Supplementary Information

Phosphate modified ceria as a Brønsted acidic/redox multifunctional catalyst

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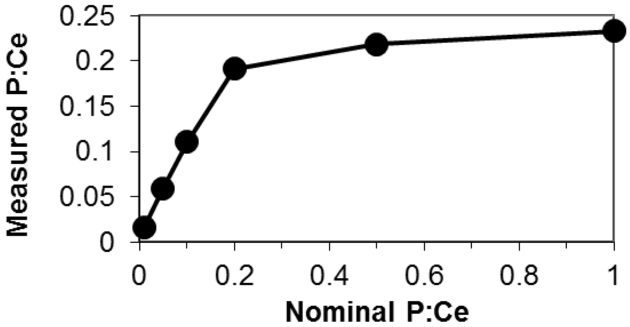


Fig. S1 Measured P:Ce mole ratio after trimethylphosphate deposition onto CeO2 followed by calcination versus the nominal P:Ce mole ratio.

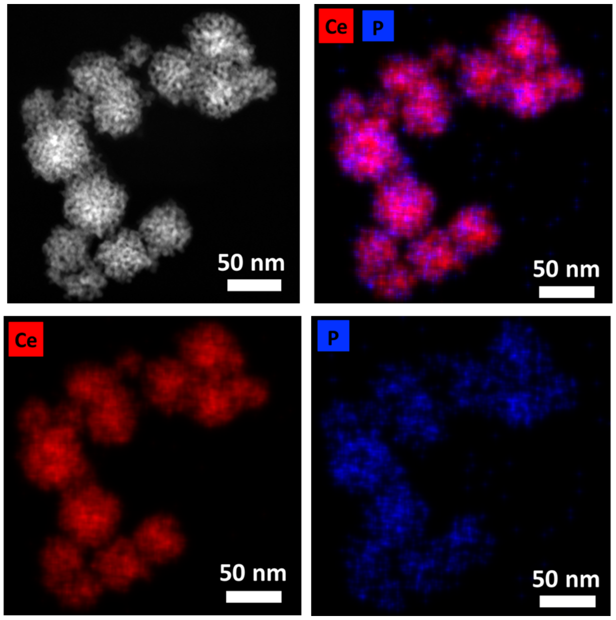


Fig. S2 STEM image and corresponding EDS elemental maps for CeO_2-0.1PO_x. STEM analysis of CeO_2-0.2PO_x is expected to be similar. STEM images of CeO_2 have been reported previously.[1]

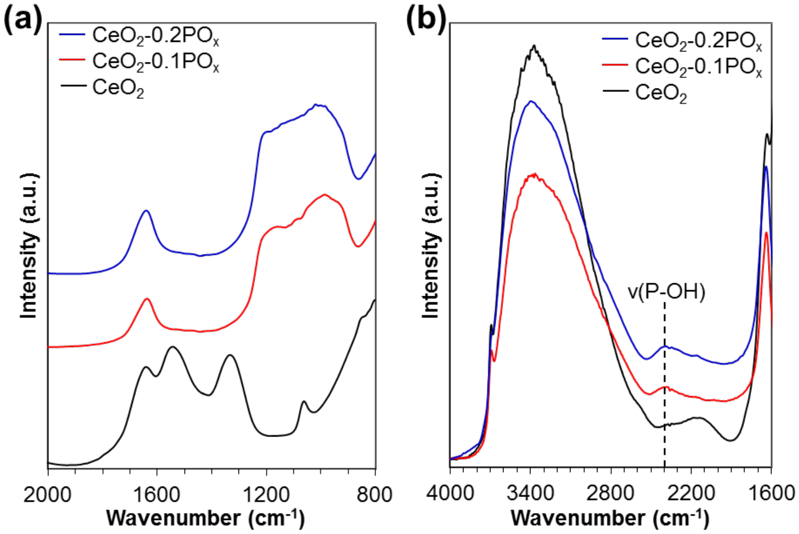


Fig. S3 DRIFT spectra of the materials with no pretreatment (i.e. as-synthesized) and no baseline correction in the (a) carbonate/phosphate and (b) hydroxyl regions. The band around 2100 cm-1 for CeO$_2$ has been proposed as either an electron transition from donor levels located near the conduction band such as Ce3+ or oxygen vacancies or the forbidden 2F$^{5/2}$ → 2F$^{7/2}$ electronic transition of Ce^{3+} located at subsurface (or bulk) defective lattice sites.[2-4]

