Electronic Supplementary Information (ESI) for:

Tailoring the Morphology of Co-doped MoS$_2$ for Enhanced

Hydrodeoxygenation Performance of *p*-cresol

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Experimental Section

Materials

All reagents were of analytical grade and used without further purification. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), Ammonium molybdate (VI) tetrahydrate (($NH_4)_6Mo_7O_{24} \cdot 4H_2O$), $N_2H_4 \cdot H_2O$ (85 wt% solution in water), thioacetamide (CH_3CSNH_2, TAA) and absolute ethanol were obtain from Sinopharm Chemical Reagent Co., Ltd. Deionized water (DI) was prepared using an OPK apparatus (Shanghai Lakecore, One instrument type short for "OPK" in that company).

Synthesis method

All Co-doped MoS_2 nanostrutures were synthesized using MoO_3 nanobelt as precursor and thioacetamide as sulfur sources. MoO_3 nanobelt was fabricated via a simple hydrothermal route. Briefly, 1.0 g ($NH_4)_6Mo_7O_{24} \cdot 4H_2O$ was dissolved in 33 mL H_2O under constant stirring. Then, after added 6 mL of HNO_3 (65%), the aqueous solution was transferred to a 50 mL Teflon-lined stainless steel autoclave and maintained at 180 °C for 36 h. The resultant white products were collected via centrifugation and washed several times with distilled water and absolute ethanol, and then dried in vacuum at 60 °C for 12 h.

For synthesis of Co-doped MoS_2 nanorods, 0.12 g CH_3CSNH_2 was dissolved in 30 mL ethanol solution which contains 50 mg of the MoO_3 nanobelts and 47 mg $Co(NO_3)_2 \cdot 6H_2O$. Next, the mixture was transferred into a Teflon-lined autoclave and heated at 180 °C for 36 h. This protocol was repeated for the synthesis of Co-doped MoS_2 nanotubes with introducing 0.4 g urea in the precursor solution. As for Co-doped MoS_2 nanoparticles, the same Co and Mo precursors were dissolved in 30 mL ethanol/hydrazine hydrate mixed solution (2:1 v/v) under vigorous stirring to form a homogeneous solution. After adding 0.12 g CH_3CSNH_2, the obtained solution was maintained at 180 °C as described above. As a control, the Co-doped MoS_2 nanoflowers were fabricated in a similar procedure for nanoparticles except using H_2O instead of ethanol.

Catalyst Characterization

X-ray diffraction (XRD) measurements were performed with a D/MAX 2500/PC powder diffractometer (Rigaku) using a Cu Kα radiation source (λ = 0.15406 nm) operated at 40 kV and 100 mA. Nitrogen adsorption measurement was performed on a Micromeritics Tristar 3020 adsorption automatic instrument at liquid nitrogen temperature. SEM images were obtained using a field emission scanning electron microscopy (FESEM) instrument (Zeiss SIGMA, Germany). Transmission electron microscopy (TEM) experiments were performed using JEM-2100 operated at the accelerating voltage of 100 kV. For elemental analyses, X-ray fluorescence spectroscopy (XRF) tests were conducted on a S8 TIGER (BRUKER) operated at 60 kV and 50 mA to measure the Co, Mo and S contents. X-ray photoelectron spectroscopy (XPS) was operated using PHI Quantum-2000 instrument under ultrahigh vacuum with a pressure close to 2×10^{-9} mbar. The C 1s peak at 284.6 eV was used as an internal standard to compensate for sample charging, and the corresponding spectra were fitted by Gaussian-Lorentzian curves using XPSPEAK software.

Catalyst Evaluation

HDO of *p*-cresol was carried out in a 100 mL sealed autoclave. In a typical test, 20 mg of the as-prepared catalyst, 560 mg of *p*-cresol and 560 mg of dodecane (internal standard) were dispersed in 20 ml decalin and then transferred to the reactor. Air in the autoclave was evacuated by pressurization–depressurization cycles with nitrogen and subsequently with hydrogen. After heated to the chosen temperature (260-300 °C), the autoclave was pressured to 4 MPa. A small volume of liquid sample was collected at regular time intervals and then analyzed

by gas chromatography (FID detector and a HP-5 capillary column). The rate of the HDO of 4-methylphenol was calculated by assuming a pseudo-first-order reaction as below,

$$\ln(1-conv.)=-kt \tag{1}$$

where conv. is the conversion of p-cresol, k is the pseudo-first-order rate constant (h^{-1}) and t is the reaction time (h). All rates are estimated at a low conversion (<50%). All the experimental data were repeated three times to ensure the repeatability and the accuracy of the measurement was estimated to below 5%.

