Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting information

Efficient hydrodeoxygenation of sulfoxides into sulfides under mild conditions using heterogeneous cobalt-molybdenum catalysts

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1. Experimental section

1.1 Materials

All of the chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). The solvents used in this study were supplied from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemicals and solvents were used directly without any purification.

1.2 Catalyst preparation

Firstly, ZIF-67 (ZIF indicates zeolitic imidazolate framework) was initially prepared. 2-Methylimidazole (5.5 g) was firstly dissolved in 20 mL of water. Then the mixture was magnetically stirred at room temperature for 1 h. To this mixture, $Co(NO_3)_2.6H_2O$ (0.45 g) in 3 mL of water was added dropwise. After the addition of $Co(NO_3)_2$ solution, the mixture was continuously stirred at 25 ^oC for another 6 h. The resulting purple precipitates were obtained via centrifugation and washed with water and methanol for twice, respectively, and finally dried in a vacuum oven to get ZIF-67.

Before the introduction of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ZIF-67 powder was further activated at 150 ^oC under vacuum for 24 h. Typically, 300 mg of ZIF-67 was dispersed in 30 mL of *n*-hexane with an assist of sonication for 2 h. $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (24 mg) in 100 μL of distilled water with was slowly added dropwise. After addition, the mixture was stirred for 1 h. During this period, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water was dispersed in the framework of ZIF-67. The supernatant was decanted, and the precipitate was dried in an oven at 70 °C overnight to remover water in the sample. Next the sample were transferred to a quartz boat and calcined at three representative temperatures (400, 600 and 800 °C) for 3 h in hydrogen atmosphere with a temperature ramp of 5 °C min^{-1}. The as-prepared catalyst was abbreviated as the Co-Mo/NC-T catalysts, where T represents the reduction temperature.

1.3 Catalyst characterization

Transmission electron microscope (TEM) was performed on a FEI Tecnai G^2 20 Tecnai G^2 F20 S-TWIN. X-ray powder diffraction (XRD) measurements of the nitrogen-doped carbon materials were performed on a Bruker advanced D8 powder diffractometer (Cu Kα), which was operated with 2θ range of 10–80° at a scanning rate of 0.016 °/s. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV. Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566). Spectra were obtained at a laser output power of 1 mW (532 nm), and a 0.2 s acquisition time with 900 lines/mm grating (Grating serial number: AJG1200531). Nitrogen physisorption measurements were conducted at 77 K on a quantachrome Autosorb-1-C-MS instrument.

1.4 General procedure of the catalytic deoxygenation of sulfoxide

The catalytic dehydrogenation of sulfoxide was conducted in a stainless steel autoclave. Generally, the Co-Mo/NC-T catalyst (20 mg), sulfoxide (0.5 mmol) and

CH_3OH (10 mL) were placed into the reactor. The air in the autoclave was precluded by the flush of hydrogen for five times and then hydrogen was pressurized to 10 bar. The autoclave was then heated from room temperature to the desired temperature and the reactions were stirred for 10 h with a magnetic stirring at a rate of 1000 RPM. After reaction, the autoclave was cooled down to room temperature, and the products were analyzed by GC and GC-MS with diphenyl ether as internal standard.

1.5 Analytic methods

The products in the reaction mixture were analyzed by Agilent 7890A GC, which was equipped with autosampler and a flame ionization detector. The products could be well separated by a HP-5 capillary column (30 m × 530 μm × 1.5 μm). The temperature of the column was initially kept at 80 °C for 3 min, and then increased at a rate of 20 °C min^{-1} to 220 °C. Products were identified by the comparison of the retention time with the authentic chemicals, and further confirmed by GC-MS (Agilent 7890A GC/5973 MS, HP-5 column). The amounts of products were determined based on GC data using the internal standard method.

1.6 Catalyst recycling experiments

After the reaction, the catalyst was separated from the reaction system with an-assist of a magnet, and washed with water and methanol for three times, respectively. Then it was dried in a vacuum oven at 50 ^oC.

