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Highly selective catalytic conversion of phenols to aromatic hydrocarbons on CoS₂/MoS₂ synthesized by two steps hydrothermal method

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CoS₂/MoS₂ catalysts were prepared by two-step hydrothermal procedure for the first time, i.e., MoS₂ was synthesized and then CoS₂ was prepared and deposited on the surface of MoS₂. The characterization results presented that CoS₂ and MoS₂ were separated in the resultant catalysts and the surface area of CoS₂/MoS₂ was much higher than that of Co-Mo-S prepared by one step method. In the hydrodeoxygenation (HDO) of *p*-cresol, the presence of CoS₂ enhanced the conversion, but excessive CoS₂ on the surface of MoS₂ reduced its activity. With an appreciate of CoS₂, the catalyst presented unprecedented HDO activity and direct deoxygenation (DDO) selectivity: 98% deoxygenation degree with a selectivity of 99% toluene at 250 °C for 1 h. This CoS₂/MoS₂ catalyst also exhibited high DDO activity for other phenolic monomers, which minimized hydrogen consumption and improved the economic efficiency.

The rapid growth in global energy demand, steadily decline in fossil fuels reserves and worldwide serious environment problems had motivated us to look for other renewable sources.¹ Bio-oil, derived from the biomass by liquefaction or pyrolysis, was an interesting alternative to supplement fuels.² However, lignocellulosic-derived bio-oil contained a relatively high amount of phenols, furans, esters and ketones, which led to some detrimental properties such as low heating value, high viscosity, chemical and thermal instability.³ This bio-oil required to be lowered its oxygen content if it was used as a supplementary fuel. Hydrodeoxygenation (HDO) was one of the most common and efficient technologies to selectively remove oxygen in a form of water in the presence of hydrogen, and the deoxygenation degree and product selectivity depended on the selected catalysts.⁴

Phenols, as the important lignin based monomeric model substrates and recalcitrant oxygenated species in bio-oil, were

always chosen to study the activity of the catalysts and the HDO reaction mechanism.^{5–11} It had been inferred that oxygen in phenols was removed via two parallel pathways: hydrogenation-dehydration (HYD) and direct deoxygenation (DDO).^{4, 5} The former involved the saturation of the aromatic ring of phenols, which resulted in a high hydrogen consumption and a decrease in octane number after HDO.¹² Therefore, allowing C–O bond scission without substantial phenyl ring saturation was an economical and favorable process for the HDO of phenols.¹³

Based on that Fe-based catalysts were effective for the activation of aromatic carbon–oxygen bond of phenols, Sun et al.¹⁴ studied the activity of Fe/C in the gas-phase HDO of guaiacol and confirmed its high DDO activity but a low HYD activity. After adding Pd to form Pd-Fe/C, the HDO activity enhanced markedly: 83.2% yield to aromatics at 450 °C. In addition, MoS₂ was established to be a good HDO catalyst and its DDO activity was further improved by adding Co.¹⁵ We had obtained a 100% *p*-cresol conversion with a selectivity of 92.2% toluene on Co-Mo sulfide catalyst at 275 °C for 4 h.¹⁶ These demonstrated that Co-Mo sulfide was a potential catalyst for the HDO of phenols, but its activity was structure-dependent, which could be improved by optimizing the preparation methods.

Until now, various technologies had been developed for the preparation of Mo based sulfide catalysts.^{11, 15, 17, 18} Previous literatures had almost adopted Co–Mo–S phase to elucidate the HDO mechanism when added Co promoter into MoS₂ catalysts.^{6, 15} However, this phase was unstable and would decompose during the reactions, which was just regarded as the precursor of the real active phase.¹⁹ Fortunately, Gil-Llambías et al.²⁰ had evidenced the synergism between the separated CoS_x and MoS₂. Recently, it had been concluded that the catalytic activity of Co-Mo sulfide was directly proportional to the increase of the contact surface area between MoS₂ and Co₉S₈ phases.²¹ For a uniformly simultaneous precipitation procedure, Co sulfides inserted into MoS₂ and were not always accessible, leading that the prepared catalyst had low surface area and much of promoter Co could not play its role,²² which in turn reduced the overall activity. Hence, to emphasize the effect of Co and enhance the HDO activity, CoS₂/MoS₂ catalysts were synthesized by

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two-step hydrothermal method for the first time and applied into the HDO of phenols.

