Supplementary Information (SI) for Green Chemistry.

Supporting Information

Selective C-O bond cleavage enhances aromatics production from lignin-derived platform molecules with ethanol as a hydrogen donor

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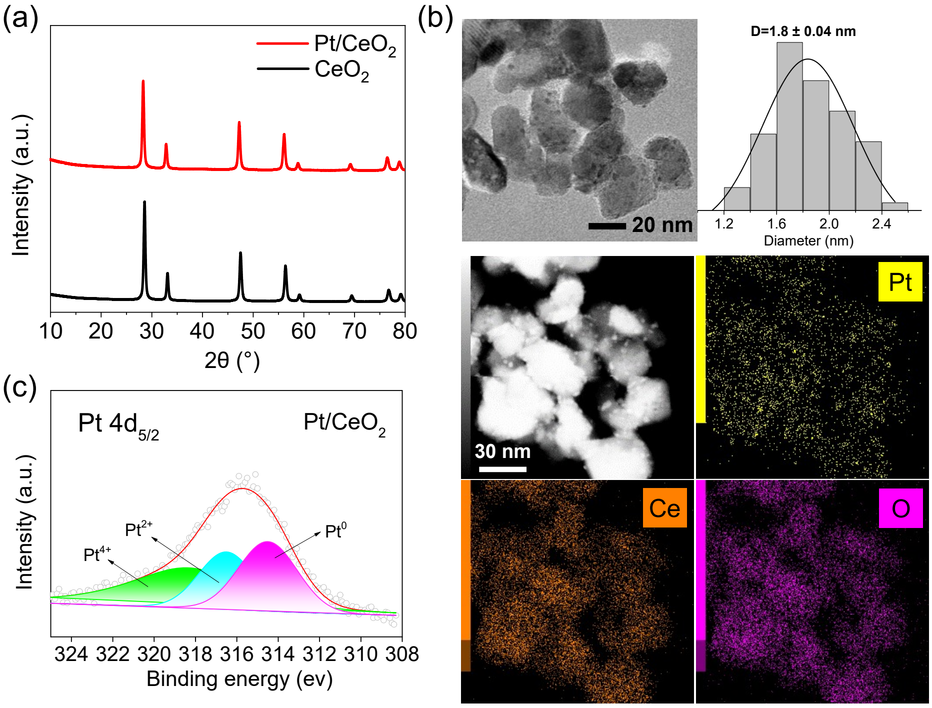

Fig. S1. XRD patterns of CeO_2 and Pt/CeO_2 (a); TEM images, particle size distribution, and elemental mapping results for Pt/CeO_2 (b); Pt $4d_{5/2}$ XPS spectra of Pt/CeO_2 catalysts (c).

