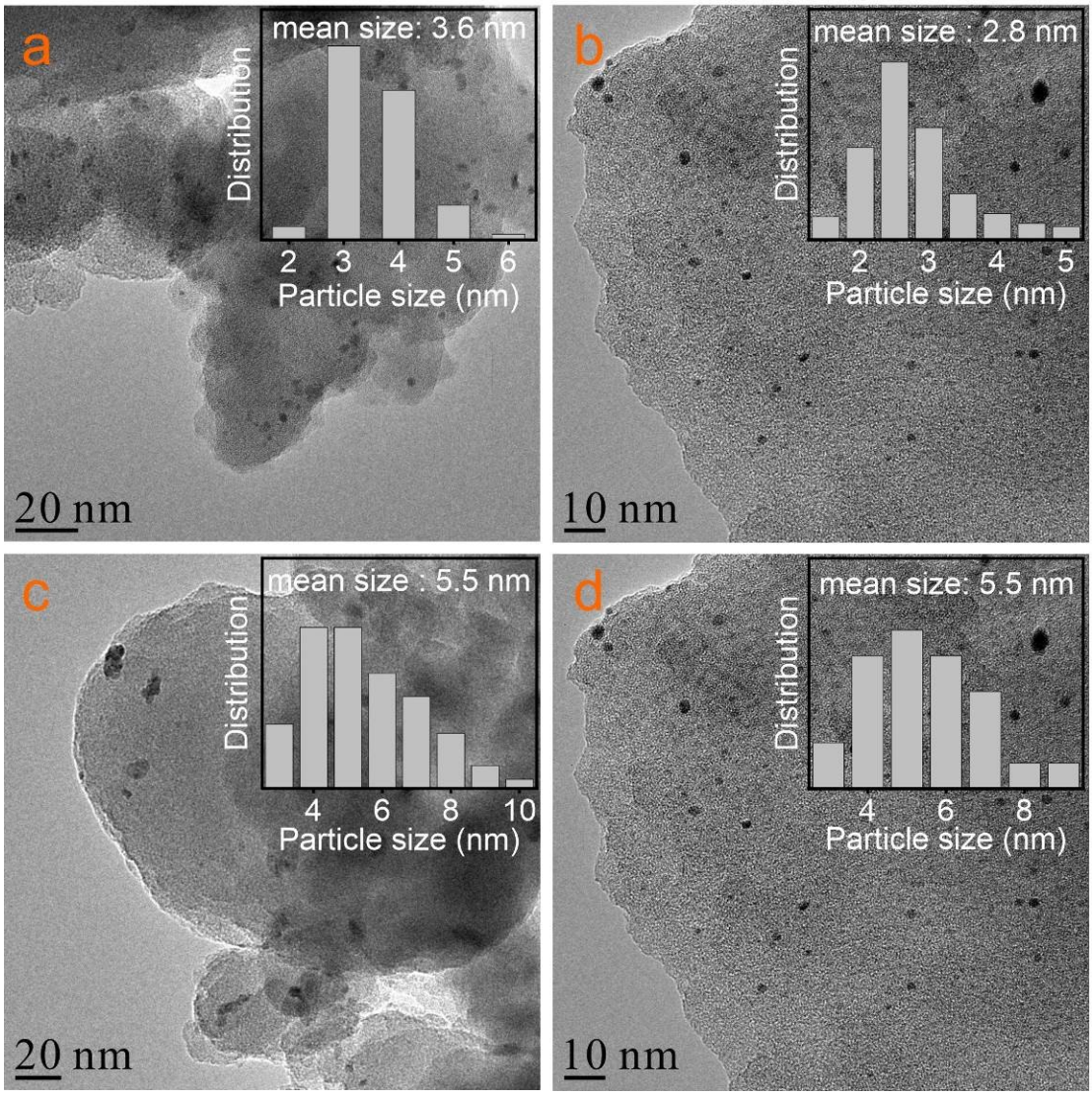

Fig. S3 TEM images of the (a) Ru/ETS-10, (b) Pt/ETS-10, (c) Rh/ETS-10, and (d) Au/ETS-10. Insets: metal particle size distributions.