In a typical procedure for the synthesis of CoS₂/MoS₂, 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 to room temperature and opened and added 30 mL solution contained cobalt nitrate and thiourea, and sealed and heated to 200 °C for 12 h again. After reaction, the black precipitate was collected and washed with water and ethanol and dried under vacuum at 50 °C for 8 hours. The resultant catalysts were denoted as Co-Mo-X, where X represented the initial molar ratio of Co/Mo. The HDO activity tests were carried out in a 100-mL sealed autoclave. The prepared catalyst (0.03 g), *p*-cresol (4.8 g) and dodecane (28.3 g) were placed into the autoclave. Air was evacuated by pressurization-depressurization cycles with nitrogen and subsequently with hydrogen. The system was heated to desired temperature, then pressurized with hydrogen and adjusted the stirring speed to 900 rpm. During the reaction, liquid samples were withdrawn from the reactor and analysed. Conversion = (the amount of aromatic-ring change during reaction/total amount of aromatic-ring) × 100 %; Selectivity = (C atom in each product/total C atom in the products) × 100 %; Deoxygenation degree (D.D., wt %) is defined as [1-oxygen content in the final organic compounds / total oxygen content in the initial material] × 100%.

As shown in Fig. 1, the XRD pattern of Mo-S presented four diffraction peaks at 2θ=14°, 33°, 39° and 59°, matching to (002), (100), (103) and (110) crystal plane of hexagonal MoS₂ (JCPDS Card No. 37-1492),²³ respectively, suggesting that MoS₂ structure had been completely formed after hydrothermal reaction for 12 h. With the increment of Co sulfide, there appeared some diffraction peaks at 2θ= 28°, 32°, 36°, 39°, 46° and 55°, corresponding to crystalline CoS₂ (JCPDS Card No. 41-1471).²⁴ These indicated that Co existed in the form of CoS₂ phase after the second hydrothermal synthesis. Previous studies had claimed that the promoter Co incorporated into the MoS₂ structure to form Co-Mo-S active phase and the excessive Co presented as Co₉S₈ phase,^{15, 21} but which were different from our results that CoS₂ and MoS₂ were separated and no Co₉S₈ phase was detected in the resultant catalysts.

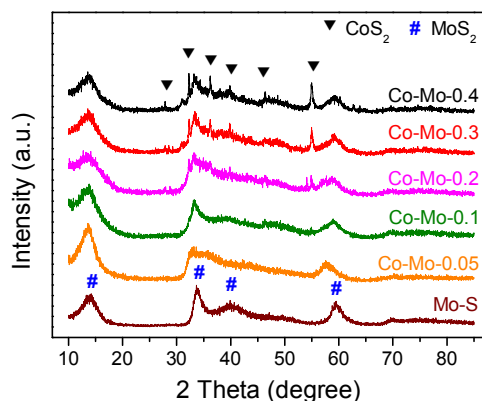


Fig. 1 XRD patterns of Mo-S and CoS₂/MoS₂ catalysts

The separated CoS₂ and MoS₂ phases were further confirmed by the XPS characterization on the electron bonding energy of each element. As presented in Fig. S1 (ESI⁺), three peaks at 226.6 eV, 229.3

eV and 232.5 eV presented in the Mo 3d level of each catalysts, assigning to the S 2p contribution for S²⁻, Mo 3d_{5/2} and Mo 3d_{3/2} of MoS₂,^{25, 26} respectively. Two peaks located at 162.2 eV and 163.6, matching well with the S 2p_{3/2} and S 2p_{1/2} in MoS₂ and CoS₂ phases,^{25, 26} respectively. Previous study had claimed that the binding energy of Co 2p_{3/2} in Co₉S₈ was at ranging between 777.8 eV and 778.1 eV while that for Co-Mo-S phase was 778.6 eV.²⁷ However, there only displayed one main peak appeared at 779.0 eV in the Co 2p level spectrums, corresponding to CoS₂. In addition, another peak at higher binding energy (782.1 eV) was assigned to Co oxides.^{21, 28} These demonstrated that Co did not decorate in MoS₂ slab to form Co-Mo-S phase and it presented as a CoS₂ phase rather than Co₉S₈ phase.

