

## Supporting Information for

### Highly selective catalytic conversion of phenols to aromatic hydrocarbons on CoS<sub>2</sub>/MoS<sub>2</sub> synthesized by two steps hydrothermal method

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#### Experimental Details

**Preparation of catalysts** CoS<sub>2</sub>/MoS<sub>2</sub> catalysts were synthesized in a 300 mL batch reactor by two step hydrothermal method. All solvents and reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. in high purity ( $\geq 99\%$ ) and used without further purification. In a typical experiment for CoS<sub>2</sub>/MoS<sub>2</sub>, ammonium heptamolybdate (2.3 g) and thiourea (3.0 g) were dissolved in 150 mL ultra-pure water and its pH value was adjusted to 0.9 by hydrochloric acid. This mixed solution was added into a reactor, and sealed and heated to 200 °C for 12 h. Then the reactor was cooled and opened and added 30 mL cobalt nitrate solution, and sealed and heated to 200 °C for 12 h again. The composition of the samples was adjusted by changing the initial Co/Mo molar ratio. After reaction, the resultant catalysts were separated and washed with absolute ethanol several times to remove the residual water and water-soluble impurities. Finally, the resulting product was dried under vacuum at 50 °C for 8 hours and stored in nitrogen environment. The prepared catalysts were denoted as Co-Mo-X, where X represented the molar ratio of Co/Mo. For comparison, MoS<sub>2</sub> without adding Co, denoted as Mo-S, was also prepared by the hydrothermal method at 200 °C for 12 h.

**Catalyst characterization** X-ray diffraction (XRD) measurements were carried on a D/max2550 18KW Rotating anode X-Ray Diffractometer with monochromatic Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) radiation at voltage and current of 40 kV and 300 mA. The  $2\theta$  was scanned over the range of 10-85° at a rate of 10°/min. The specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at -196 °C. The samples were dehydrated at 300 °C using vacuum degassing for 12 h before experiments. The scanning electronic microscopy (SEM) images of the catalysts were obtained on a JEOL JSM-6360 electron microscopy. The morphologies of catalysts were determined by transmission electron microscopy

(TEM) on a JEOL JEM-2100 transmission electron microscope with a lattice resolution of 0.19 nm and an accelerating voltage of 200 kV. The samples for the TEM study were prepared by the ultrasonic dispersing in ethanol and consequent deposition of the suspension upon a “holey” carbon film supported on a copper grid. The samples were kept under inert atmosphere until the last process. The surface composition and surface electronic state were analyzed by X-ray Photoelectron Spectroscopy (XPS) using Kratos Axis Ultra DLD instrument at 160eV pass energy. Al K $\alpha$  radiation was used to excited photoelectrons. The binding energy value of each element was corrected using C<sub>1s</sub> = 284.6 eV as a reference. The XP spectrum of each element in the prepared catalysts was deconvoluted using a convolution of Lorentzian–Gaussian function under a continuous background of secondary electrons (Shirley method).

**Catalyst activity measurement** The HDO activity tests were carried out in a 100-mL sealed autoclave. The prepared catalyst without any further treatment (0.03 g), *p*-cresol (4.8 g) and dodecane (28.3 g) were placed into the autoclave. Air in the autoclave was evacuated by pressurization-depressurization cycles with nitrogen and subsequently with hydrogen. The system was heated to 250 °C, then pressurized with hydrogen to 4.0 MPa and adjusted the stirring speed to 900 rpm. During the reaction, liquid samples were withdrawn from the reactor and analysed by Agilent 6890/5973N GC-MS and 7890 gas chromatography using a flame ionization detector with a 30 m AT-5 capillary column. To separate the reaction products, the temperature in the GC oven was heated from 40 °C to 85 °C with the ramp of 20 °C/min, held at 85 °C for 4.0 min, then heated to 200 °C at a rate of 20 °C/min and kept at 200 °C for 5.0 min. Duplicate or triplicate experiments were performed and the average of these tests was reported here. The errors for conversion values were typically within plus/minus 5.0 mol%. The conversion, selectivity and deoxygenation degree for each experiment were calculated as follows:

