Supplementary Information

Support morphology-dependent catalytic activity of Co/CeO_2 catalyst for the aqueous-phase hydrogenation of phenol

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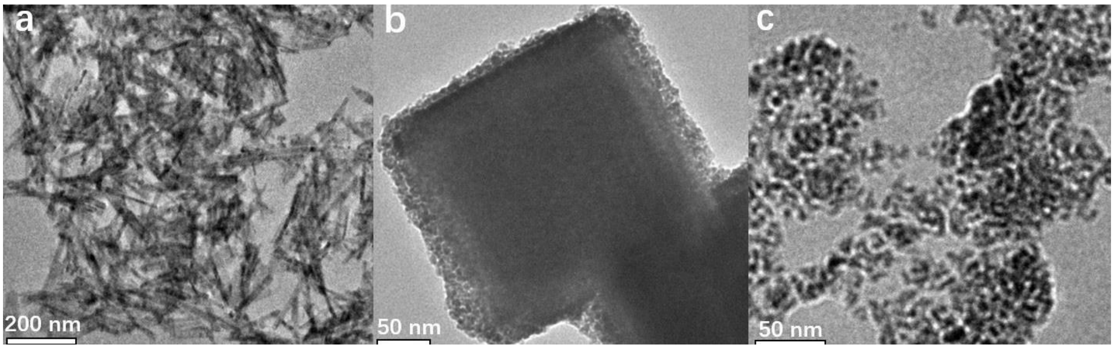


Fig. S1 TEM image of Co/CeO_2 catalysts, (a) Co/r-CeO_2, (b) Co/c-CeO_2, and (c) Co/p-CeO_2.

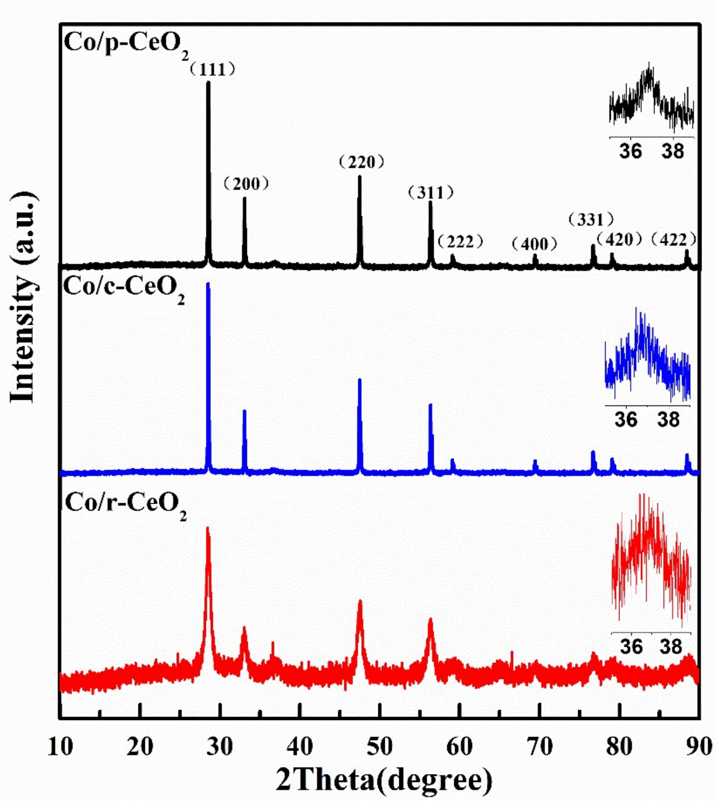


Fig. S2 XRD spectra of cobalt catalysts supported on different morphologies of CeO_2.