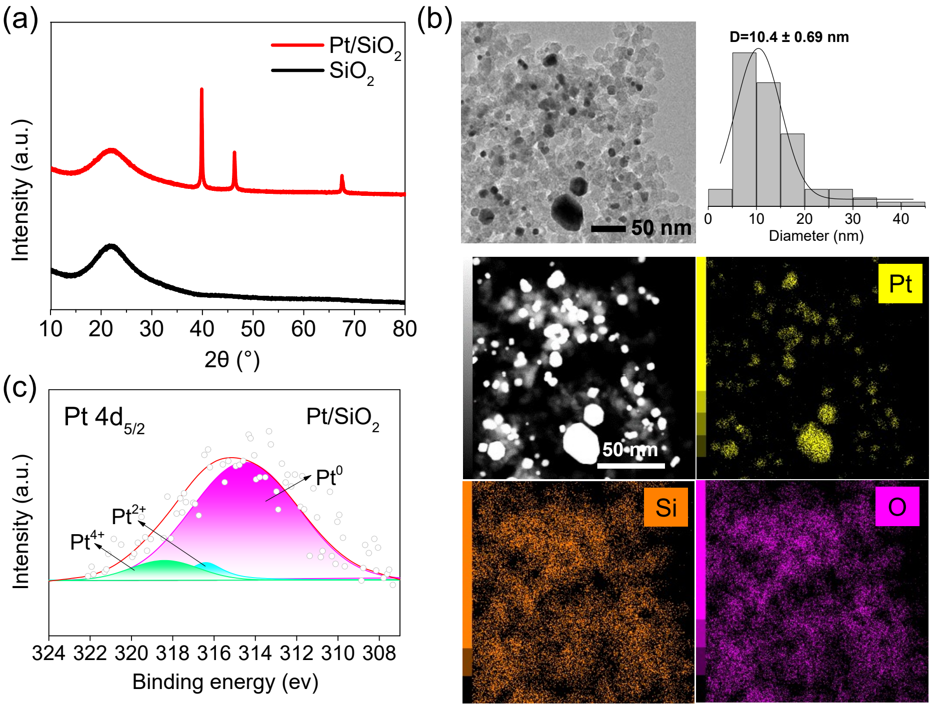

Fig. S2. XRD patterns of SiO_2 and Pt/SiO_2 (a); TEM images, particle size distribution, and elemental mapping results for Pt/SiO_2 (b); Pt $4d_{5/2}$ XPS spectra of Pt/SiO_2 catalysts (c).

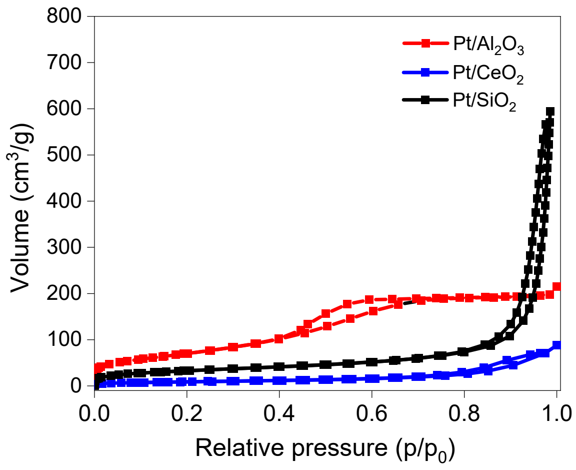

Fig. S3. N_2 adsorption-desorption isotherms of Pt/Al_2O_3, Pt/CeO_2 and Pt/SiO_2 catalysts.

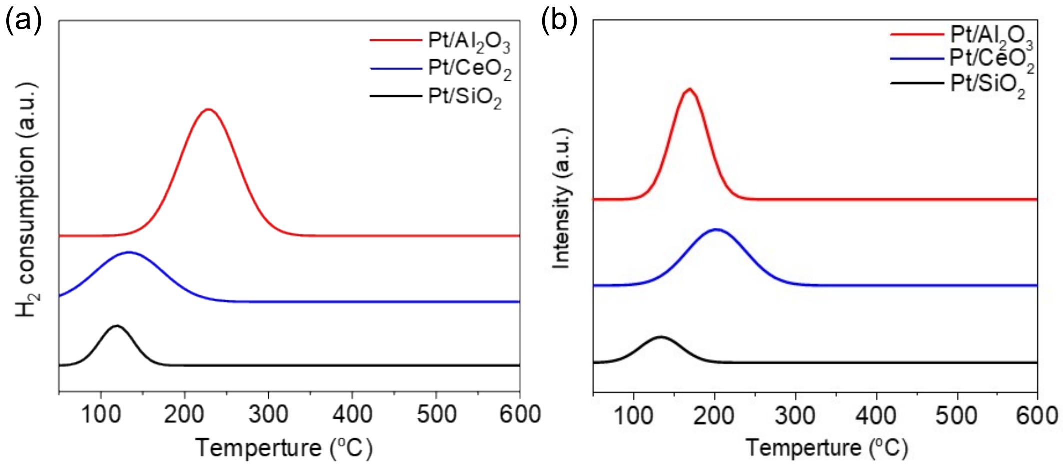

Fig. S4. H_2-TPR (a) and H_2-TPD (b) profiles of Pt/Al_2O_3, Pt/CeO_2 and Pt/SiO_2 catalysts.