Supplementary Figures
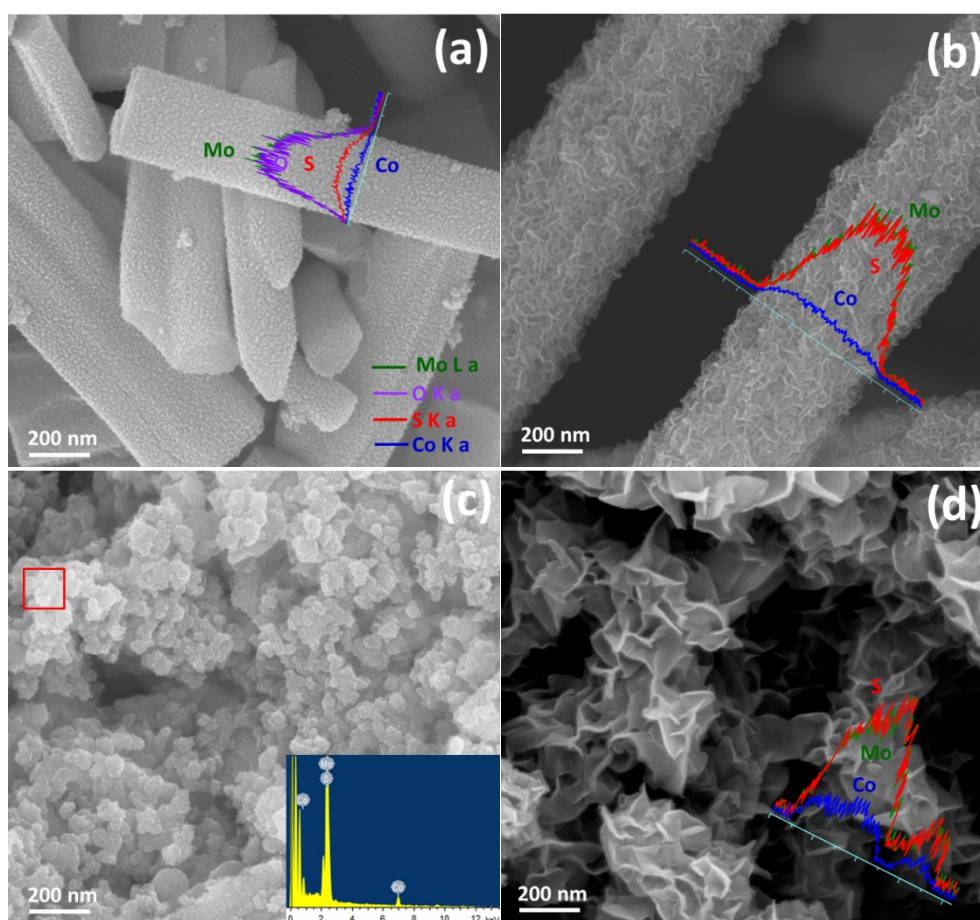
Figure S1 SEM images (line-scan elemental distributions spectrum inset) of the Co-doped MoS$_2$ nanostructures: (a, b) nanorods; (c, d) nanotubes; (e, f) nanoparticles; (g, h) nanoflowers. Green, red, blue