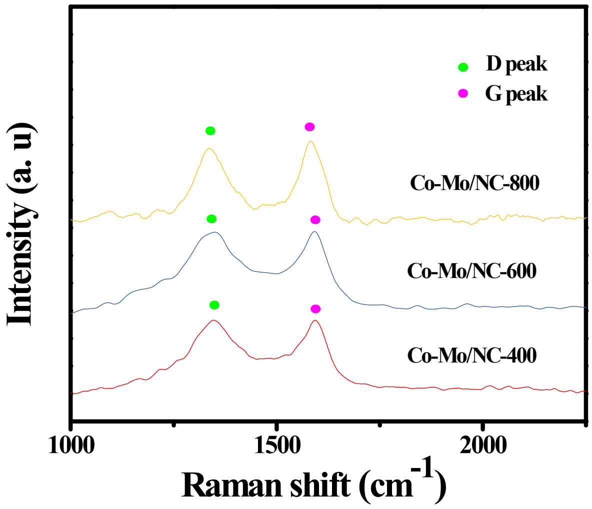


Figure S1. Raman spectra of the Co-Mo/NC-400, Co-Mo/NC-600 and Co-Mo/NC-800 catalysts.

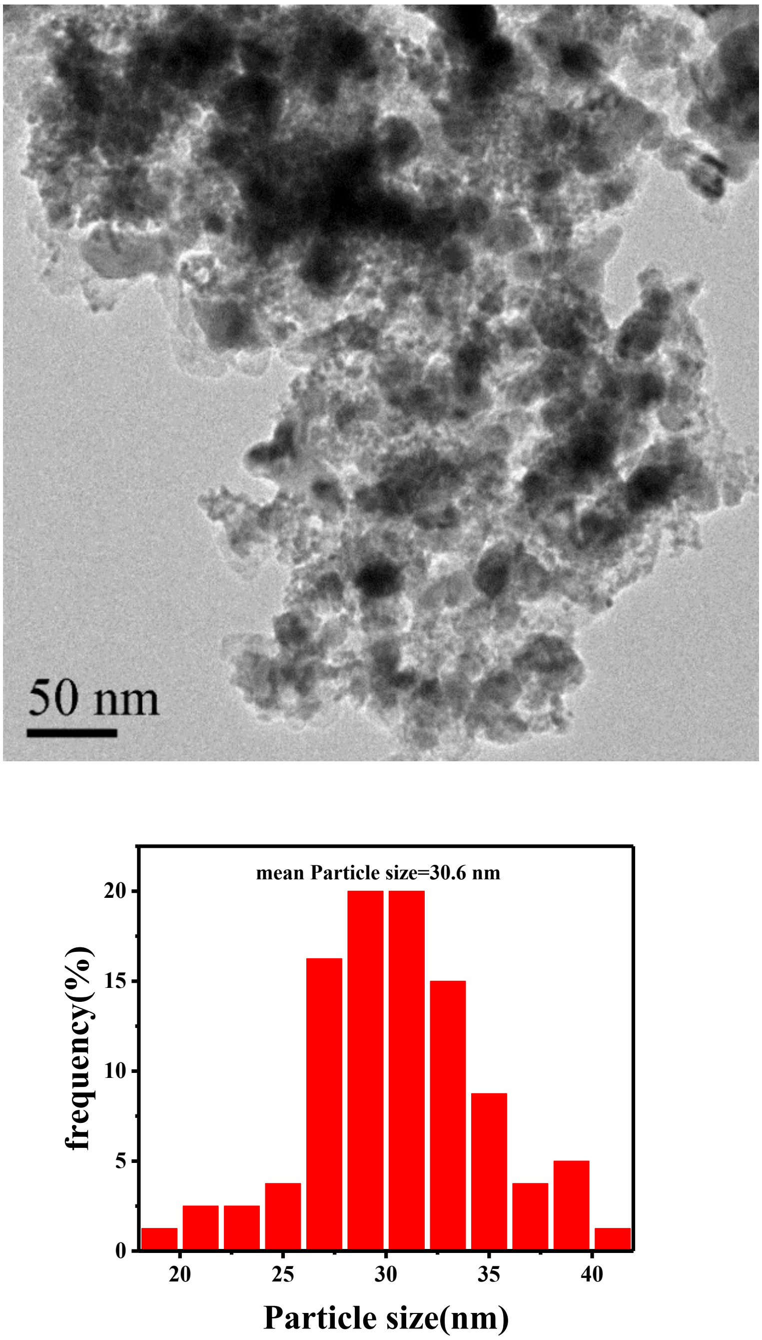


Figure S2. TEM image of the Co-Mo/NC-600 and particle size distribution of Co nanoparticles.