Generally, CoS₂ was deposited on the surface of MoS₂, resulting in a enrichment of Co and high Co/Mo molar ratio on the catalyst surface. However, the XPS results showed that the Co/Mo molar ratio on the surface of Co-Mo-0.05, Co-Mo-0.1, Co-Mo-0.2, Co-Mo-0.3 and Co-Mo-0.4 was 0.03, 0.05, 0.09, 0.16 and 0.24, respectively, being much lower than the corresponding ratio in the raw solution. These suggested that much of CoS₂ was not dispersed uniformly but aggregated together on the catalyst surface. The SEM images provided the direct evidence (Fig. S2, ESI⁺). Mo-S presented a loose flower-like structure composed of nanosheets in random orientation. Co-Mo-0.2 and Co-Mo-0.3 displayed some spinel-like particles, coexisting with the flower-like morphology, which was attributed to CoS₂. After adding excessive Co, e.g., Co-Mo-0.4, the flower-like MoS₂ was not obvious and there appeared large spinel CoS₂ particles, suggesting more CoS₂ and less MoS₂ active sites on this catalyst surface. These also demonstrated that MoS₂ and CoS₂ phases were separated and CoS₂ only deposited on the surface of MoS₂ and tended to aggregate together.

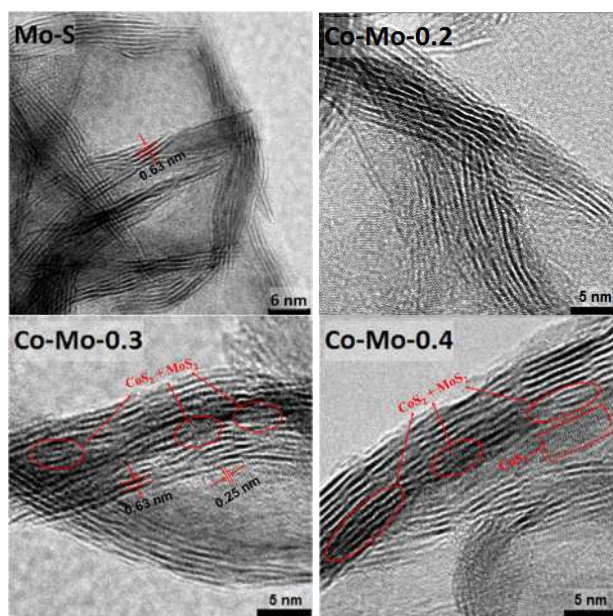


Fig. 2 HRTEM images of Mo-S and CoS₂/MoS₂ catalysts

HRTEM was taken to measure the microstructure of Mo-S and CoS₂/MoS₂ catalysts, which could provide tracks from direct observations to determine the interaction between CoS₂ and MoS₂ sulfide phases.²¹ Fig. 2 presents that Mo-S has a highly disordered organization of stacked layers with a spacing of fringe of 0.63 nm,

typifying the d_{002} interplanar spacing of MoS_2 .^{23, 29} After the deposition of Co sulfide on MoS_2 , such as for Co-Mo-0.3 and Co-Mo-0.4, another group of lattice fringes with an interplanar spacing of 0.25 nm were observed, corresponding to (210) plane of cubic CoS_2 pyramids,³⁰ and these fringes increased with the amount of Co sulfide. From these HRTEM images, it clearly showed that CoS_2 covered and spreaded on the MoS_2 slabs substrate, resulting that some MoS_2 slabs were invisible or some HRTEM zones presented both MoS_2 and CoS_2 phases.

The surface area, pore volume, and pore size distribution of Mo-S and $\text{CoS}_2/\text{MoS}_2$ catalysts are listed in Table 1. Mo-S had a surface area of $183 \text{ m}^2/\text{g}$ with a pore volume of $0.8 \text{ cm}^3/\text{g}$ and bi-modal pore distribution centered at 2.3 nm and 10.7 nm. With the increment of

Co/Mo mole ratio, the surface area gradually decreased to $78 \text{ m}^2/\text{g}$ and the small pores dramatically decreased (Fig. S3, ESI[†]). These were resulted from the deposition of CoS_2 on the surface or in the pore channel of MoS_2 . For the one-step synthesis, Co and Mo dispersed uniformly in Co-Mo bimetallic sulfide and consequently the obtained catalyst had a very small surface area (lower than $10 \text{ m}^2/\text{g}$). However, in this study, MoS_2 produced in the first step had large surface area, when CoS_2 produced and deposited on the surface of MoS_2 in the second step, only a small part of CoS_2 particles inserted into MoS_2 pores, preventing the decrease of surface area and exposing more active sites for the reaction, which was expected to enhance its catalytic activity.