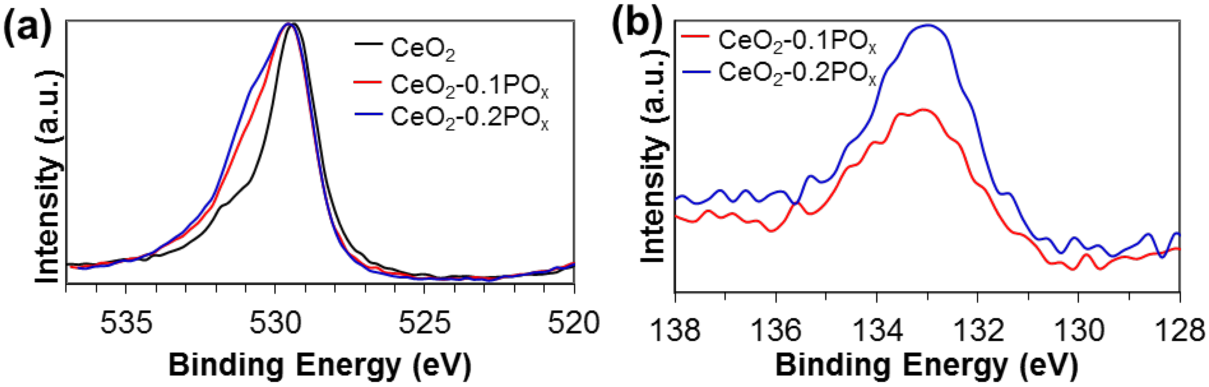


Fig. S4 XPS spectra in the (a) O 1s spectral region for CeO$_2$, CeO$_2$-0.1PO$_x$, and CeO$_2$-0.2PO$_x$. (b) P 2p spectral region for phosphate functionalized materials.

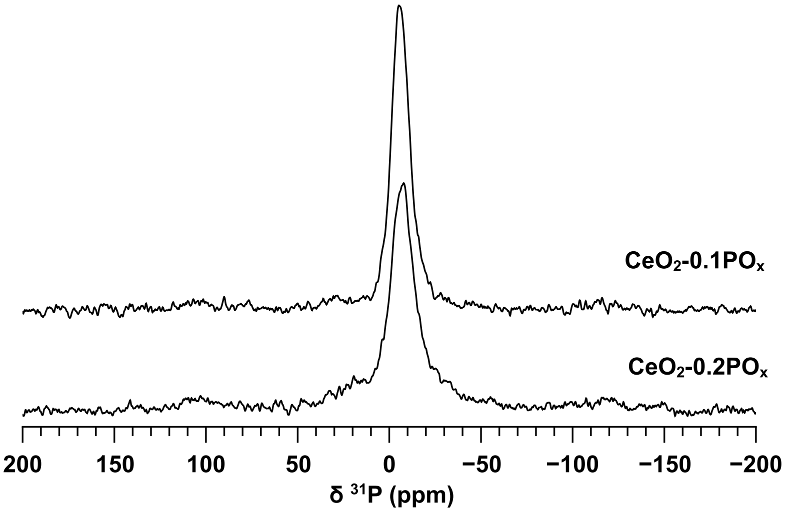


Fig. S5 ^{31}P{1H} CPMAS spectra of CeO2-0.1POx and CeO2-0.2POx. The spectra were obtained at 9.4 T using v_R = 18 kHz, t_{CP} = 2.1 ms, v_{RF}(^{1}H CP) = 96 kHz, v_{RF}(31P CP) = 78 kHz, v_{RF}(^{1}H SPINAL-64) = 96 kHz and 1024 scans.