and purple lines represent Mo, S, Co and O, respectively.
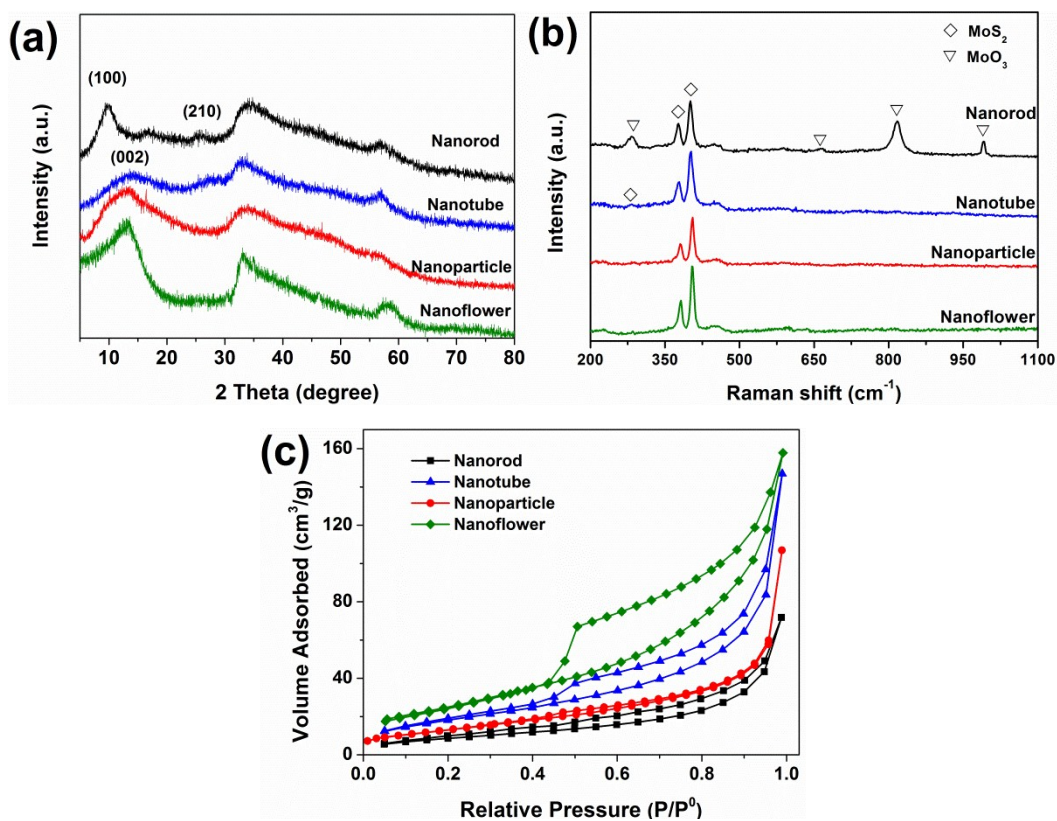
Figure S2 (a) X-ray diffraction patterns, (b) Raman spectra and (c) nitrogen adsorption-desorption isotherms obtained on the catalyst of