$$\text{Conversion (mol\%)} = \left(1 - \frac{\text{moles of residual reactant}}{\text{moles of initial reactant}}\right) \times 100 \%$$

$$\text{Selectivity (A, mol\%)} = \frac{\text{C atoms in each product}}{\text{total C atoms in the products}} \times 100 \%$$

$$\begin{aligned} &\text{Deoxygenation degree (D. D., wt\%)} \\ &= \left(1 - \frac{\text{oxygen content in the final organic compounds}}{\text{total oxygen content in the initial material}}\right) \times 100 \% \end{aligned}$$

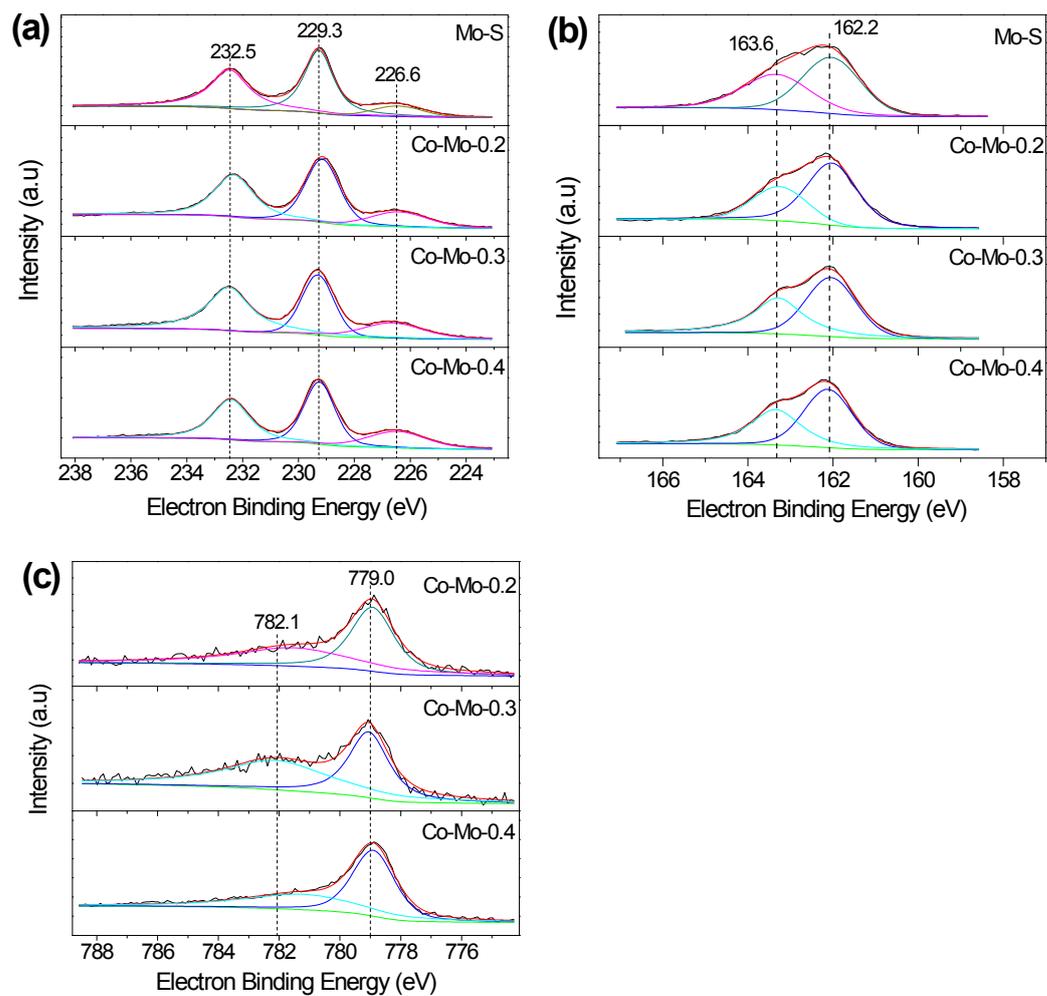


Fig. S1 XPS spectrums of (a) Mo 3d, (b) S 2p and (c) Ni 2p levels of Mo-S, Co-Mo-0.2, Co-Mo-0.3 and Co-Mo-0.4 catalysts