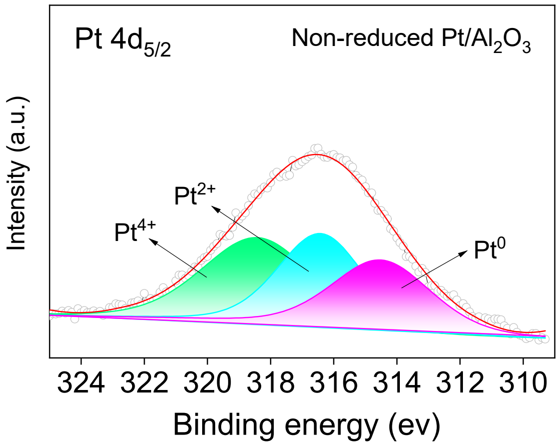

Fig. S5. Pt $4d_{5/2}$ XPS spectra of the calcined (unreduced with H_2) Pt/Al_2O_3 catalyst.

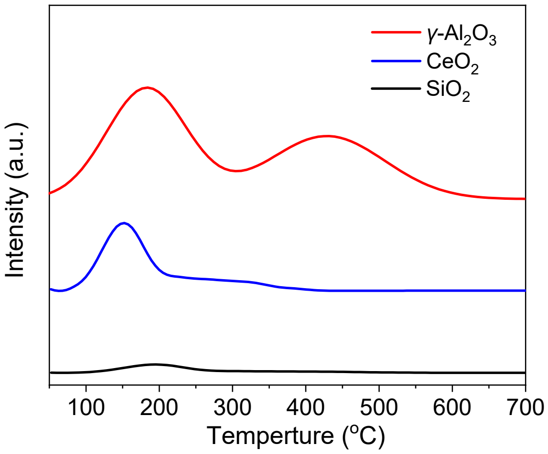

Fig. S6. NH_3-TPD profiles of the three employed catalyst supports.

NH_3-TPD was conducted on the three supports to investigate their acidity properties. For γ-Al_2O_3, two desorption peaks at approximately 180 °C and 420 °C were attributed to weak and medium Lewis acidity, respectively. On CeO_2, desorption peaks at approximately 150 °C and 280 °C were associated with NH_3 coordinated on weak and medium LASs. In comparison, SiO_2 exhibited very few weak acid sites, which originated from its surface hydroxyl groups.