Nanorod (black curve), nanotube (blue curve), nanoparticle (red curve) and nanoflower (green curve).
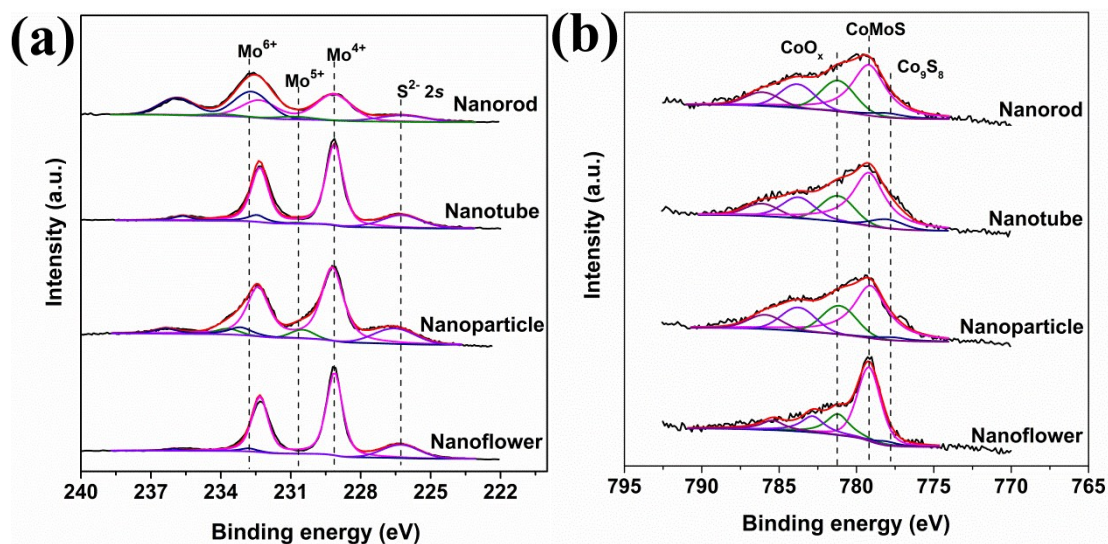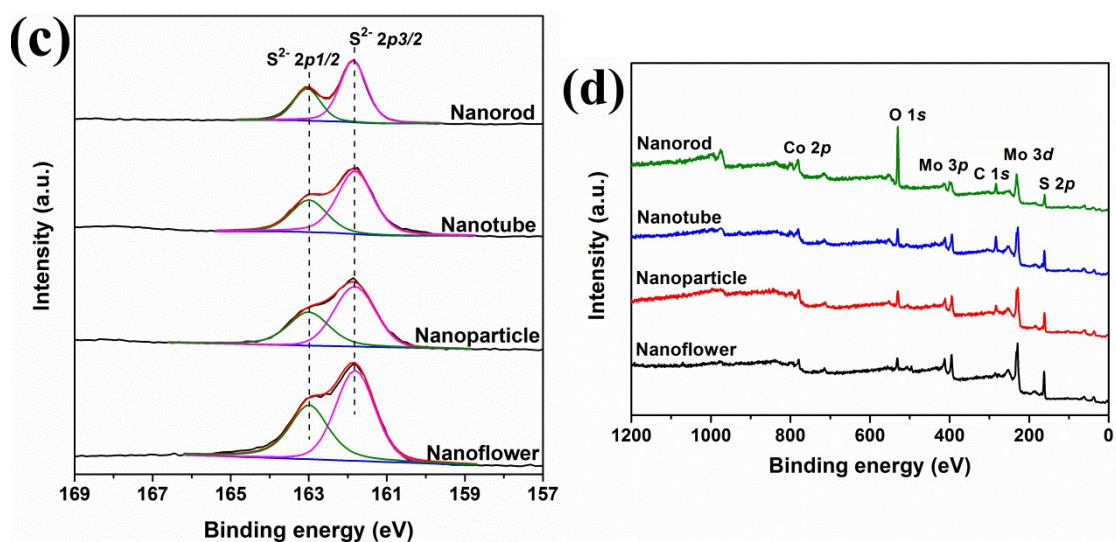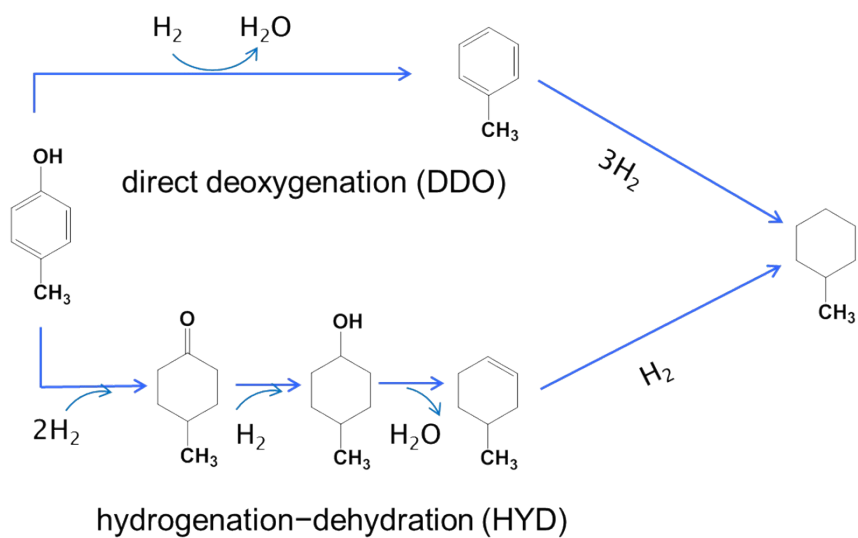