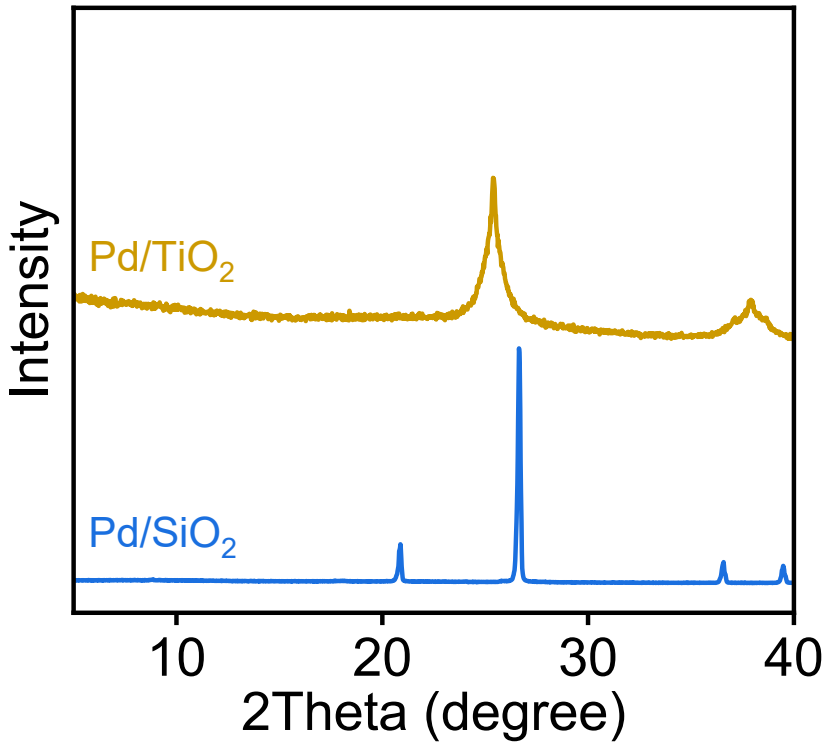

Fig S4. XRD patterns of the Pd/TiO_2 and Pd/SiO_2 samples.

Note: The TiO_2 and SiO_2 were of anatase and quartz phase, respectively.

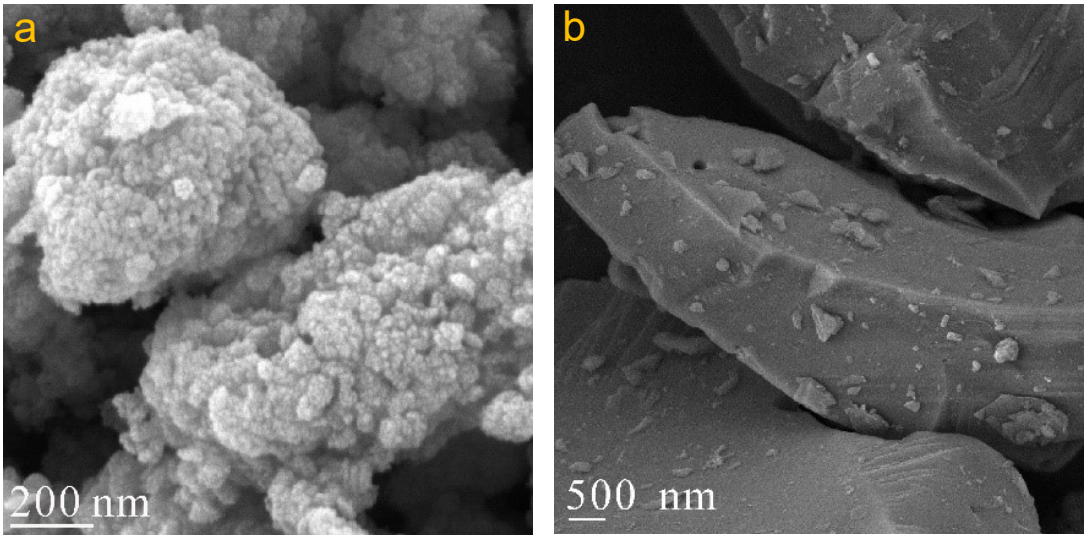

Fig S5. SEM images of the (a) Pd/TiO_2 and (b) Pd/SiO_2 samples.