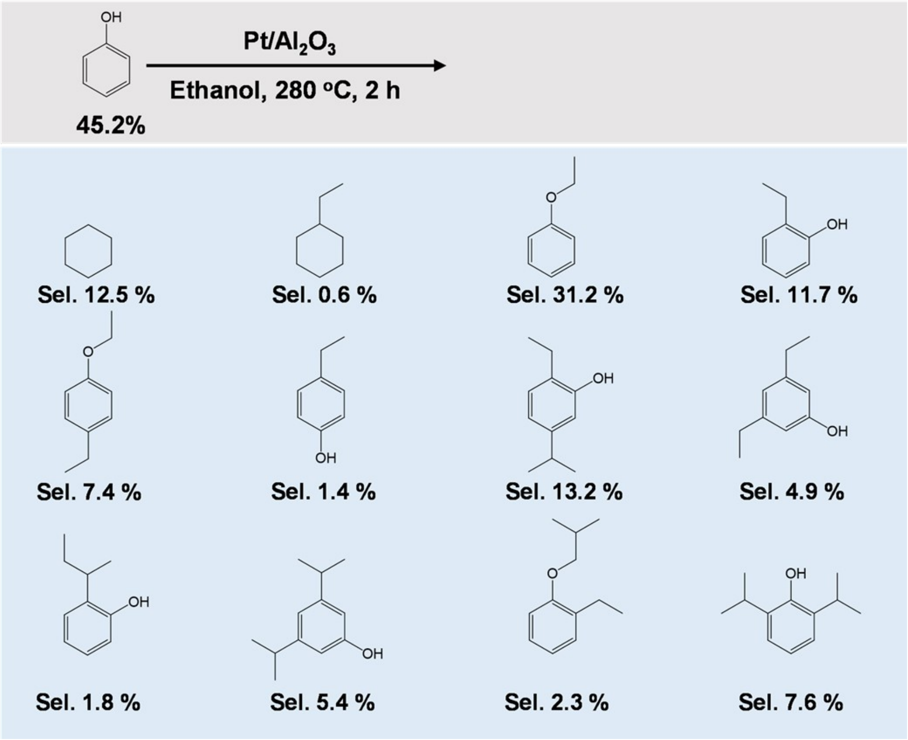

Fig. S7. Phenol conversion and products distribution with pure ethanol as the hydrogen donor. Reaction conditions for 500 mg phenol, 200 mg catalyst, 8 mL ethanol, 280 °C, 2 h.

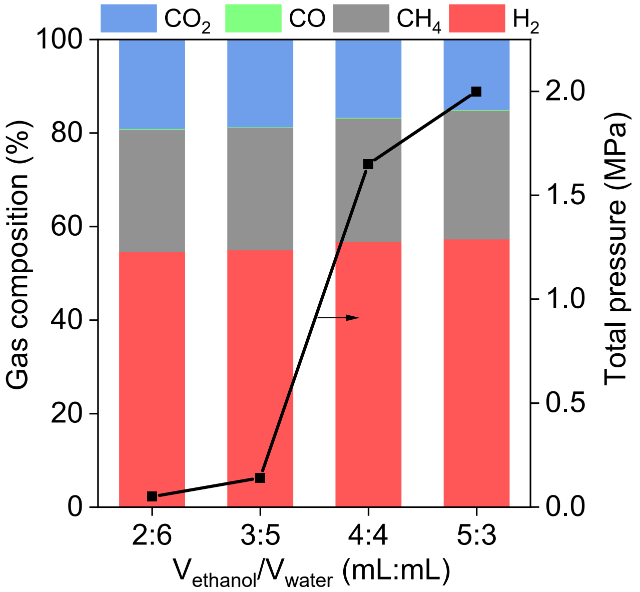

Fig. S8. The effect of ethanol-to-water ratio on the total pressure and gas composition in the APR of ethanol. Reaction conditions: 200 mg Pt/Al_2O_3 catalyst, 8 mL ethanol + water, 280 °C, 2 h. The total pressure was measured after the reactor was cooled to room temperature.

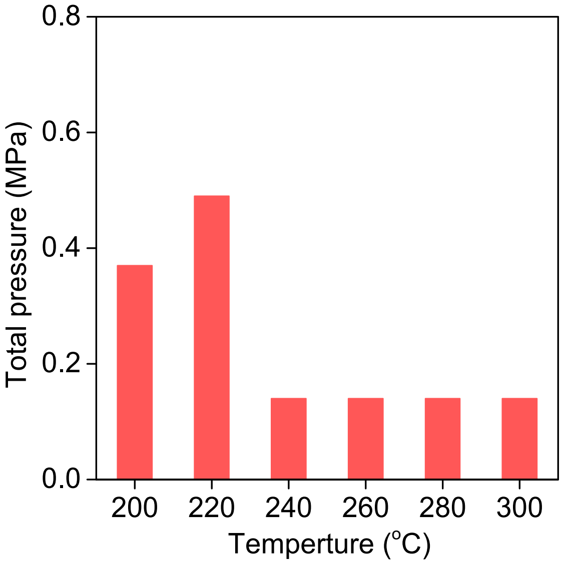

Fig. S9. The effect of reaction temperature on the H_2 production from APR of ethanol. Reaction conditions: 200 mg Pt/Al_2O_3 catalyst, 3 mL ethanol, 5 mL H_2O, 2 h.