Figure S3 High-resolution XPS spectra for (a) Mo 3*d*, (b) Co 2*p*$_{3/2}$, (c) S 2*p* and (d) XPS survey spectra of the Co-doped MoS$_2$ nanocatalysts with different species obtained by decomposition.
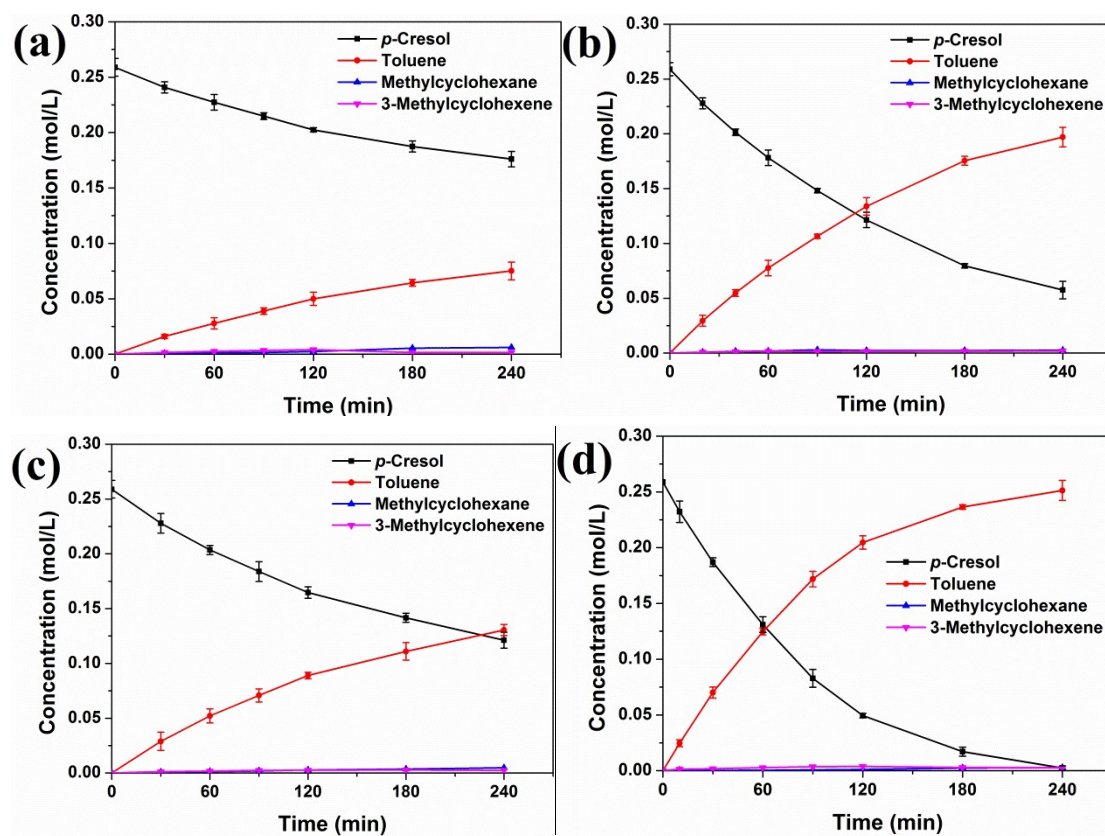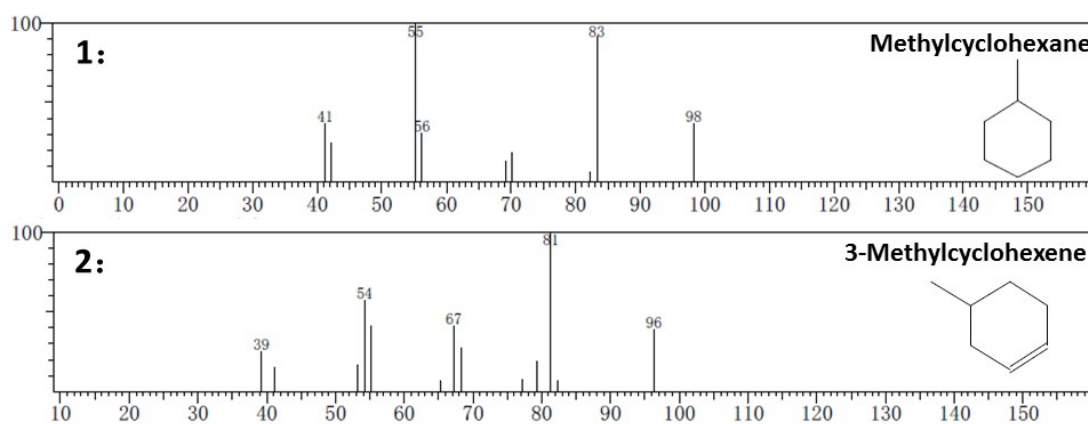