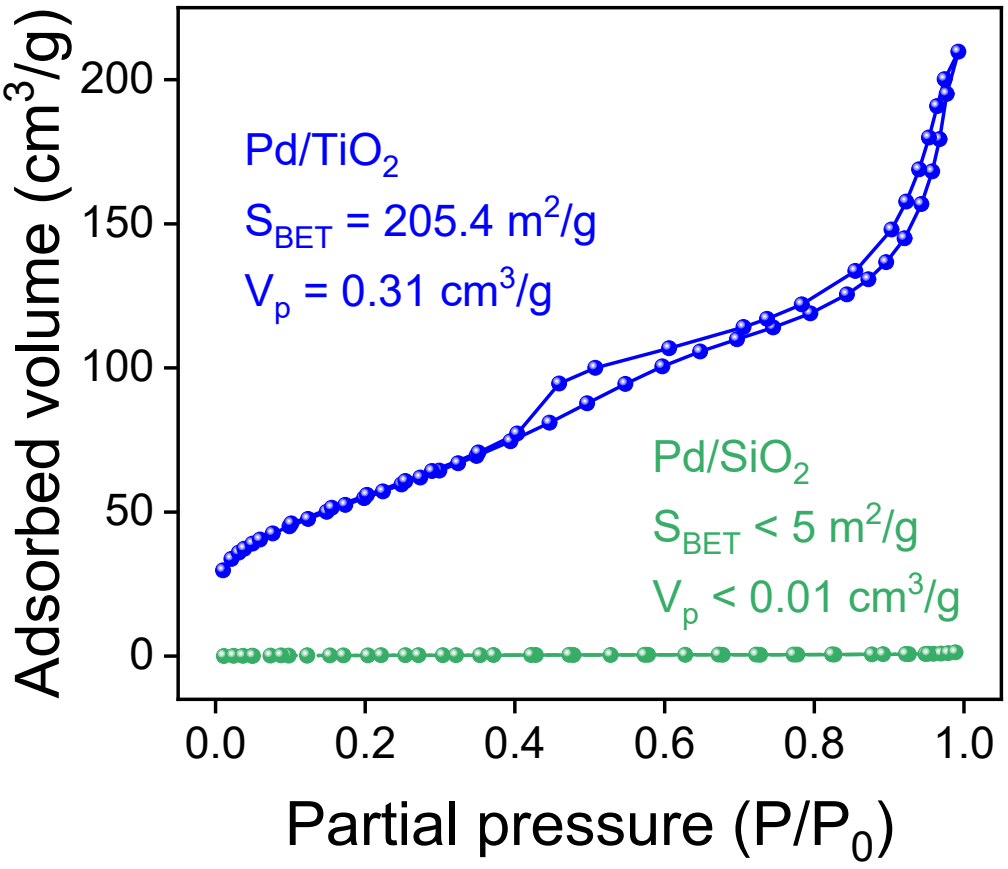

Fig S6. N_2 sorption isotherms of the Pd/TiO_2 and Pd/SiO_2 samples.

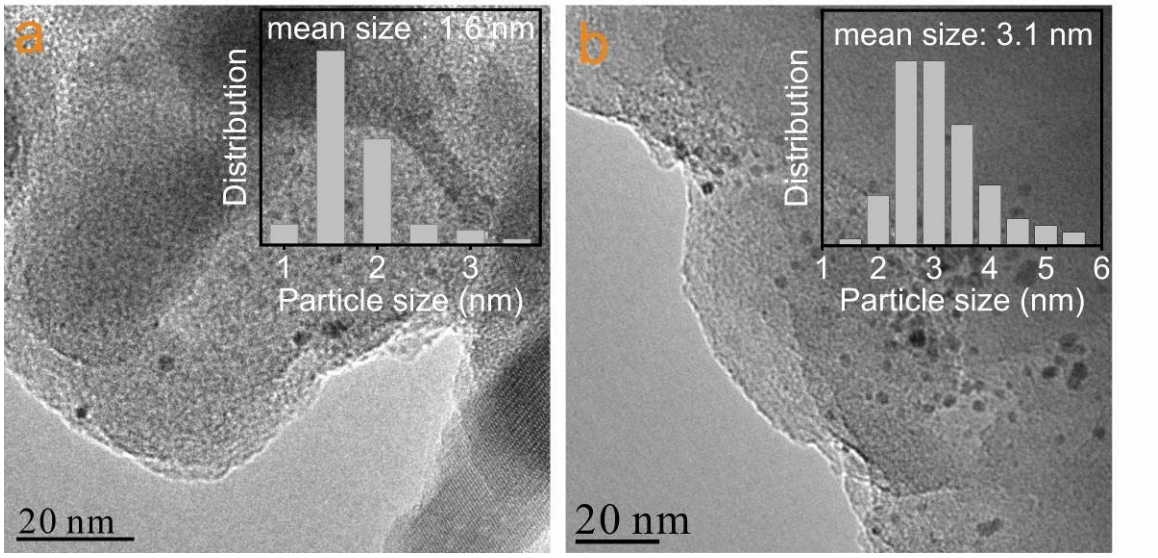

Fig. S7 TEM images of the (a) Pd/TiO_2 and (b) Pd/SiO_2 samples. Insets: metal particle size distributions.