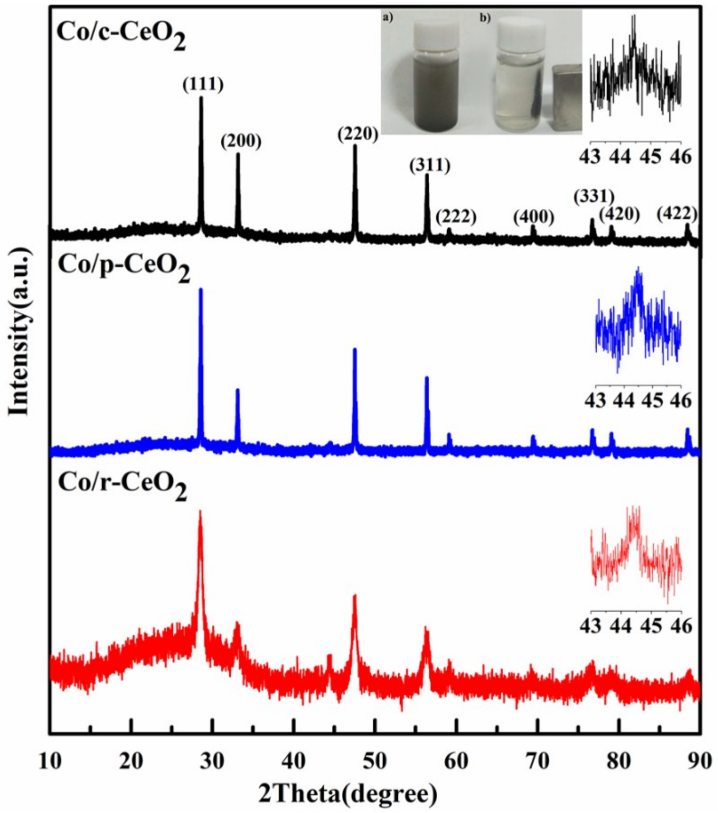


Fig. S3 XRD pattern of the catalysts after the reaction.

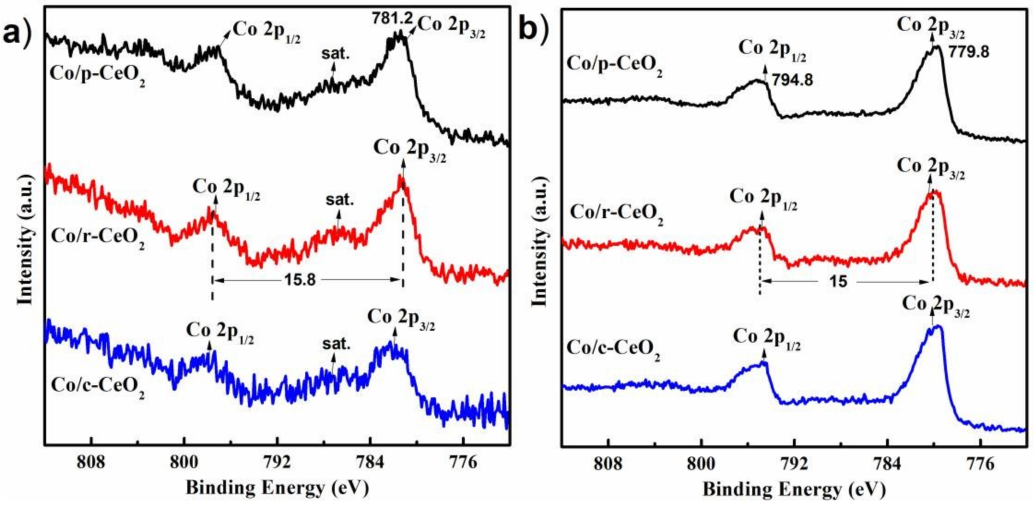
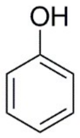
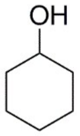
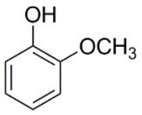
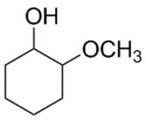
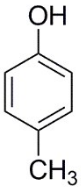


Fig. S4 High resolution XPS spectra of Co 2p before reaction (a) and after reaction (b)

Fig. S4(a) shows the high-resolution XPS spectrum of Co 2p before the reaction. The two peaks at approximately 781.2 and 797 eV can be attributed to the binding energies of the Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively, and the binding energy gap was 15.8 eV, which indicated the Co species was Co_3O_4.[1] The lower bonding energy at 779.8 eV and 794.8 eV can be assigned to metallic Co^0.[2]

Table S1. Catalytic hydrogenation of phenol derivatives using different Co catalysts.[a]

Entry	Sample	Catalyst	Temp.	Products	**Conv. (%)**	Sel. (%)
1		Co/r-CeO$_2$	150 ℃		82.5	⩾99
		r-CeO$_2$	150 °C		0	0
		c-CeO$_2$	150 °C		0	0
		p-CeO$_2$	150 °C		0	0
		Co_3O_4	150 °C		26.5	⩾99
		Co/r-CeO$_2$[b]	150 °C		81.6	⩾99
2		Co/r-CeO$_2$	150 °C		40.0	⩾99
3		Co/r-CeO$_2$	150 °C		56.0	⩾99

[a] Reaction condition: 250 mg of phenol, 100 mg of catalyst, 10 mL of deionized water and 3 MPa H_2 for 16 h. [b] Co/r-CeO_2 was reduced at 200 °C and H_2 atmosphere for 2 hours.