Figure S4 Changes of *p*-cresol and products concentration versus reaction time on the catalyst of (a) nanorods; (b) nanotubes; (c) nanoparticles; (d) nanoflowers at 300 °C.
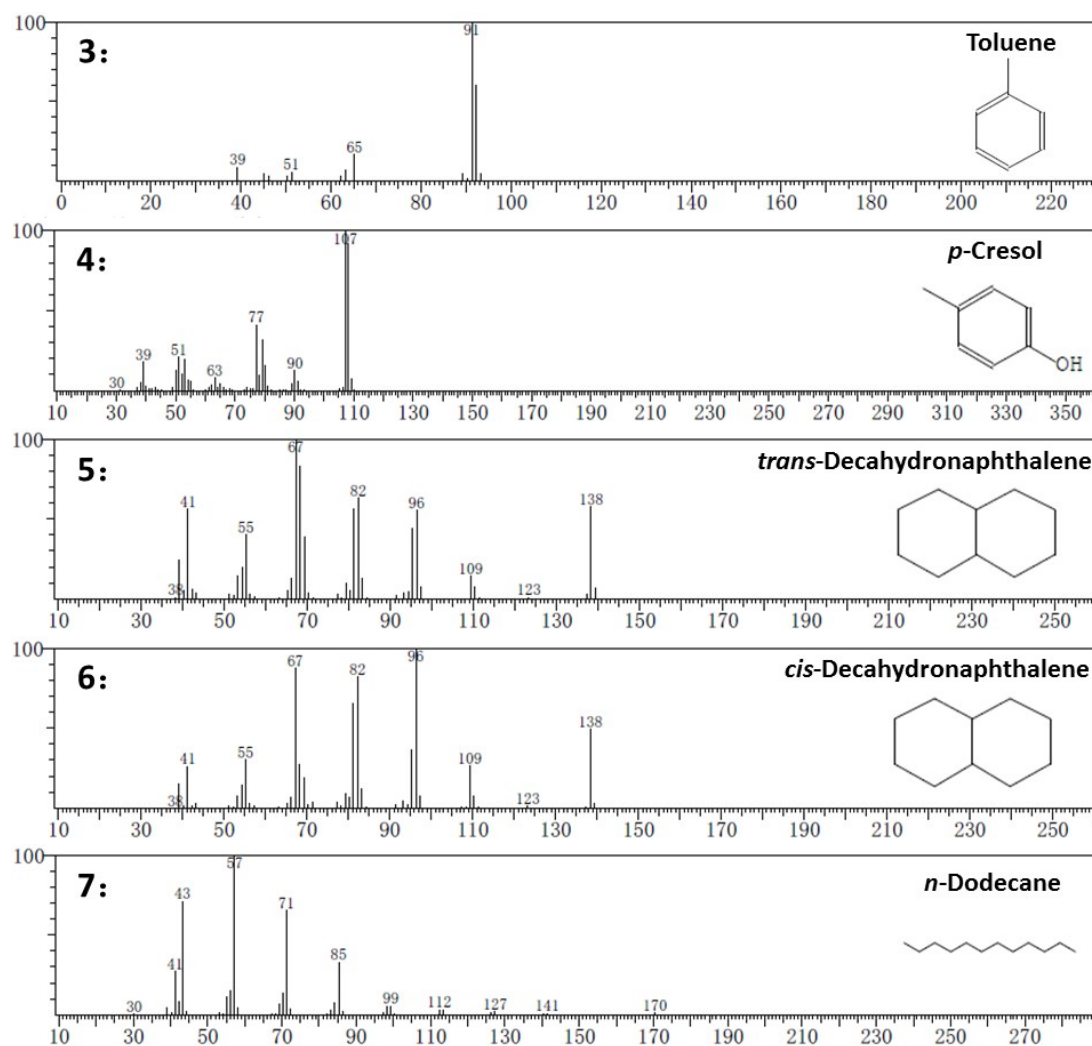
Figure S5 Reaction scheme of the conversion of *p*-cresol on Co-MoS$_2$ catalysts.
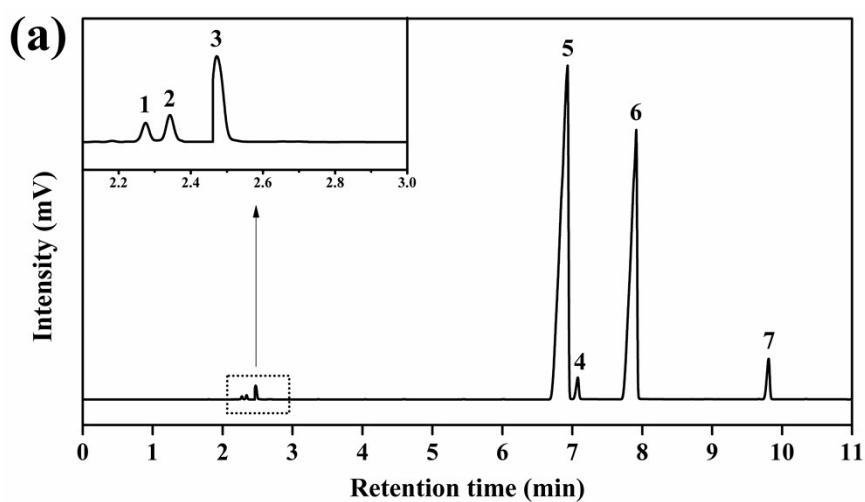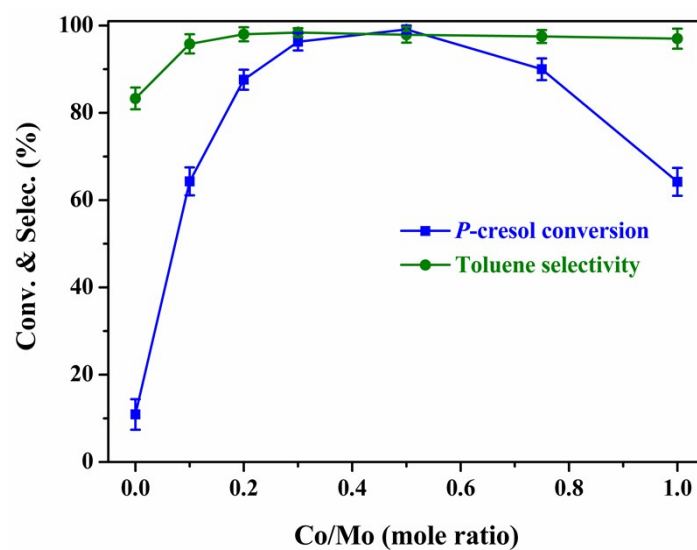