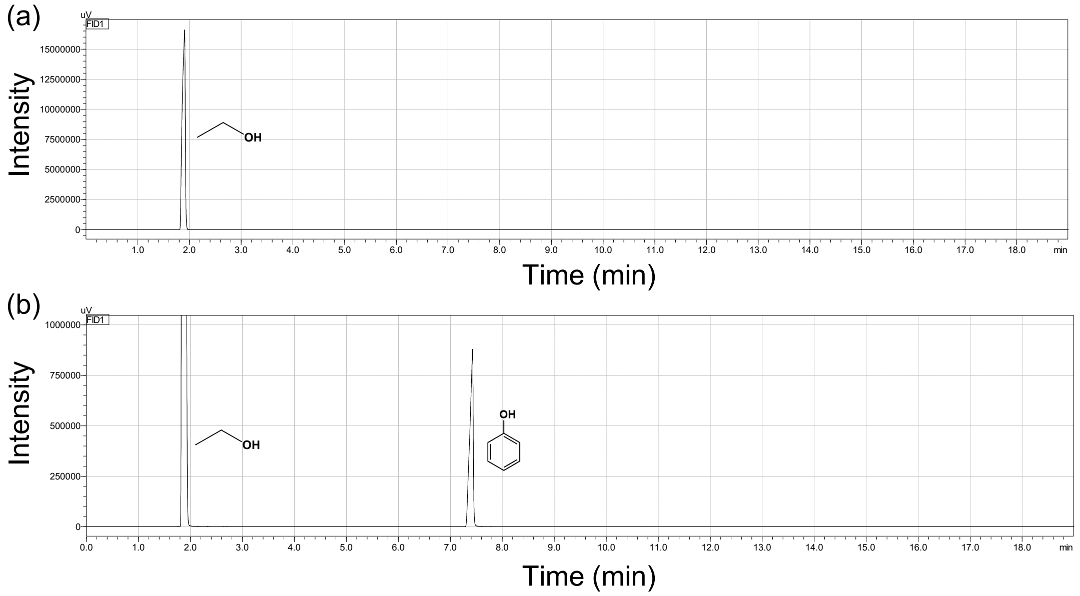

Fig. S10. The GC spectrum of liquid products from ethanol reaction on γ-Al_2O_3 (a). and the GC-MS spectrum of liquid products from *in situ* HDO of phenol on γ-Al_2O_3 (b). Reaction conditions for (a): 200 mg γ-Al_2O_3, 3 mL ethanol, 5 mL H_2O, 280 ℃, 2 h. Reaction conditions for (b): 200 mg γ-Al_2O_3, 500 mg phenol, 3 mL ethanol, 5 mL H_2O, 280 ℃, 2 h.

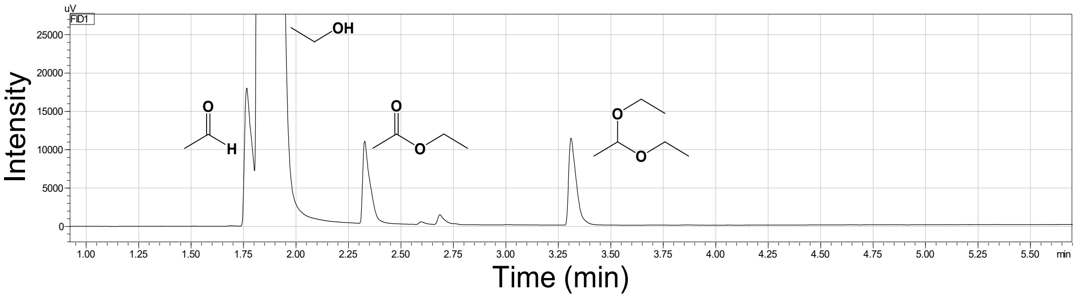

Fig. S11. GC spectrum of the liquid products from APR of ethanol over Pt/Al_2O_3. Reaction conditions: 200 mg Pt/Al_2O_3, 3 mL ethanol, 5 mL H_2O, 280 ℃, 2 h.