Table 1 The structure properties of Mo-S and $\text{CoS}_2/\text{MoS}_2$ catalysts and their activities in the HDO of *p*-cresol^[a]

Catalyst	Mo-S	Co-Mo-0.05	Co-Mo-0.1	Co-Mo-0.2	Co-Mo-0.3	Co-Mo-0.4	$\text{CoS}_2+\text{MoS}_2$ ^[b]
Surface area (m^2/g)	183	165	149	105	91	78	--
Pore volume (cm^3/g)	0.8	0.7	0.7	0.6	0.6	0.5	--
Pore size (nm)	2.3, 10.7	2.2, 11.6	2.2, 12.8	2.4, 16.5	2.1, 16.0	19.2	--
Conversion (mol %)	18	40	53	77	98	93	19
Products selectivity (mol %)							
Methylcyclohexane	12	<1	1	<1	<1	<1	14
3-Methylcyclohexene	8	2	<1	<1	<1	<1	7
Toluene	80	98	98	99	99	99	79
D. D. (wt %)	16	36	49	74	98	92	17

[a] Reaction conditions: 0.03 g catalyst, 4.8 g *p*-cresol, 28.5 g dodecane, 4.0 MPa hydrogen pressure, temperature 250 °C and time 1 h.

[b] The catalysts was composed by 0.01 g CoS_2 and 0.03 g MoS_2 .

The comparison of Mo-S and $\text{CoS}_2/\text{MoS}_2$ catalysts on the activity and product distribution in HDO of *p*-cresol is shown in Table 1. The conversion over Mo-S was 18% with a selectivity of 80% toluene and a deoxygenation degree of 16% at 250 °C for 1 h. In the presence of CoS_2 , the products remained unchanged, but both the conversion and toluene selectivity were increased greatly, suggesting that CoS_2 was beneficial to significantly enhance the HDO activity and DDO activity, which was in line with previous investigations.^{6, 15} With the increment of CoS_2 , the conversion increased firstly and then decreased but toluene selectivity increased continually. When the Co/Mo mole ratio in the raw solution increased to 0.3, the catalyst exhibited the highest HDO activity. The deoxygenation degree reached to 98%, which was 6-fold higher than that on Mo-S. In contrast, at high Co/Mo molar ratio, e.g., for Co-Mo-0.4, because of the excessive coverage of MoS_2 by CoS_2 , the conversion decreased to 93%. Consequently, an appropriate CoS_2 on MoS_2 surface maximized the HDO activity. We also tested the HDO activity of physically mixed CoS_2 and MoS_2 under the same reaction conditions. The conversion was 19% with a selectivity of 79% toluene. This meant that large CoS_2 particles had little promoting effect on the HDO activity of MoS_2 and only CoS_2 disperse on MoS_2 surface with small size could enhance the HDO activity. Hence, the change of *p*-cresol conversion versus Co/Mo molar ratio on the catalyst surface obtained from XPS data was summarized (Fig. S4, ESI[†]). Under a low CoS_2 content, the conversion was linearly related to the Co/Mo molar ratio in the catalyst surface. Therefore, CoS_2 should be dispersed on MoS_2 surface uniformly and its monolayer dispersion would maximize the HDO activity.

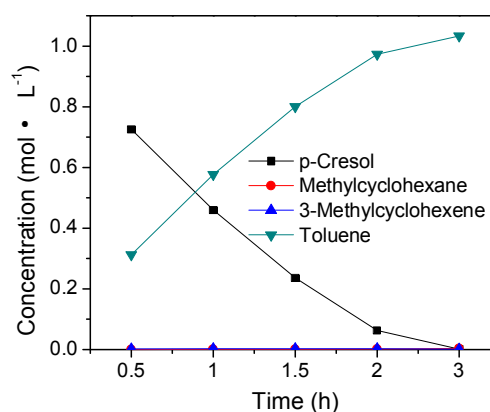


Fig. 3 The curves of concentration changes of *p*-cresol and product versus reaction time on Co-Mo-0.3 at 225 °C

Fig.3 presents the curves of concentration changes of *p*-cresol and product versus reaction time on Co-Mo-0.3 at 225 °C. With the increase of time, *p*-cresol concentration decreased while toluene concentration increased. During the whole reaction, both methylcyclohexane and 3-methylcyclohexene concentrations were very low. Obviously, the dominant reaction route for the HDO of *p*-cresol on Co-Mo-0.3 was DDO. After reaction for 3 h, the conversion was higher than 99% with a selectivity of 99% toluene. These suggested that Co-Mo sulfide catalysts prepared by this new method had very high HDO activity and direct deoxygenation activity. The above characterization results demonstrated that CoS_2 and MoS_2 phases but no Co-Mo-S phase presented in $\text{CoS}_2/\text{MoS}_2$ catalysts.