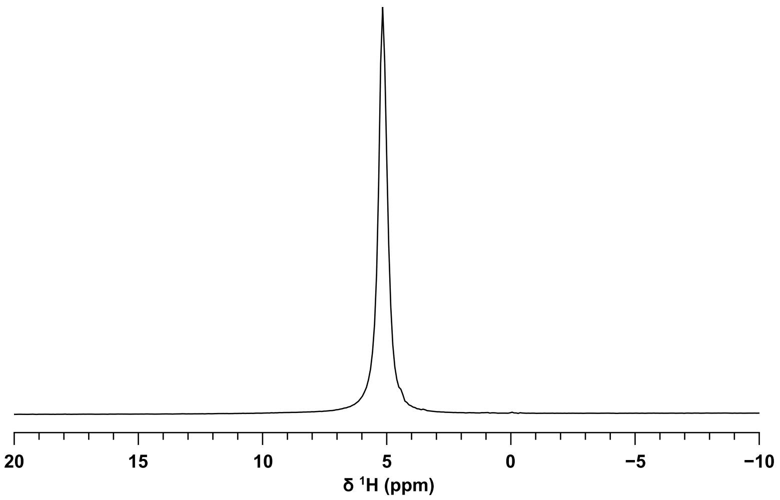


Fig. S6 ^{1}H DPMAS spectrum of CeO_2, obtained at 14.1 T using v_R = 38 kHz, v_{RF}(^{1}H 90˚) = 83.3 kHz, t_{rd} = 3 s and 16 scans. The probe background was subtracted.