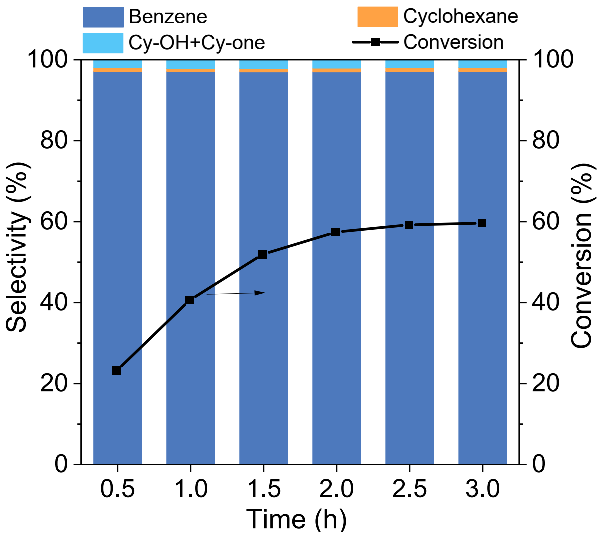

Fig. S12. Time-dependent conversion and product selectivity involved in the *in situ* HDO of phenol over Pt/Al_2O_3. Reaction conditions: 500 mg phenol, 200 mg Pt/Al_2O_3, 3 mL ethanol, 5 mL H_2O, 280 °C.