Consequently, Remote Control model was reasonable to explain the HDO reaction mechanism on these $\text{CoS}_2/\text{MoS}_2$ catalysts^{20, 31, 32}, as presented in Fig. 4. CoS_2 acted as a donor phase while MoS_2 acted as acceptor phase. Hydrogen adsorbed on CoS_2 active sites and converted into spillover hydrogen and migrated to MoS_2 active site for the HDO reaction. It had been reported that *p*-cresol molecules were adsorbed on catalyst surface via two modes: vertical adsorption and co-plane adsorption, which decided the DDO route and HYD route.¹⁷ However, according to the reaction equation, it required 6 mol spillover hydrogen for the hydrogenation of 1 mol *p*-cresol to 4-methylcyclohexanol, which was 3-fold larger than that for the deoxygenation of 1 mol *p*-cresol to toluene. Due to the low activity of CoS_2 for the creation of spillover hydrogen, the hydrogen for saturating phenyl ring became hard with the increase of CoS_2 on MoS_2 surface and then the HYD route was inhibited, resulting in a very high toluene selectivity.

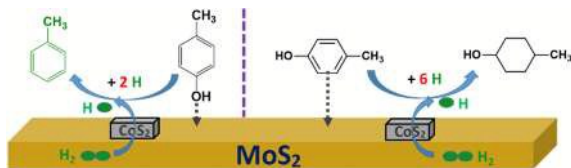


Fig. 4 The proposed reaction mechanism for *p*-cresol HDO on $\text{CoS}_2/\text{MoS}_2$ catalysts

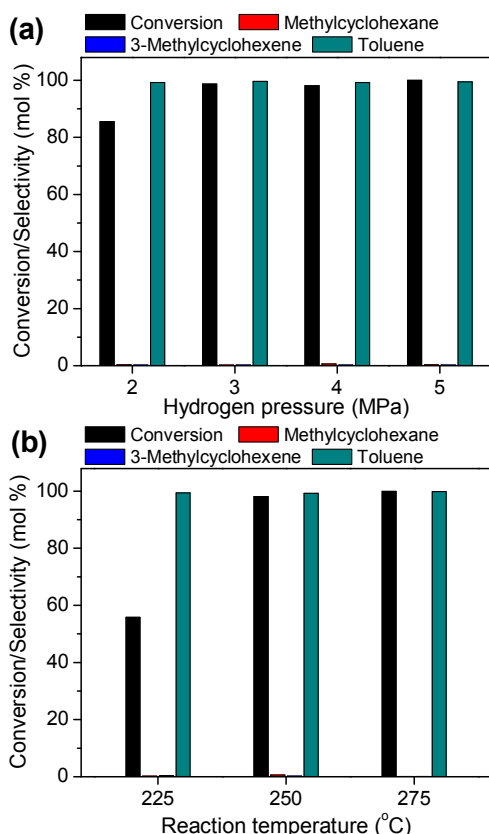


Fig. 5 The conversion and products distribution in the HDO of *p*-cresol on Co-Mo-0.3 under different hydrogen pressure (a) and reaction temperature (b) for 1 h

The hydrogen pressure had a great effect on the conversion in the HDO of phenols, especially for the product distribution.³³ Generally, high hydrogen pressure enhances the hydrogenation

reaction. Fig. 5 shows the HDO of *p*-cresol on Co-Mo-0.3 under different hydrogen pressures and reaction temperatures. After reaction for 1 h, the conversion was 86% with a selectivity of 99% toluene under 250 °C and 2 MPa hydrogen pressure. When the hydrogen pressure was raised to 5.0 MPa, the conversion increased to 100% and toluene selectivity was still higher than 99%. These suggested that high hydrogen pressure favored the *p*-cresol conversion but had little effect on toluene selectivity. As presented in Fig. 4, hydrogen was activated into spillover hydrogen on CoS_2 , but CoS_2 had a very low activation ability. Even though the hydrogen pressure was very high, the spillover hydrogen created on Co-Mo-0.3 was still insufficient to meet the required spillover hydrogen for the saturation of phenyl ring. These suggested that it did not need to consider the increase of hydrogen consumption with the hydrogen pressure in the HDO of *p*-cresol on Co-Mo-0.3 at high hydrogen pressure, which was industrially desirable.