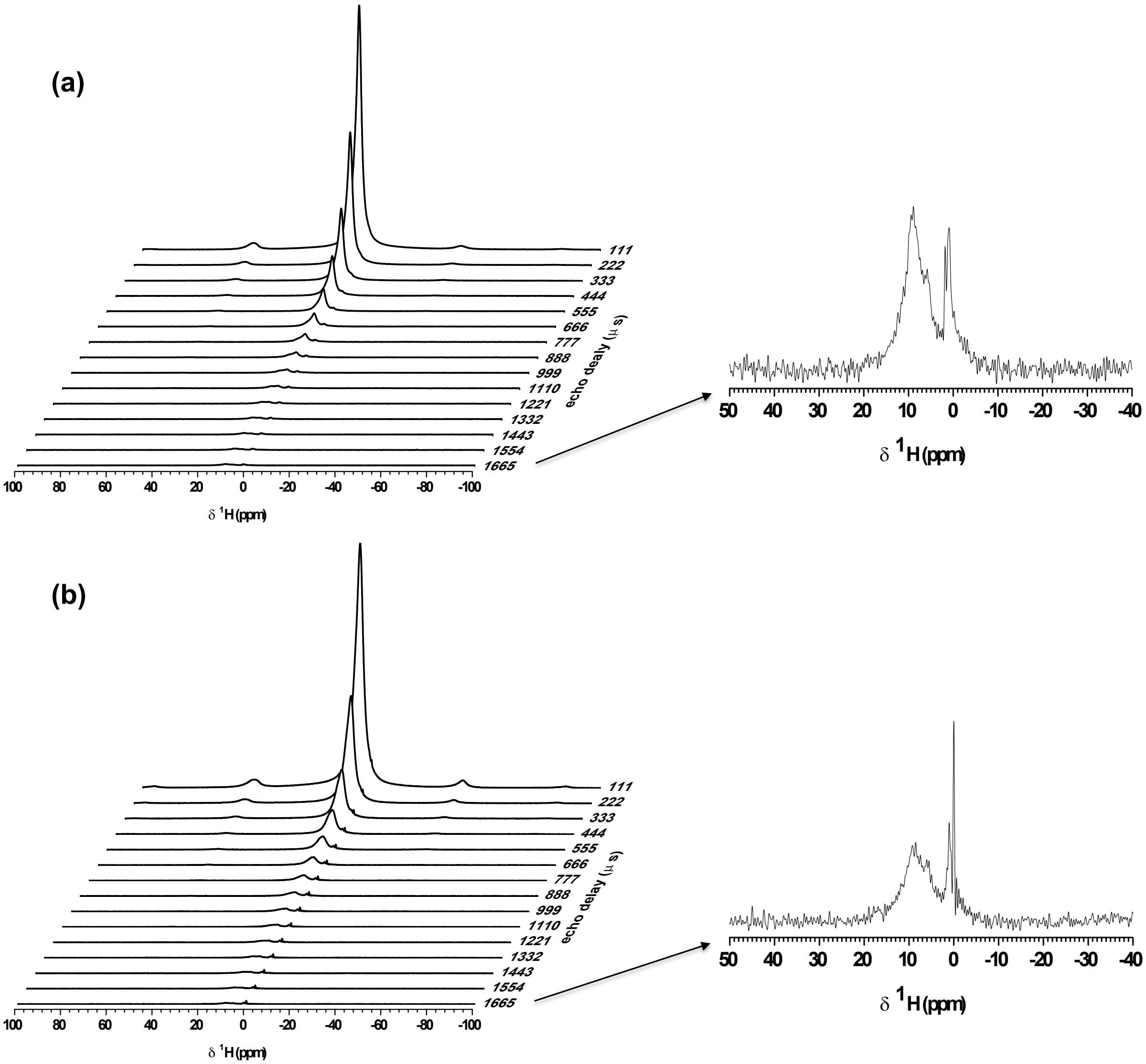


Fig. S7 ^{1}H DPMAS Hahn echo spectra of (a) CeO_2-0.1PO_x and (b) CeO_2-0.2PO_x. The spectra were obtained at 9.4 T using v_R = 18 kHz, v_{RF}(^{1}H 90°) = 96 kHz, t_{rd} = 7 s, 64 scans/delay, and echo delays indicated in the figure.

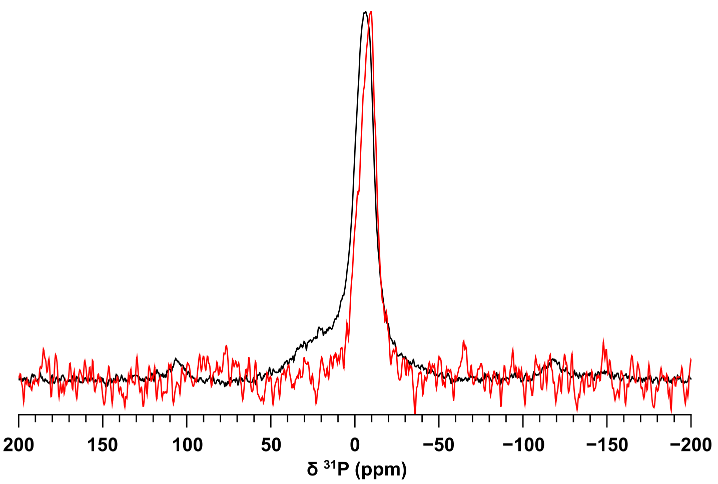


Fig. S8 Comparison between ^{31}P DPMAS (black) and ^{31}P DQ-filtered DPMAS (red) spectra of CeO$_2$-0.2PO$_x$ measured at 9.4 T. The ^{31}P DPMAS spectrum was obtained using ν_R = 18 kHz, ν_{RF}(^{31}P 90°) = 83.3 kHz, ν_{RF}(^{1}H SPINAL-64) = 100 kHz, and 128 scans with t_{rd} = 6 s. ^{31}P DQ-filtered DPMAS spectrum was obtained using ν_R = 18 kHz, ν_{RF}(^{31}P 90°) = 83.3 kHz, ν_{RF}(^{1}H SPINAL-64) = 100 kHz, and 2048 scans with t_{rd} = 5 s.