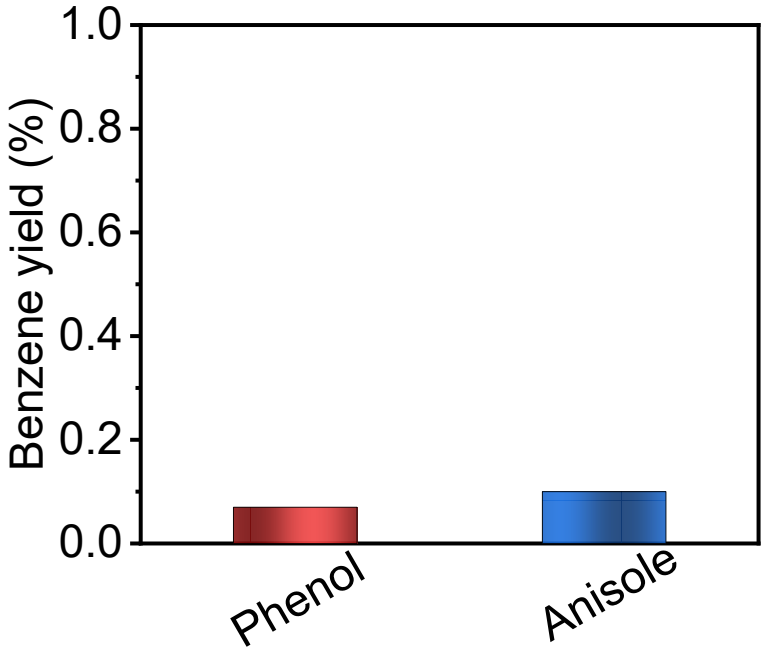

Fig. S8 Catalytic hydrodeoxygenation of phenol and anisole over various catalysts. Typical reaction conditions: 6.6 mmol of substrate, 0.2 g of catalyst, 50 g of H_2O, 1 MPa of H_2, 120 °C, and 1.5 h.

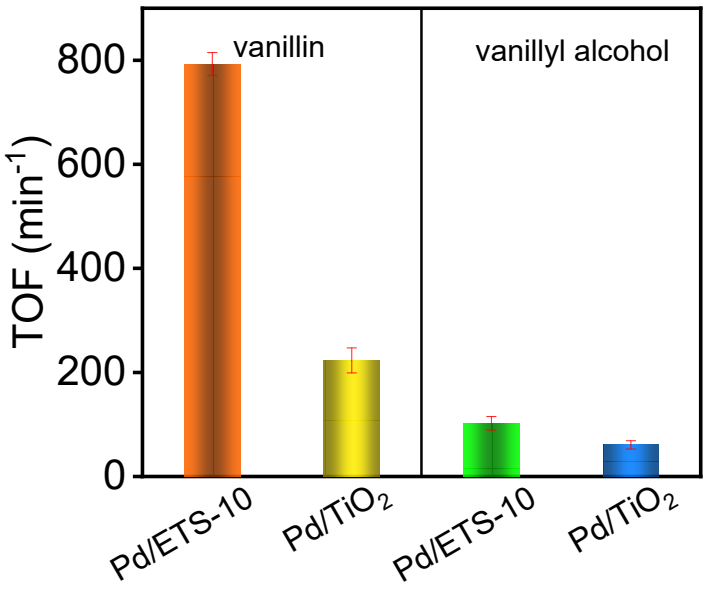

Fig. S9 TOF values in the catalytic hydrodeoxygenation of vanillin and vanillyl alcohol.