However, low temperature was beneficial to create spillover hydrogen on the catalyst surface because of a high hydrogen solubility in the solvent in this case,³⁴ which supplied more hydrogen for the HDO reaction and enhanced the HYD products selectivity. As shown in Fig. 5(b), the conversion was dropped from 98% to 56% when the reaction temperature decreased from 250 °C to 225 °C, but toluene selectivity changed very little, which was still higher than 99%. This was also attributed to the low hydrogen activation ability of Co-Mo-0.3. Although the hydrogen concentration in the solvent at low temperature was higher than that at high temperature, but the created spillover hydrogen was still insufficient and presented a very high toluene selectivity.

The high HDO activity of $\text{CoS}_2/\text{MoS}_2$ catalyst was attributed to the following reasons. At first, $\text{CoS}_2/\text{MoS}_2$ catalyst had a large surface area and supplied sufficient active sites for *p*-cresol adsorption. Compared with our previous study¹⁶ that *p*-cresol conversion was 94% with a toluene selectivity of 90% on Co-Mo sulfide catalyst prepared by one-step hydrothermal method at 250 °C for 6 h with a *p*-cresol/catalyst weight ratio of 50, the surface area of Co-Mo-0.3 catalyst in this study was high to 91 m²/g, which exposed more active sites for the reaction and exhibited higher HDO activity. Secondly, the spillover hydrogen could promote the metal-sulfur bond scission,¹⁹ creating more coordinatively unsaturated sites for the adsorption of *p*-cresol molecules. When the spillover hydrogen on CoS_2 was sufficient, the DDO reaction would proceed smoothly and enhance the deoxygenation degree. Although more spillover hydrogen was provided for the HDO reaction when CoS_2 was excessive, but which was still insufficient for the HYD route and then presented an increase on toluene selectivity. In this case, the serious coverage of CoS_2 on MoS_2 active sites prevented the adsorption of *p*-cresol molecules and resulted in a decrease on deoxygenation degree. Compared with other catalysts (Table S1, ESI[†]), it obviously showed that $\text{CoS}_2/\text{MoS}_2$ catalyst prepared by two-step hydrothermal method presented unprecedented HDO activity and DDO selectivity: the deoxygenation degree and toluene selectivity reached to 98% and 99% in the HDO of *p*-cresol at 250 °C for 1 h, respectively.

The reusability of Co-Mo-0.3 in the HDO of *p*-cresol is shown in Fig. 6(a). Because the catalyst loss was inevitable during the reaction and separation, more parallel reactions were carried and recovered more catalyst to compensate the lost catalyst. It could observe that both *p*-cresol conversion and toluene selectivity were still higher

than 99% after cycle 3. These results suggested that Co-Mo-0.3 catalyst had a good stability, but which did not mean that there was no deactivation for this catalyst during HDO reaction. Previous study had reported that the sulfide catalyst underwent a continuous sulfur-oxygen exchange at its edge sites.³⁵ Hence, the recovered catalyst after each cycle reaction was characterized by XRD, as presented in Fig 6(b). We noticed that the peaks to MoS₂ became sharper after reaction and the intensity of (0 0 2) peak to MoS₂ edge decreased but others' intensity changed very little with the cycle number. These indicated that the enlarged MoS₂ crystallite size and the continuous destruction of (0 0 2) plane might be the reason for the catalyst deactivation during the HDO reaction, and it needed to be further confirmed.