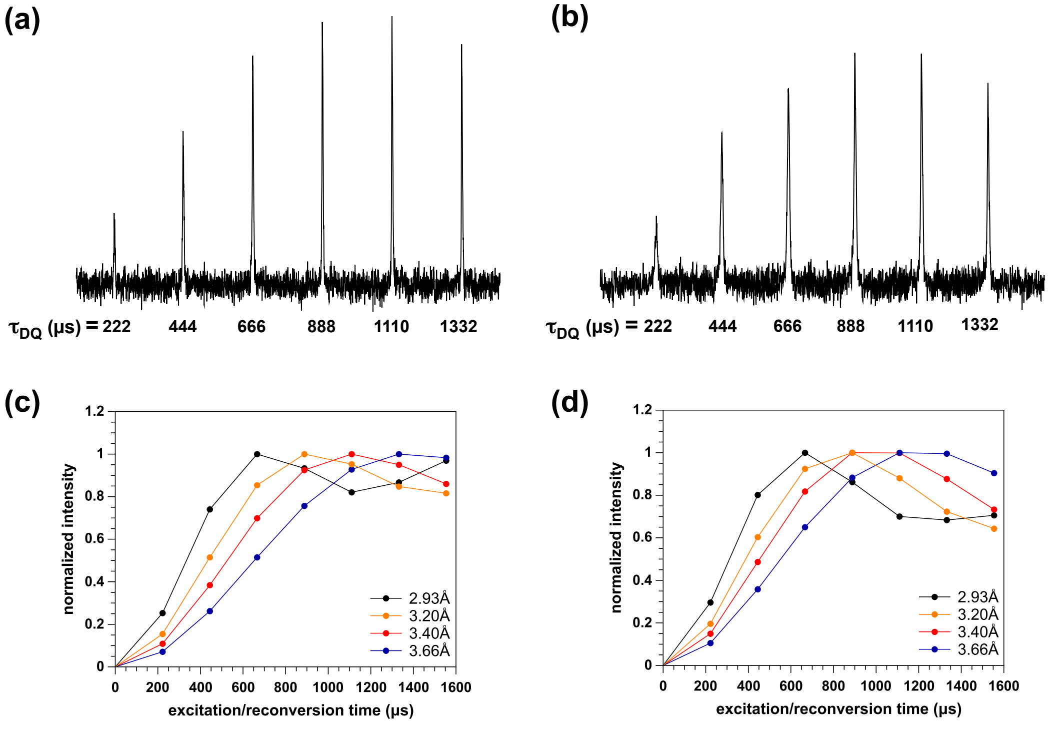


Fig. S9 Experimental DQ build-up curves measured at 9.4 T for (a) CeO$_2$-0.1PO$_x$ and (b) CeO$_2$-0.2PO$_x$, using ν_R = 18 kHz, ν_{RF}(^{31}P 90°) = 83.3 kHz, ν_{RF}(^{1}H SPINAL-64) = 100 kHz, and 2048 scans with t_{rd} = 10 s for CeO$_2$-0.1PO$_x$ and t_{rd} = 5 s for CeO$_2$-0.2PO$_x$. SIMPSON simulations of the DQ build-up curves for 2-spin model, without (c) and with (d) taking into account the effect of spin-spin relaxation (for the main ^{31}P peak in CeO$_2$-0.2PO$_x$, a T2` value of 5.6 ms was measured at ν_R = 18 kHz).