(b) Corresponding mass spectrum:

Figure S6 GC-MS spectrum of hydrodeoxygenation of *p*-cresol on Co-MoS$_2$ nanorods. Reaction conditions: 20 mg of catalyst, 560 mg *p*-cresol, 560 mg dodecane, 20 mL decalin, 4 MPa H$_2$, 300 °C, 4 h. The hydrodeoxygenated products of *p*-cresol were identified as: 1: methylcyclohexane; 2: 3-methylcyclohexene; 3: toluene.

Figure S7 Hydrodeoxygenation of *p*-cresol on Co-MoS$_2$ nanoflowers with different Co/Mo molar ratio at 300 °C for 4h.
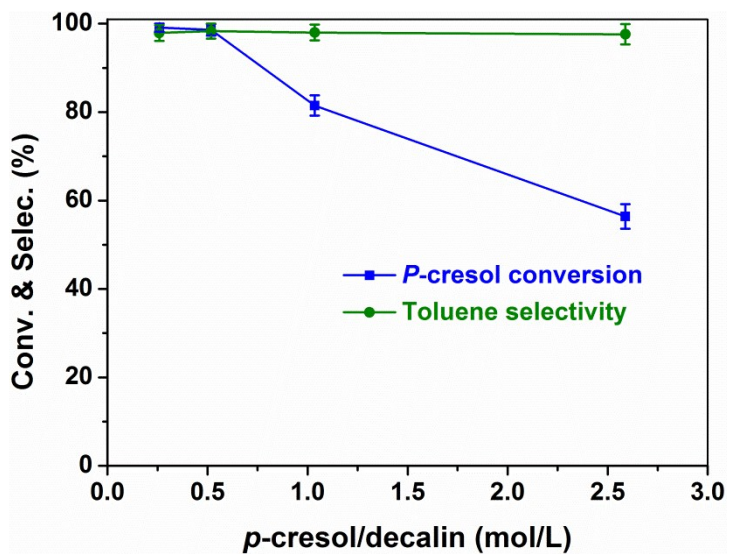
Figure S8 Effect of precursor concentration on the hydrodeoxygenation reaction of *p*-cresol to produce toluene at 300 °C for 4 h.
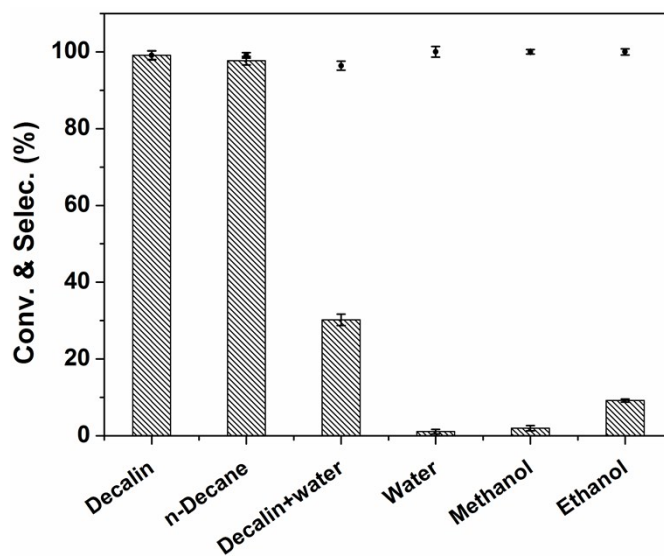
Figure S9 HDO performance of Co-MoS$_2$ nanoflowers in various solvent at 300 °C for 4h.