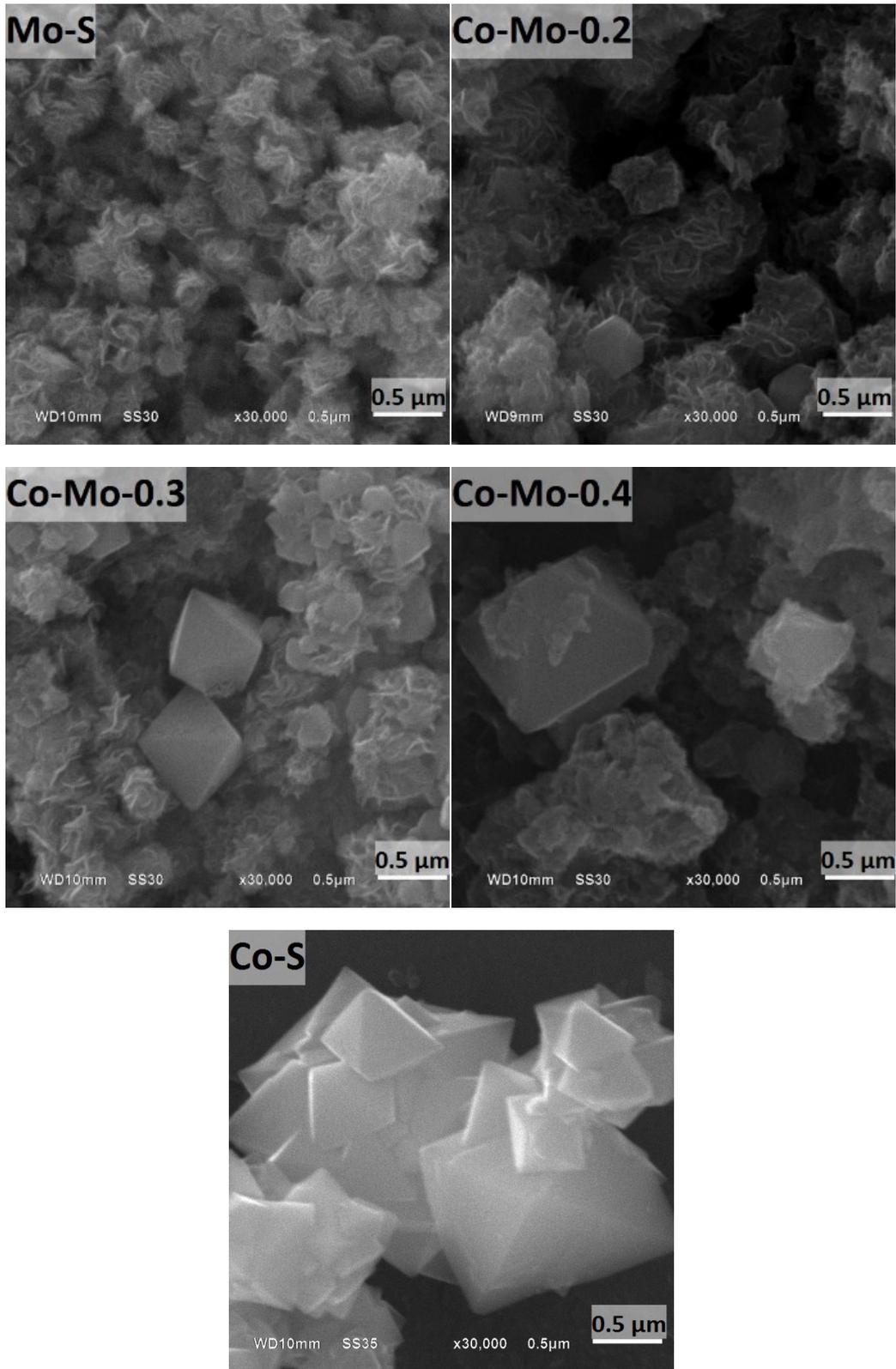


Fig. S2 SEM images of Mo-S, CoS<sub>2</sub>/MoS<sub>2</sub> and CoS<sub>2</sub>

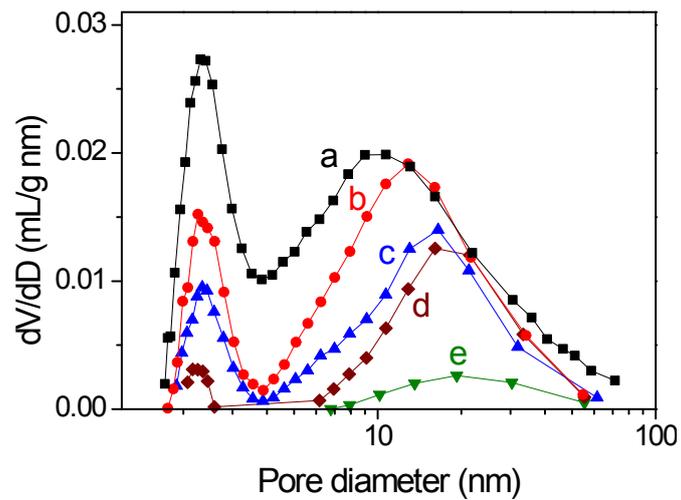


Fig. S3 Pore distribution of (a) Mo-S, (b) Co-Mo-0.1, (c) Co-Mo-0.2, (d) Co-Mo-0.3 and (e) Co-Mo-0.4 catalysts

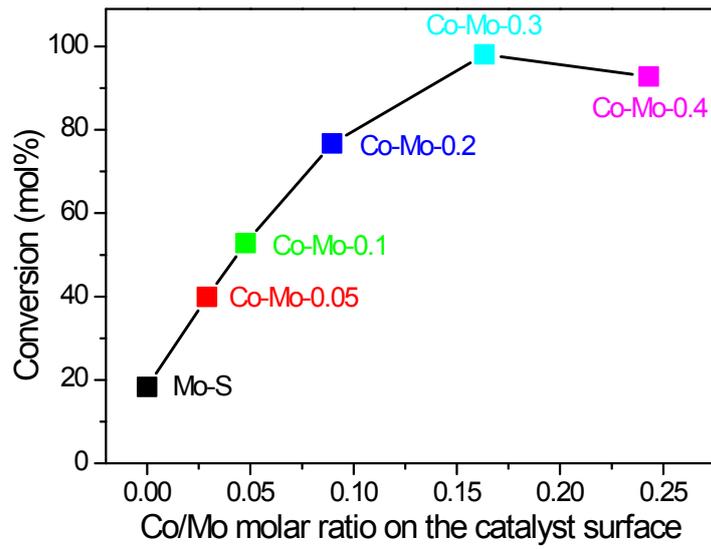


Fig. S4 The change of *p*-cresol conversion versus Co/Mo molar ratio on the catalyst surface