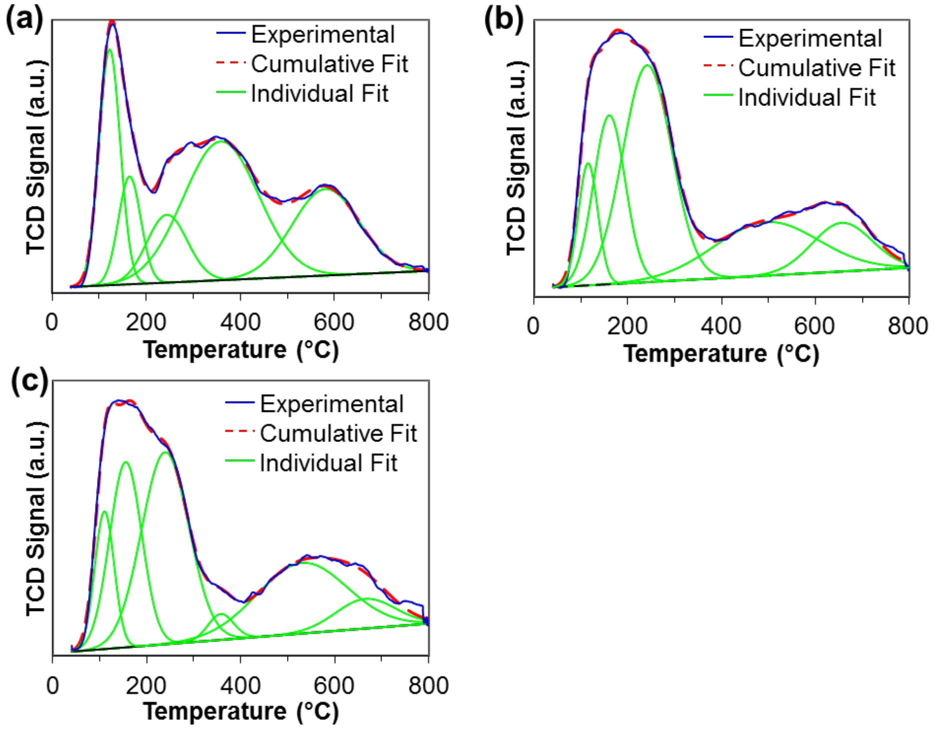


Fig. S10 Deconvoluted NH_3-TPD profiles for (a) CeO_2, (b) CeO_2-0.1PO_x, (c) CeO_2-0.2PO_x, which correspond to NH_3 integrated values of 0.61, 0.57, 0.68 mmol g^{-1}, respectively. The deconvoluted peaks with maxima around 110 °C and 160 °C (the two lowest temperature deconvoluted peaks) were common to all three materials. This indicates that the type of adsorbed NH_3 species is the same for all three materials and the low desorption temperature suggests they are multilayer and/or physisorbed species. These peaks were subtracted to determine the total number of acid sites. After correcting for physisorption, the acid site density for CeO_2 was 2.0 µmol m^{-2}. This value agrees well with prior studies using NH3 adsorption microcalorimetry (1.9 ± 0.3 µmol m^{-2}).[5-8] The similarity between the corrected CeO_2 acid site density to the literature values for ceria suggest this correction method is a good approximation to the true acid site density. The method was extended to the phosphate functionalized materials since the low temperature deconvoluted peaks are common to all materials. After correcting for physisorbed/multilayer NH3 the integrated values for CeO2, CeO2-0.1POx, and CeO_2-0.2PO_x were 0.44, 0.41, 0.44 mmol g^{-1}, respectively.