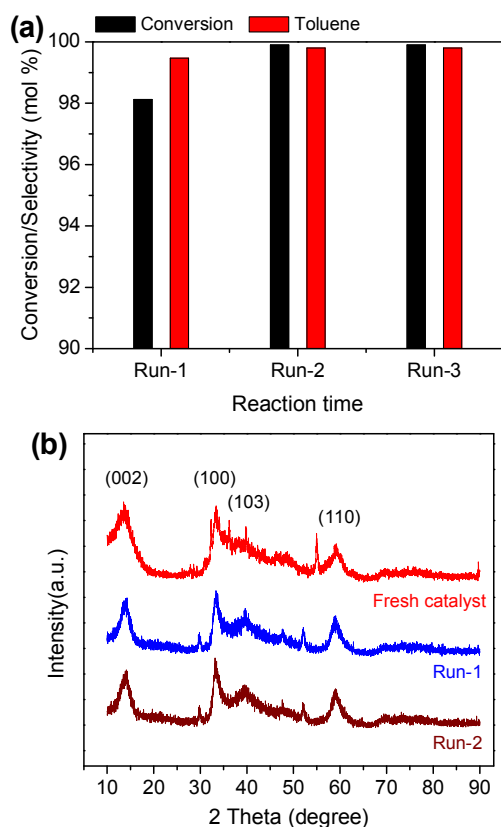















Fig. 6 (a) the reusability of Co-Mo-0.3 in the HDO of *p*-cresol and (b) the XRD patterns of fresh Co-Mo-0.3 and spent Co-Mo-0.3 after different cycles

To demonstrate the versatility of CoS₂/MoS₂ catalyst, several monomeric phenol derivatives were investigated using Co-Mo-0.3 as an optimized catalyst and the results are shown in Table 2. All the selected substrates were efficiently converted into aromatics, with a conversion of >99% and selectivity to aromatics of >98% under the investigated conditions, except for 4-methoxyphenol and guaiacol. These results indicated that CoS₂/MoS₂ had a high activity for the direct scission of C-O bonds in phenolic hydroxyl group. Moreover, previous literatures^{5, 36-38} had reported that the full conversions of phenols with the high selectivities (>90%) toward alkanes were obtained on the noble metal catalysts, where the HDO reaction temperature was reduced, but it consumed numerous hydrogen and the corresponding octane value of the products was decreased. In this study, due to the special structure of CoS₂/MoS₂ catalyst, the DDO was the predominant route in the HDO phenols on these catalysts, which minimized the consumption of precious hydrogen

energy. These CoS₂/MoS₂ catalysts also exhibited high activity in the hydrodesulfurization (HDS) of benzothiophene (seen in Table S2, ESI[†]). In the presence of CoS₂, e.g., on Co-Mo-0.2, the conversion and ethylbenzene selectivity raised to 98% and 100% at 300 °C for 3 h, respectively.

Table 2. HDO of phenol derivatives on Co-Mo-0.3^[a]

Substrate	Weight (g)	Conversion (%)	Selectivity (%)	
C6 backbone				
	4.2	100	99	1
	2.5	100	99	1
	2.8	100	85	1
	2.8	99	84	1
C7 backbone				
	4.8	100	99	1
	4.8	100	99	1
C8 backbone				
	5.4	100	99	1

^[a] Reaction conditions: 0.1 g catalyst, the total weight 33.3 g, H₂ pressure 4.0 MPa, temperature 300 °C and reaction time 1 h.

Conclusions

A new method was developed for the synthesis of Co-Mo sulfide catalysts with high activity. The characterization results showed that the prepared catalysts were composed with separate CoS₂ and MoS₂ phases rather than Co-Mo-S phase. CoS₂/MoS₂ catalysts exhibited unprecedented HDO activity and DDO selectivity: the deoxygenation degree reached to 97.8% with a toluene selectivity of 99.2% at 250 °C for 1 h, which was attributed to the synergistic effect between CoS₂ and MoS₂, uniform dispersion of CoS₂ on MoS₂ surface and large surface area. The conversion of *p*-cresol increased with the reaction temperature and hydrogen pressure, but which had little effect on toluene selectivity. These catalysts also exhibited a high direct DDO activity for other diverse substituted phenolic monomers and high HDS activity for benzothiophene, which minimized the consumption of precious hydrogen energy and exhibited a high potential superiority.

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Highly selective catalytic conversion of phenols to aromatic hydrocarbons on $\text{CoS}_2/\text{MoS}_2$ synthesized by two steps hydrothermal method

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$\text{CoS}_2/\text{MoS}_2$ composite catalysts were synthesized by two-step hydrothermal method and presented very high hydrodeoxygenation and direct deoxygenation activity in phenols conversion, which minimized the hydrogen consumption and improved the economic efficiency.