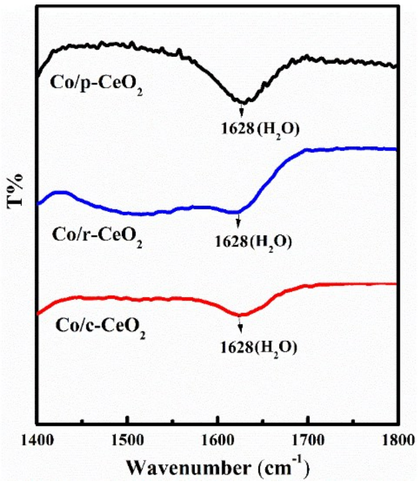


Fig. S5 The infrared fourier transform spectroscopy of Co-based catalysts.

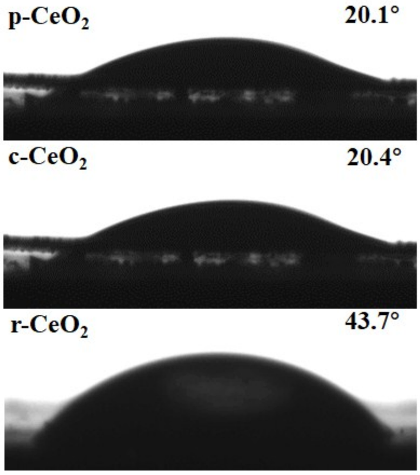


Fig. S6 Static water contact angles measurement for p-CeO_2, c-CeO_2 and r-CeO_2.

Table S2. Effect of solvents on the hydrogenation of phenol by Co/r-CeO_2 catalyst.[a]

Entry	Solvents	Conv. (%)	p^b	Sel. (%)
1	water	48.1	10.2	⩾99
2	n-hexane	86.2	0.06	⩾99
3	i-propanol	72.3	4.3	⩾99
4	ethanol	54.4	4.3	⩾99
5	THF	21.8	4.2	⩾99
6	dimethyl sulfoxide	0	7.2	0

[a] Reaction condition: phenol 200 mg, 50 mg catalyst, 20 mL solvent , 150 ^{o}C, 3 MPa H_2, 16 h. [b] Solvent polarity.

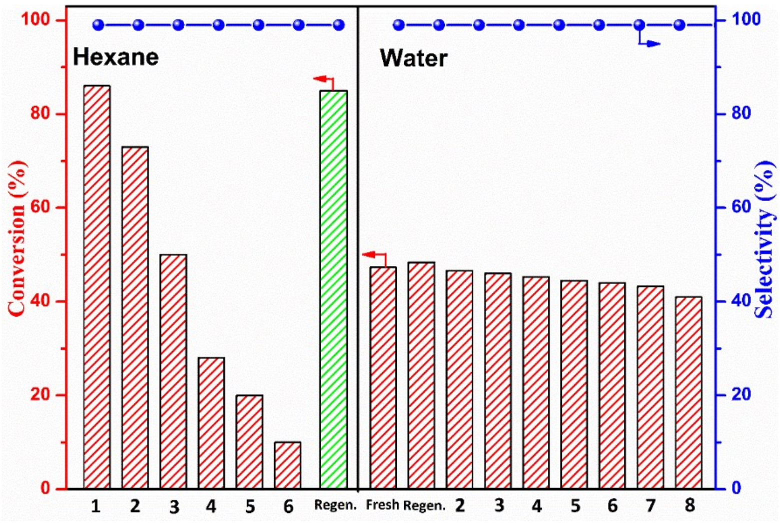


Fig. S7 Cycling experiments for the hydrogenation of phenol using Co/r-CeO_2 in hexane at T = 150 °C and in water at T = 150 °C. Reaction conditions: 8 h, 3 MPa, 200 mg of phenol, 100 mg of catalyst, 20 mL of solvent.