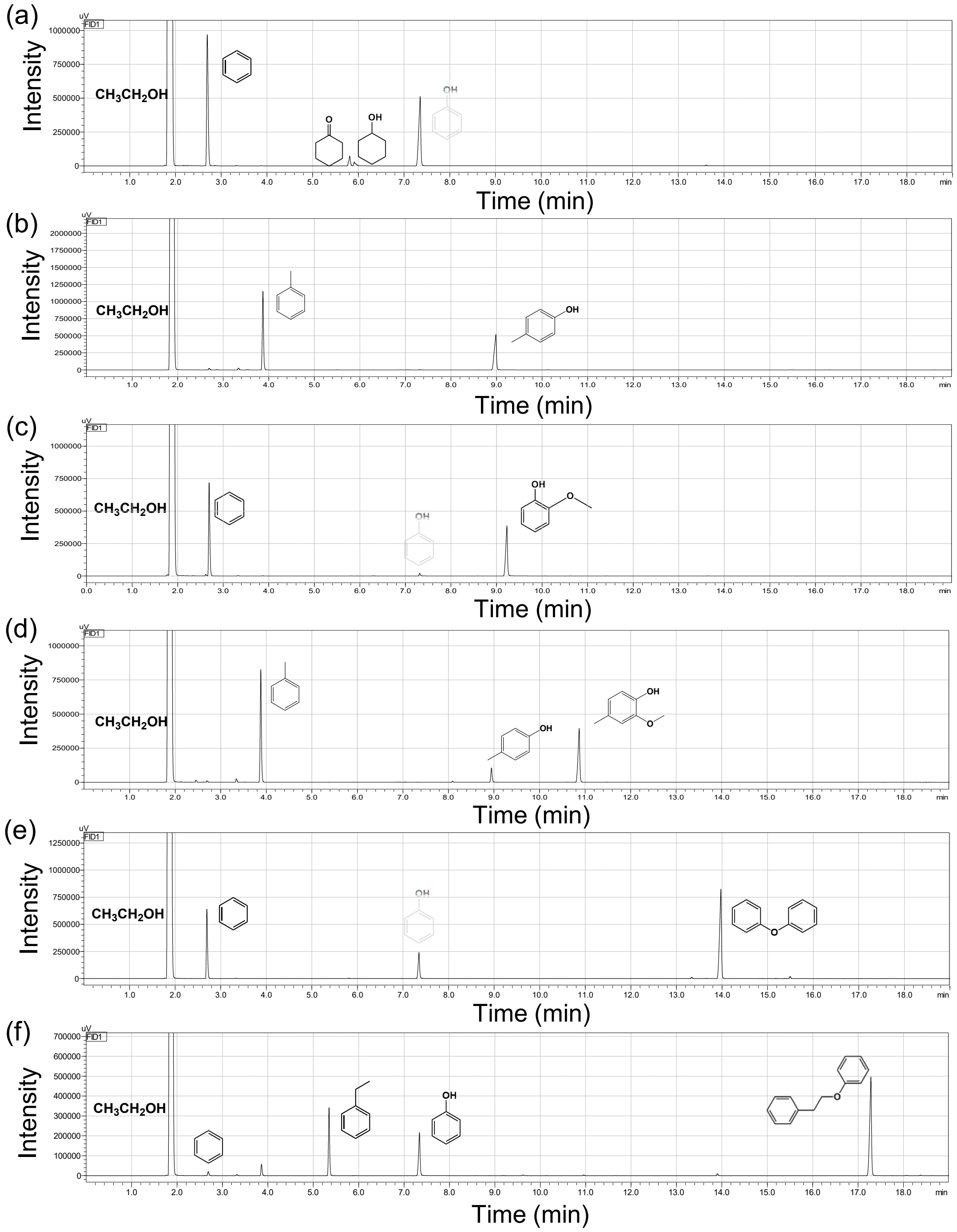

Fig. S13. The GC spectrum of liquid products from the *in situ* HDO reaction of phenol (a), p-cresol (b), guaiacol (c), 4-methylguaiacol (d), diphenyl ether (e), and phenylethyl phenyl ether (f) over Pt/Al_2O_3 catalyst. Reaction conditions: 500 mg reactants, 200 mg γ-Al_2O_3, 3 mL ethanol, 5 mL H_2O, 280 °C, 2 h.

Table S1. Textural properties of Pt/Al_2O_3, Pt/CeO_2 and Pt/SiO_2 catalysts and Pt metal dispersions on these studied catalysts.

Sample	BET surface area (m^2 g^{-1}) [a]	Pore volume (cm^3 g^{-1}) [a]	Pt dispersion (%) [b]
Pt/Al_2O_3	256.3	0.31	86
Pt/CeO_2	36.8	0.13	71
Pt/SiO_2	132.5	0.58	30

[a] The specific surface areas and pore volumes are determined by N_2 sorption analysis at -196°C. The specific surface area obtained by the BET method; The pore volume was calculated by the t-plot method; [b] The dispersion of Pt was determined by H_2 chemisorption.

Table S2. The proportion of Pt species at different valance states on Pt/Al_2O_3, Pt/CeO_2 and Pt/SiO_2 catalysts determined by XPS analysis.

Sample	Pt^0	Pt^{2+}	Pt^{4+}	$Pt^0/Pt^{\delta+}$
Pt/Al_2O_3	55.2%	32.8%	12.0%	1.23%
Non-reduced Pt/Al_2O_3	29.3%	32.9%	37.8%	0.41%
Pt/CeO_2	35.9%	28.4%	35.7%	0.56%
Pt/SiO_2	86.3%	4.20%	9.50%	6.31%

Table S3. Reactant conversion and products distribution of the *in situ* HDO of phenol, as well as the H_2 pressure generated from the APR of ethanol on non-reduced Pt/Al_2O_3 catalyst.

Conversion (%) [a]	Selectivity (%) [a]			H_2 pressure (MPa) [b]
	Benzene	Cy-OH +Cy-one	Cyclohexane	
25	97.7	1.7	0.6	0.12

[a] Reaction conditions: 500 mg phenol, 200 mg non-reduced Pt/Al_2O_3 catalyst, 3 mL ethanol and 5 mL H_2O, 280 °C, 2 h. [b] Reaction conditions: 200 mg non-reduced Pt/Al_2O_3 catalyst, 3 mL ethanol, 5mL H_2O, 280 °C, 2 h.