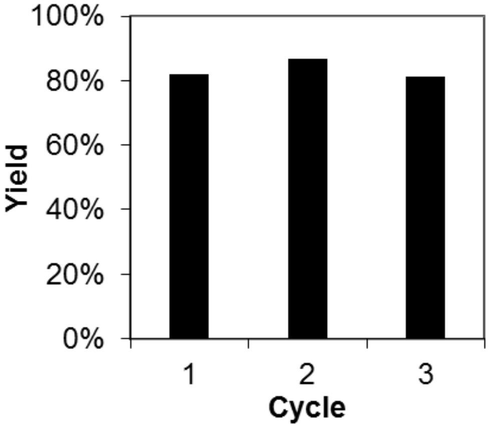


Fig. S11 Recycling experiments using CeO_2-0.2PO_x catalyst for the hydrolysis of propylene oxide. Conditions: ~40 mg catalyst, T = 60 °C, D_2O (1 mL), propylene oxide = ~2.4 mmol, t = 1 h. The catalyst:substrate ratio was maintained at 16.7 mg $mmol^{-1}$.

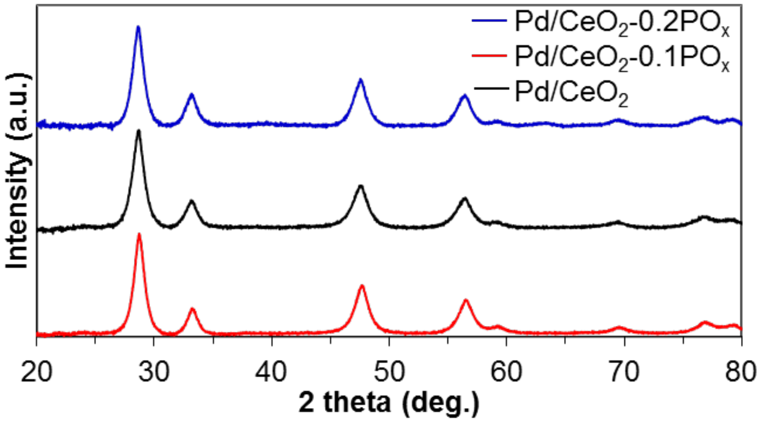


Fig. S12 PXRD patterns of the catalysts used for eugenol hydrogenolysis reaction.

Table S1 Physicochemical properties of catalysts for eugenol hydrogenolysis.

Sample	BET Surface Area (m^2 g^{-1})[a]	CeO_2 Crystallite Size (nm)[b]	Pd Dispersion (%)[c]	Pd Loading (wt. %)[d]
Pd/CeO_2	121	7	64	1.0
Pd/CeO_2-0.1PO_x	111	9	7	1.0
Pd/CeO_2-0.2PO_x	112	10	9	1.1

[a] Surface areas calculated using BET approximation. [b] Obtained from PXRD data using Scherrer equation. [c] Calculated from H_2 chemisorption data. [d] Loadings obtained from ICP analysis.

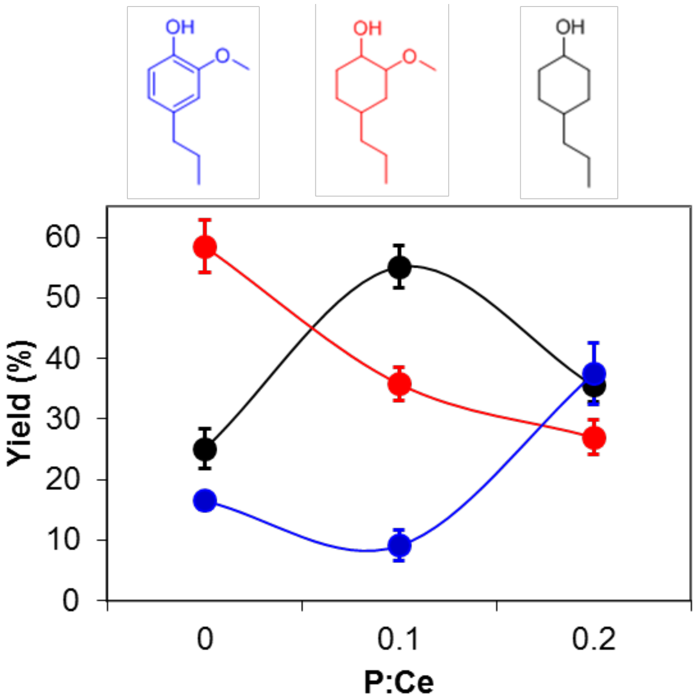
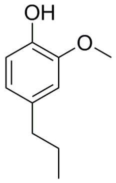
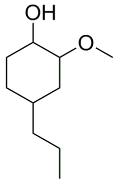
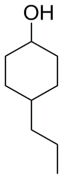