Supplementary Tables

Table S1 Surface area and pore texture of the catalysts.

Sample	S_{BET} (m²·g⁻¹)	V_{Pore} (cm³·g⁻¹)	d_{Pore} (nm)
Nanorod	32.8	0.10	13.5
Nanotube	68.1	0.22	13.3
Nanoparticle	49.6	0.16	13.3
Nanoflower	93.6	0.24	10.2

Table S2 HDO of p-cresol on MoO_3, MoS_2 and Co-MoS_2 nanocatalysts at 300 °C for 4 h[a].

Catalyst	MoO_3 nanorod	MoS_2 nanoparticle	Co-MoS_2 nanorod
Conversion (%)	16.0	10.9	33.1
Products selectivity (%)			
Toluene	77.2	83.3	90.7
3-Methylcyclohexene	12.4	8.3	4.4
Methylcyclohexane	10.4	8.4	4.9
HYD/DDO[b]	0.29	0.20	0.10

[a] Reaction conditions: 560 mg p-cresol; 20 mL decalin; 560 mg of dodecane (internal standard); 20 mg catalyst. The relatively errors for these experiments were less than 5 %.

[b] HYD/DDO=selectivity to (methylcyclohexane + 3-methylcyclohexene) / selectivity to toluene.

Table S3 HDO of p-cresol on Co-MoS_2 nanocatalysts at different temperature for 4 h[a].

	Nanorod		Nanoparticle		Nanotube		Nanoflower		
Temperature	280	300	280	300	280	300	260	280	300
Conversion (%)	11.0	33.1	28.0	53.2	38.5	78.3	62.2	81.6	99.8
Products selectivity (%)									
Toluene	89.7	90.7	93.4	94.7	96.3	97.8	96.1	97.6	97.9
3-methylcyclohexene	1.9	4.4	3.4	1.0	1.1	0.1	2.0	0.3	0
methylcyclohexane	8.4	4.9	3.2	4.3	2.6	2.1	1.9	2.1	2.1
HYD/DDO[b]	0.11	0.10	0.07	0.06	0.04	0.02	0.04	0.02	0.02

[a] Reaction conditions: 560 mg p-cresol; 20 mL decalin; 560 mg of dodecane (internal standard); 20 mg catalyst. The relatively errors for these experiments were less than 5 %.

[b] HYD/DDO=selectivity to (methylcyclohexane + 3-methylcyclohexene) / selectivity to toluene.