

Supporting Information for

Facile synthesis of hydrophobic MoS₂ and its activity and stability in the hydrodeoxygenation reaction

Kui Wu^a, Chao Wang^a, Xiangxiang Chen^a, Weiyan Wang^a †, Yunquan Yang^a †

*School of Chemical Engineering, Xiangtan University, Xiangtan, Hunan, 411105, PR
China*

† Corresponding Author

E-mail: wangweiyan@xtu.edu.cn (W. Wang), yangyunquan@xtu.edu.cn (Y. Yang)

Preparation of hydrophobic MoS₂ catalysts

All solvents and reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. in high purity (≥99%) and used without further purification. Sodium molybdate (0.73 g), thiourea (1.14 g) and silicomolybdic acid (0 g, 2 g, 4 g, 6 g and 8 g) were dissolved in 100 mL water, and hydrochloric acid was added to adjust the pH value to 0.8, and then transferred to a 200 mL Teflon-lined stainless-steel autoclave and treated at 240 °C for 24 h. After reaction, the resulting black precipitate was separated and washed with water and absolute ethanol, and dried under vacuum at 60 °C for 5 hours. The resultant catalysts were denoted as Mo-S-X, where X represented the weight of silicomolybdic acid.

Catalyst characterization

X-ray diffraction (XRD) measurements were carried on a D/max2550 18KW Rotating

anode X-Ray Diffractometer with monochromatic Cu K α radiation ($\lambda=1.5418\text{\AA}$) radiation at voltage and current of 40 kV and 300 mA. The 2θ was scanned over the range of $10\text{-}90^\circ$ at a rate of $10^\circ/\text{min}$. The specific surface area was measured by a Quantachrome's NOVA-2100e Surface Area instrument by physisorption of nitrogen at 77 K. The samples were dehydrated at $300\text{ }^\circ\text{C}$ using vacuum degassing for 12 h before experiments. 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. Water contact angle was measured by a contact angle meter (Cam 200, KSV Instrument Ltd.) at $24\text{ }^\circ\text{C}$. A droplet of water in a size of $10\text{ }\mu\text{L}$ was used to test static contact angle.

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 (1.50 g) and dodecane (15.00 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 $300\text{ }^\circ\text{C}$, 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 (FID) 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. The experiments have been repeated twice at least and the results showed that the standard deviations of conversion and selectivity were less than 3.0%. The conversion, selectivity and deoxygenation degree for each experiment were calculated as follows:

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

$$\text{Selectivity (A, mol\%)} = \frac{\text{moles of product (A)}}{\text{moles of reacted } p\text{-cresol}} \times 100\%$$

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

To study the catalyst stability, the spent catalyst was separated and washed by ethanol for several times, dried under vacuum and then further used in the HDO of *p*-cresol under the same reaction conditions. Because the catalyst loss was inevitable during the reaction and separation, more parallel reactions were carried out and collected more catalysts to compensate the lost catalyst.

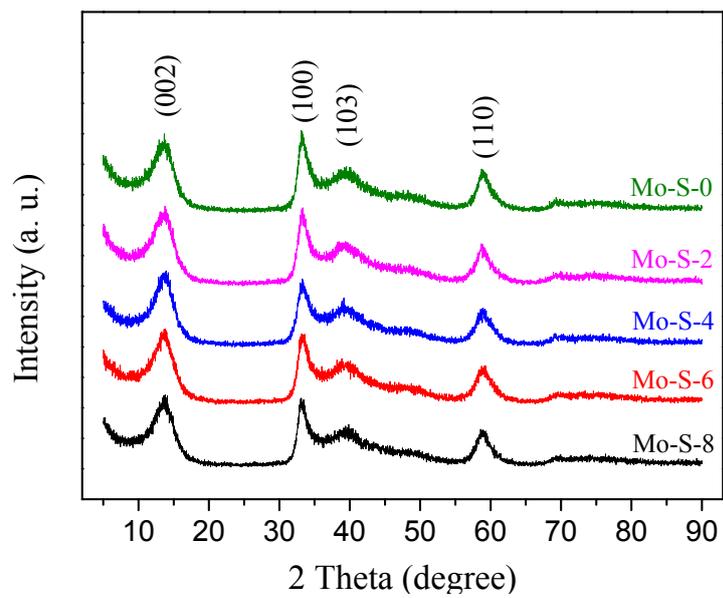


Fig. S1 XRD patterns of spent MoS₂ catalysts

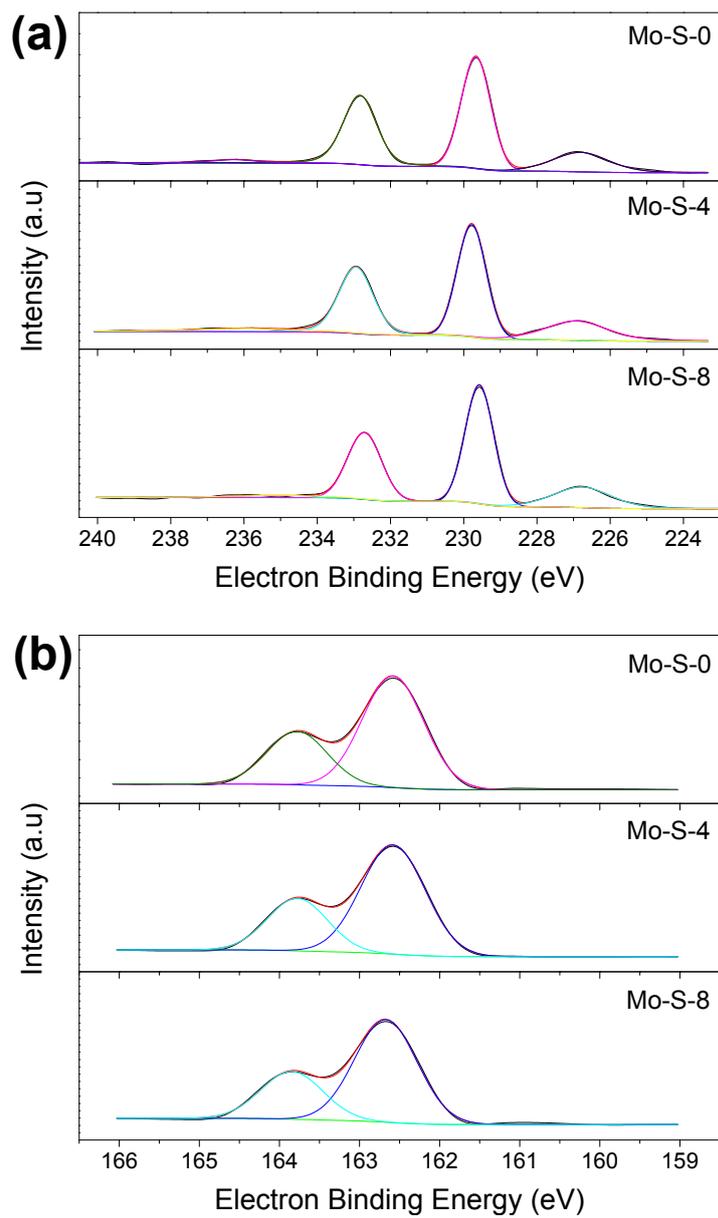


Fig. S2 XPS spectra of (a) Mo 3d and (b) S 2p levels of spent Mo-S-0, Mo-S-4 and

Mo-S-8