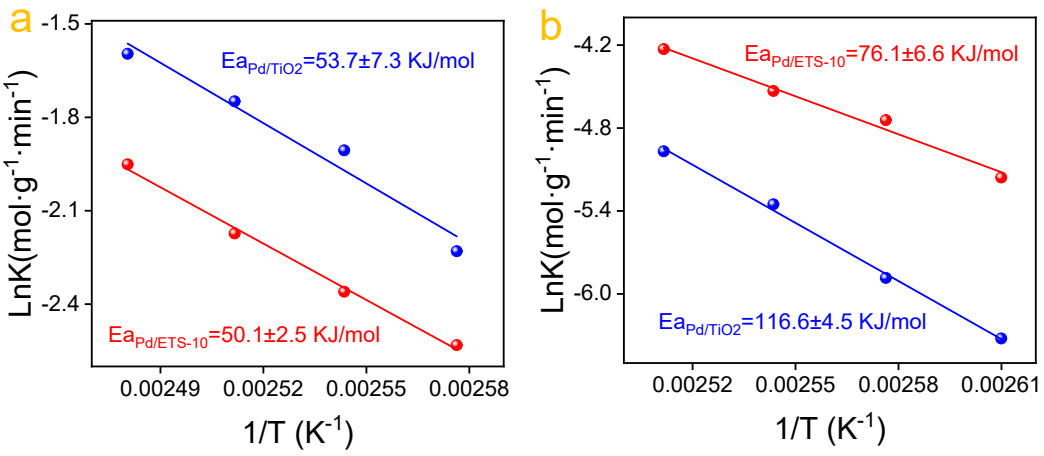

Fig. S10 Activation energies of (a) vanillin and (b) vanillyl alcohol over the Pd/ETS-10 and Pd/TiO_2 catalysts. Reaction conditions for vanillin reaction: 400 mg of vanillin, 2 mg of catalyst, 20 g of H_2O, 1 MPa of H_2, 120 °C, 0.083 h. Reaction conditions for vanillyl alcohol: 100 mg of vanillyl alcohol, 1 mg of catalyst, 5 g of H_2O, 1 MPa of H_2, 120 °C, and 0.083 h.

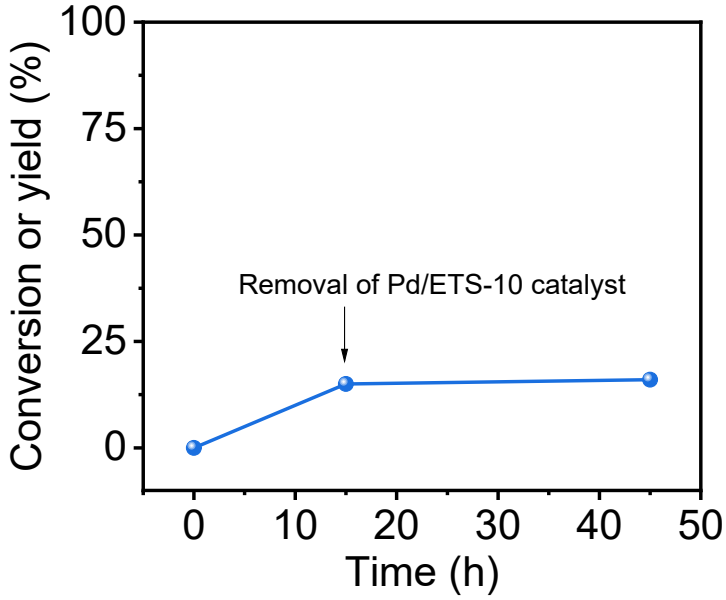

Fig. S11 Dependence of catalytic activity in hydrodeoxygenation of vanillin on time for a reaction system before and after separation of Pd/ETS-10 catalyst. Reaction conditions: 200 mg of vanillin, 5.1 mg of catalyst, 10 g of H_2O, 1 MPa of H_2, 120 °C.

Supplementary Table

Table S1. Textual parameters of the Pd catalysts.

Sample	metal loading amount (*wt*%)[a]
Pd/ETS-10	0.33
Pd/TiO_2	0.46
Pd/SiO_2	0.20
Pt/ETS-10	0.67
Au/ETS-10	0.12
Rh/ETS-10	0.91
Ru/ETS-10	1.04

[a] determined by ICP analysis

Table S2. Comparison of the catalytic results between the Pd/ETS-10 catalyst and the selected examples of some representative Pd and no-noble catalysts in the hydrodeoxygenation of vanillin.

Catalyst	Temperature (°C)	Time (h)	P_{H2} (MPa)	Conversion (%)	Selectivity (%)	Reference
Pd/C	100	3	3	100	92	[1]
Pd-PTA/ZrO_2	80	1.5	0.1	>99	>99	[2]
Pd/PHS	R.T.	8	2	>99	98.2	[3]
Pd/BC	60	4	2	>99	92.8	[4]
Ga-Cu/HNZY	180	2.5	1	>99	>99	[5]
Ni_2P/HY	220	5	2	>99	>99	[6]
Ni_3Co@NC@C	170	2	1	>99	>99	[7]
Pd/ETS-10	60	5	2	>99	93.0	This work

Note: The selection criteria are as-follows: Pd catalysts are active for the hydrodeoxygenation of vanillin at different reaction temperatures. Therefore, we chose several representative Pd-based catalysts performed at different reaction temperatures (references 1-4). Notably, at the same temperature, our Pd/ETS-10 catalyst exhibited comparable activity to that of the Pd/BC catalyst (reference 4). In addition, we also compared our catalyst with representative non-noble metal catalysts (references 5-7). Notably, our Pd/ETS-10 catalyst is more active than the Ni, Co, and Cu catalysts.

References

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