Fig. S13 Product distribution for the hydrogenolysis of eugenol over Pd/CeO_2, Pd/CeO_2-0.1PO_x, and Pd/CeO_2-0.2PO_x. The error bars represent the standard deviation from three separate reactions. Conditions: T = 100 °C, t = 4 h, P_{H2} = 10 bar, Pd:Eugenol = 5 mol. %, 25 mL H_2O.

Table S2 Product distribution for the hydrogenolysis of eugenol over the three catalysts.[a]

Reaction			
	Allyl hydrogenation	Allyl + aromatic hydrogenation	Allyl + aromatic + methoxy hydrogenation/lysis
Product			
Catalyst	 4-propyl-2-methoxyphenol Yield (%)	 4-propyl-2-methoxycyclohexanol Yield (%)	 4-propylcyclohexanol Yield (%)
Pd/CeO_2	16 ± 1	59± 4	25 ± 3
Pd/CeO_2-0.1PO_x	9.1 ± 2.5	36 ± 3	55 ± 4
Pd/CeO_2-0.2PO_x	37 ± 5	27 ± 3	36 ± 3

[a] Error bars represent the standard deviation from three separate reactions. Conditions: T = 100 °C, t = 4 h, P_{H2} = 10 bar, Pd:Eugenol = 5 mol. %, 25 mL H_2O.

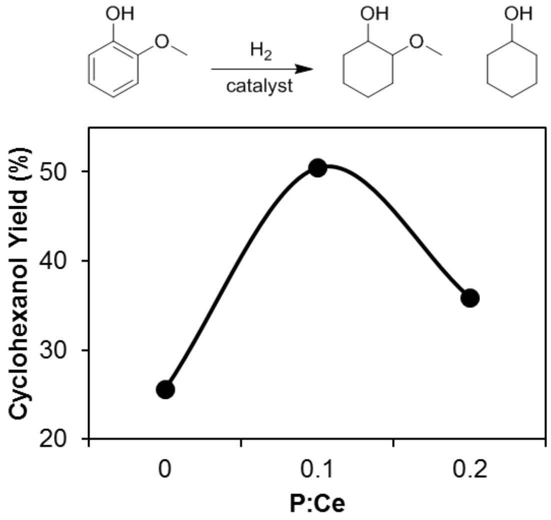
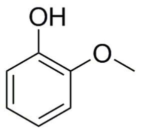
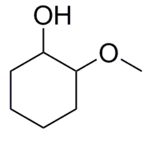
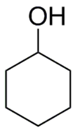


Fig. S14 Cyclohexanol yield for the hydrogenolysis of guaiacol over Pd/CeO_2, Pd/CeO_2-$0.1PO_x$, and Pd/CeO_2-$0.2PO_x$. Conditions: T = 100 °C, t = 4 h, P_{H2} = 10 bar, Pd:Guaiacol = 5 mol. %, 25 mL H_2O.

Table S3 Conversion and selectivity data for guaiacol hydrogenolysis over the three catalysts.

Reaction			
		Aromatic hydrogenation	Aromatic+ methoxy hydrogenation/lysis
	Reactant	Products	
			
Catalyst	Conversion	2-methoxycyclohexanol Yield	Cyclohexanol Yield (%)
Pd/CeO_2	84	59	25
Pd/CeO_2-$0.1PO_x$	97	46	50
Pd/CeO_2-$0.2PO_x$	89	53	36

REFERENCES

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