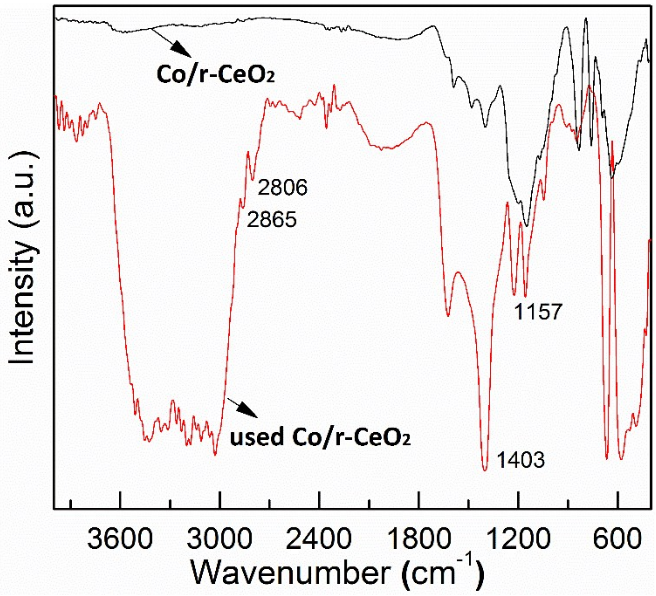


Fig. S8 The FTIR spectra of Co/r-CeO_2 and the used Co/r-CeO_2 in hexane.

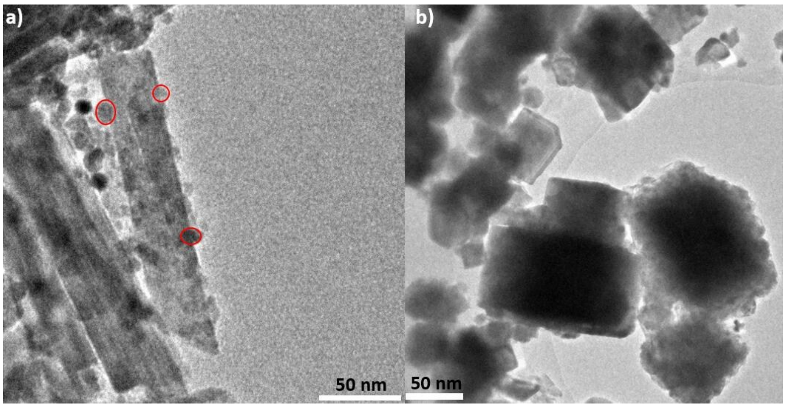


Fig. S9 The TEM images of Co/r-CeO_2 (a) and Co/c-CeO_2 catalyst after the reaction.

Table S3. The relative amount of different components.

Sample	Ce^{4+}	Ce^{3+}	Ce^{3+}/Ce^{4+}	O_C	O_V	O_L	O_V/O_L
Co/p-CeO_2[a]	74.2%	25.8%	0.35	50.7%	32.1%	17.2%	1.87
Co/r-CeO_2[a]	73.4%	26.6%	0.36	15.1%	38.5%	46.4%	0.83
Co/c-CeO_2[a]	77.0%	23.0%	0.30	54.4%	18.3%	27.3%	0.67
Co/p-CeO_2[b]	72.8%	27.2%	0.37	17.4%	35.5%	47.1%	0.75
Co/r-CeO_2[b]	66%	34%	0.52	29.6%	33.8%	36.6%	0.92
Co/c-CeO_2[b]	73.8%	26.2%	0.36	18.2%	32.1%	49.7%	0.65

[a] The catalysts before reaction; [b] the catalysts after reaction.