**Table S1** Comparison of the activity of different catalysts in the HDO of phenols

No	Catalyst	Reactant	Reactant/Catalyst weight ration	T (°C)	P (MPa)	T (h)	Con. (%)	Aromatics selectivity	Ref.
0	CoS <sub>2</sub> /MoS <sub>2</sub>	<i>p</i> -cresol	160	250	4.0	1	98	99	This work
1	Ni-Mo-S	<i>p</i> -cresol	13.9	300	3.0	5	77	96	[1]
2	MoS <sub>2</sub>	<i>p</i> -cresol	22.5	300	4.0	3	91	93	[2]
3	Co-Mo-S	<i>p</i> -cresol	50	275	4.0	4	100	92	[3]
4	Ni-Mo-W-S	<i>p</i> -cresol	13.9	300	3.0	5	98	87	[4]
5	Mo-P	<i>p</i> -cresol	9.29	350	4.4	5	58	60	[5]
6	Ni <sub>2</sub> P	<i>p</i> -cresol	9.29	350	4.4	5	63	55	[6]
7	Ni <sub>2</sub> P	<i>p</i> -cresol	90	350	4.0	10	85	34	[7]
8	MoS <sub>2</sub>	<i>p</i> -cresol	14.4	350	2.8	7	75	36	[8]
9	Ni-Mo-W-S	<i>p</i> -cresol	22.5	300	4.0	6	98	30	[9]
10	Ru/TiO <sub>2</sub>	phenol	50	300	4.5	1	30	85	[10]
11	CoMoS <sub>2</sub>	phenol	4	350	2.8	1	98	83	[11]
12	Ni-Mo-S	phenol	4	350	2.8	1	96	30	[12]
13	MoS <sub>2</sub>	phenol	10	300	3.0	2	55	26	[13]
14	Ni	phenol	3.1	300	4	2	100	3	[14]
15	Pt-Re/ZrO <sub>2</sub>	Propylphenol	6.9	300	2	1	67	85	[15]

16	Re-Ni/ZrO <sub>2</sub>	Propylphenol	3.4	300	3	1	96	36	[16]
17	Ni/Al <sub>2</sub> O <sub>3</sub> -HZSM-5	Propylphenol	1.5	200	5.0	0.5	100	0	[17]
18	Ru-WO <sub>x</sub> /SiAl	butylpheno	1.25	270	2.0	2	88	82	[18]
19	Pd/Fe <sub>2</sub> O <sub>3</sub>	<i>m</i> -cresol	--	300	--	--	--	92	[19]
20	Pt/ $\gamma$ -Al <sub>2</sub> O <sub>3</sub>	<i>m</i> -cresol	--	300	1	--	--	86	[20]
21	MoO <sub>3</sub> /ZrO <sub>2</sub>	<i>m</i> -cresol	--	315	1.0	--	78	77	[21]
22	Pt/Na-B	<i>m</i> -cresol	--	300	--	--	--	65	[22]
23	Ni-Fe	<i>m</i> -cresol	--	300	--	--	--	60	[23]
24	Ga/HBEA	<i>m</i> -cresol	--	450	1	--	--	52	[24]
25	Ru/SiO <sub>2</sub>	<i>m</i> -cresol	--	300	--	--	5	39	[25]
26	CoMo/-Al <sub>2</sub> O <sub>3</sub>	2-ethylphenol	--	340	7		24	18	[26]

**Table S2** HDS of benzothiophene on Mo-S and CoS<sub>2</sub>/MoS<sub>2</sub> catalysts at 300 °C for 3 h

Catalyst	Mo-S	Co-Mo-0.1	Co-Mo-0.2	Co-Mo-0.3	Co-Mo-0.5
Conversion (mol %)	73	94	98	99	88
Products selectivity (mol %)					
Dihydrobenzothiophene	68	6	0	2	11
2-Ethylbenzenethiol	0	0	0	0	2
Ethylbenzene	32	94	100	98	87

The prepared CoS<sub>2</sub>/MoS<sub>2</sub> catalysts were also applied into the hydrodesulfurization benzothiophene and exhibited high HDS activity, as shown in Table S2. Benzothiophene conversion on Mo-S was 73%, but dihydrobenzothiophene selectivity was up to 68% at 300 °C for 3 h, suggesting the C-S bond scission of dihydrobenzothiophene to form 2-ethylbenzenethiol was the limited step in this HDS reaction. At the presence of CoS<sub>2</sub>, the conversion and ethylbenzene selectivity increased obviously. However, excessive CoS<sub>2</sub> covered on the surface of MoS<sub>2</sub> and then the available active sites for the adsorption of benzothiophene were decreased, leading to the reduction of the conversion at high Co/Mo molar ratio. Among these catalysts, Co-Mo-0.2 presented the highest HDS activity: 98% conversion and 100% ethylbenzene selectivity.

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