Table S4. Products distribution for phenol *in situ* HDO in pure water.

Catalyst	Reaction conditions	Total Pressure	Conversion (%)	Selectivity (%) [a]		
				Benzene	CYH	Cy-OH+ Cy-one
Pt/Al_2O_3	500 mg phenol, 200 mg Pt/Al_2O_3, 8 mL H_2O, 280 °C, 2 h	Not detectable	2.5	95.0	4.1	0.9

[a] CYH, Cy-OH, and Cy-one are the abbreviations for cyclohexane, cyclohexanol, and cyclohexanone, respectively. The total pressure was measured after the reactor was cooled to room temperature.

Table S5. Conversion of ethanol and *in situ* HDO of phenol over γ-Al_2O_3.

Catalyst	Reaction conditions	Total Pressure (MPa) [a]	Conversion (%)
γ-Al_2O_3	200 mg γ-Al_2O_3, 3 mL ethanol, 5 mL H_2O, 280 °C, 2 h	Not detectable	0 [b]
γ-Al_2O_3	200 mg γ-Al_2O_3, 500 mg phenol, 3 mL ethanol, 5 mL H_2O, 280 °C, 2 h	Not detectable	0 [c]

[a] The total pressure was measured after the reactor was cooled to room temperature. [b] The conversion of ethanol. [c] The conversion of phenol.

Table S6. Co-reaction of phenol and cyclohexene over γ-Al_2O_3 using ethanol as the hydrogen donor.

Catalyst	Reaction conditions	Phenol Conversion (%)	Selectivity (%) [a]		
			Benzene	CYH	Cy-OH+ Cy-one
Pt/Al_2O_3	500 mg phenol, 500 mg cyclohexene, 200 mg catalyst, 3 mL ethanol, 5 mL H_2O, 280 °C, 2 h	59.3	96.6	2.84	0.56

[a] CYH, Cy-OH, and Cy-one are the abbreviations for cyclohexane, cyclohexanol, and cyclohexanone, respectively.

Table S7. Relative calibration factors of different chemicals determined by GC with 2-cyclohexen-1-one as the standard (2-cyclohexen-1-one = 1).

Entry	Substrate	Relative calibration factor
1	2-cyclohexen-1-one	1.0
2	phenol	1.13
3	cyclohexanol	1.04
4	cyclohexene	0.86
5	cyclohexanone	0.93
6	cyclohexane	0.88
7	benzene	0.98
8	toluene	1.23
9	ethylbenzene	1.49
10	p-cresol	1.35
11	guaiacol	1.25
12	4-methylguaiacol	1.47
13	diphenyl ether	2.73
14	phenylethyl phenyl ether	3.23

Table S8. Metal loading measurements for the fresh Pt/Al_2O_3 and the spent Pt/Al_2O_3 catalysts after four catalytic runs.

	Fresh Pt/Al_2O_3	Spent Pt/Al_2O_3 [b]
Pt Loading (wt%) [a]	4.95	4.03

[a] Determined by ICP-OES; Every sample was test for three times and the average values were used here. [b] After four catalytic runs, the catalyst was collected, washed, calcined at 500 °C for 4 h in air, followed by reduction at 450 °C for 2 h in H_2 before the ICP-OES measurement.

Table S9. Textural properties of the fresh and spent Pt/Al_2O_3 catalyst after four catalytic runs.

Sample	BET surface area (m^2 g^{-1}) [a]	Pore volume (cm^3 g^{-1}) [a]	Pt dispersion (%) [b]
Fresh Pt/Al_2O_3	256.3	0.31	86
Spent Pt/Al_2O_3	193.7	0.26	66

[a] The specific surface areas and pore volumes are determined by N_2 sorption analysis at -196°C. The specific surface area obtained by the BET method; The pore volume was calculated by the t-plot method; [b] The dispersion of Pt was determined by H_2 chemisorption.