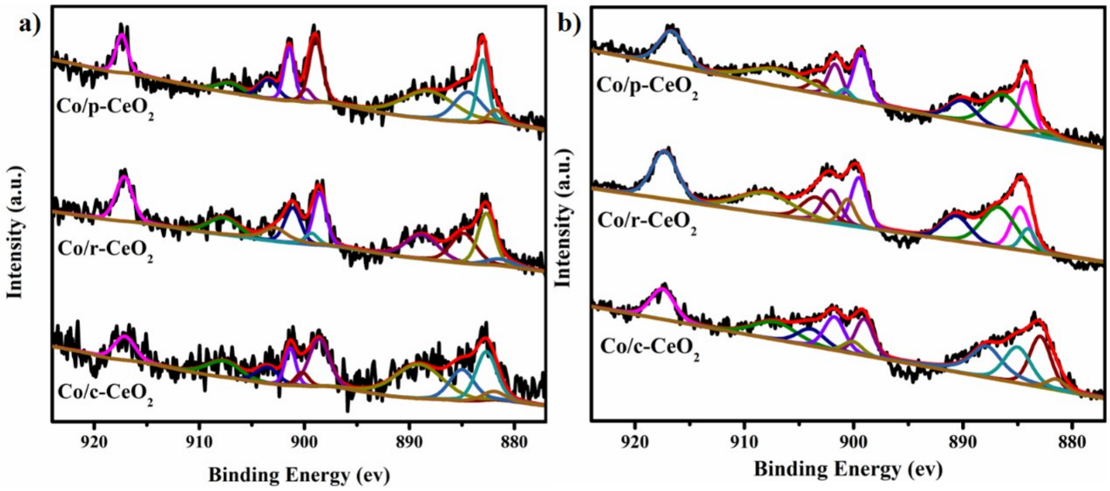


Fig. S10 High resolution XPS spectra of Ce3d before reaction (a) and after reaction (b).

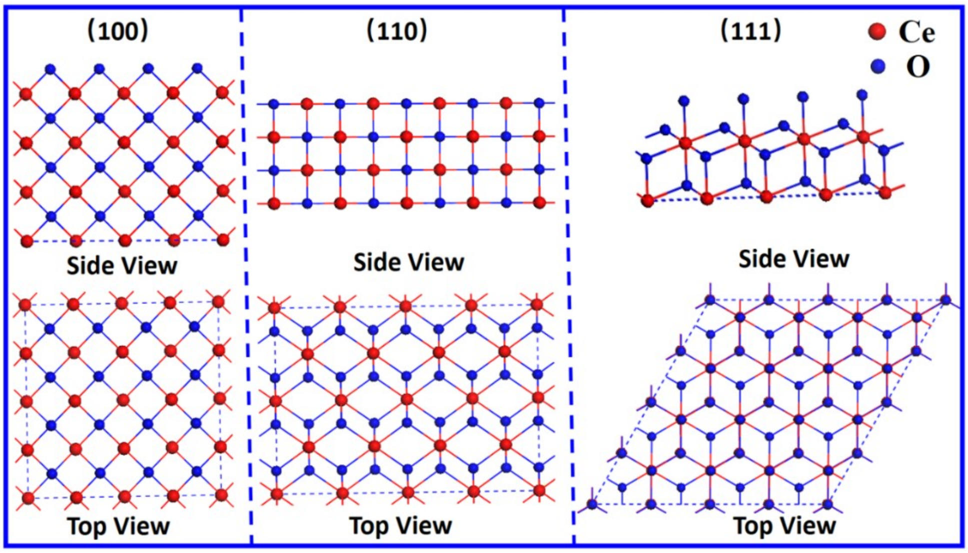


Fig. S11 The ideal CeO_2 structure seen from (100), (110) and (111) directions.

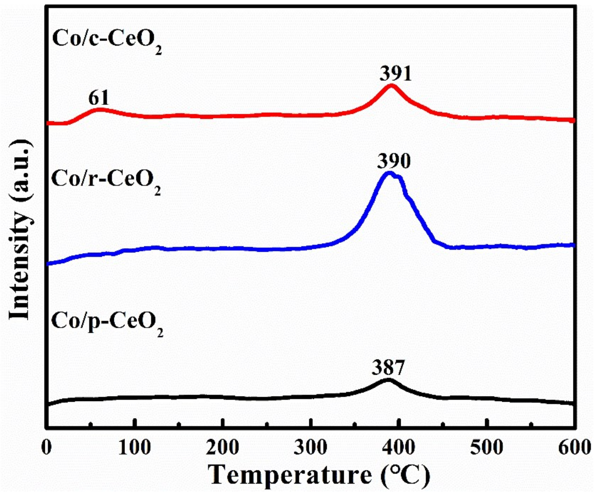


Fig. S12 The O_2-TPO images of Co/CeO_2 with different morphological supports.

Reference

1. L. Liu, J. Ding, G. V. Sarrigani, P. Fitzgerald, Z. M. Aljunid Merican, J.-W. Lim, H.-H. Tseng, F. Xie, B. Zhang and D. K. Wang, Applied Catalysis B: Environmental, 2020, 262, 118246.

2. Y. Zhan, Y. Liu, X. Peng, W. Zhao, Y. Zhang, X. Wang, C.-t. Au and L. Jiang, Catalysis Science & Technology, 2019, 9, 4928-4937.