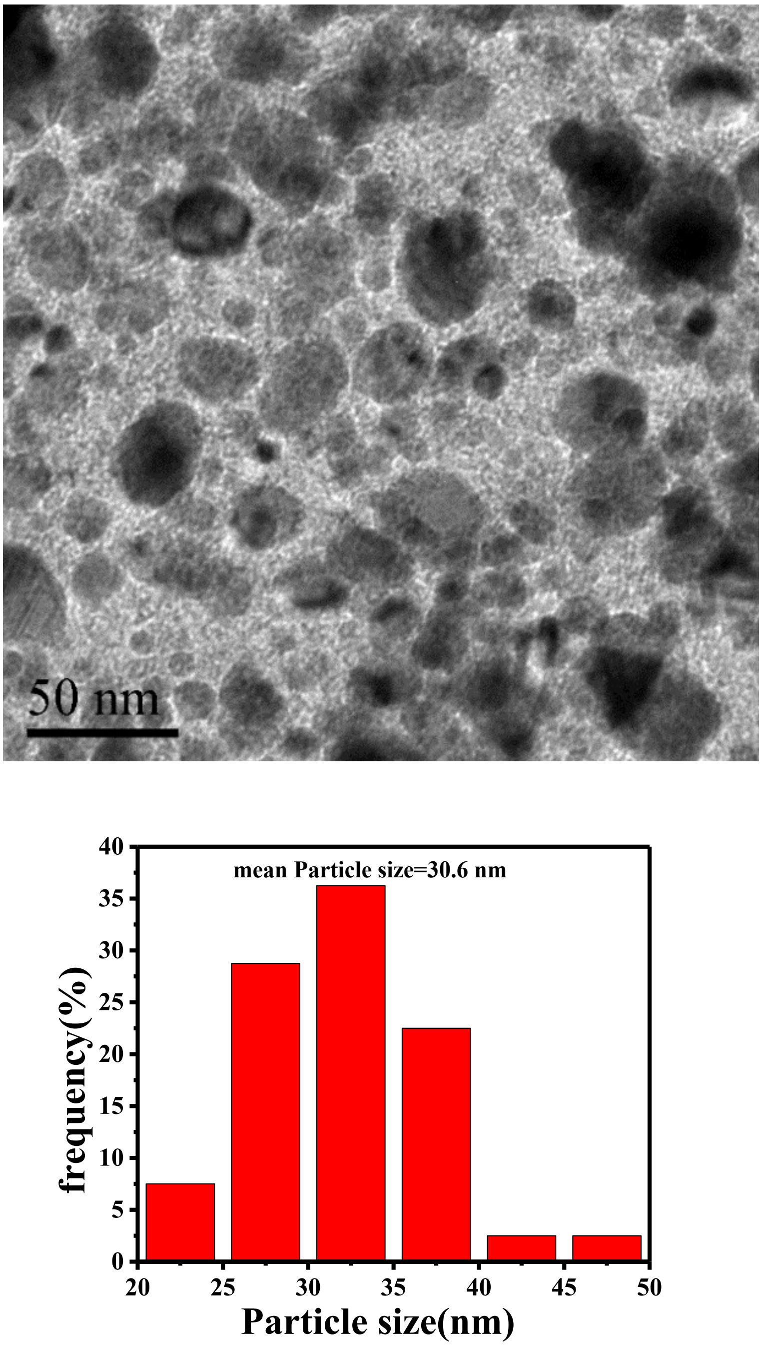


Figure S3. TEM image of the Co-Mo/NC-800 and particle size distribution of Co nanoparticles.

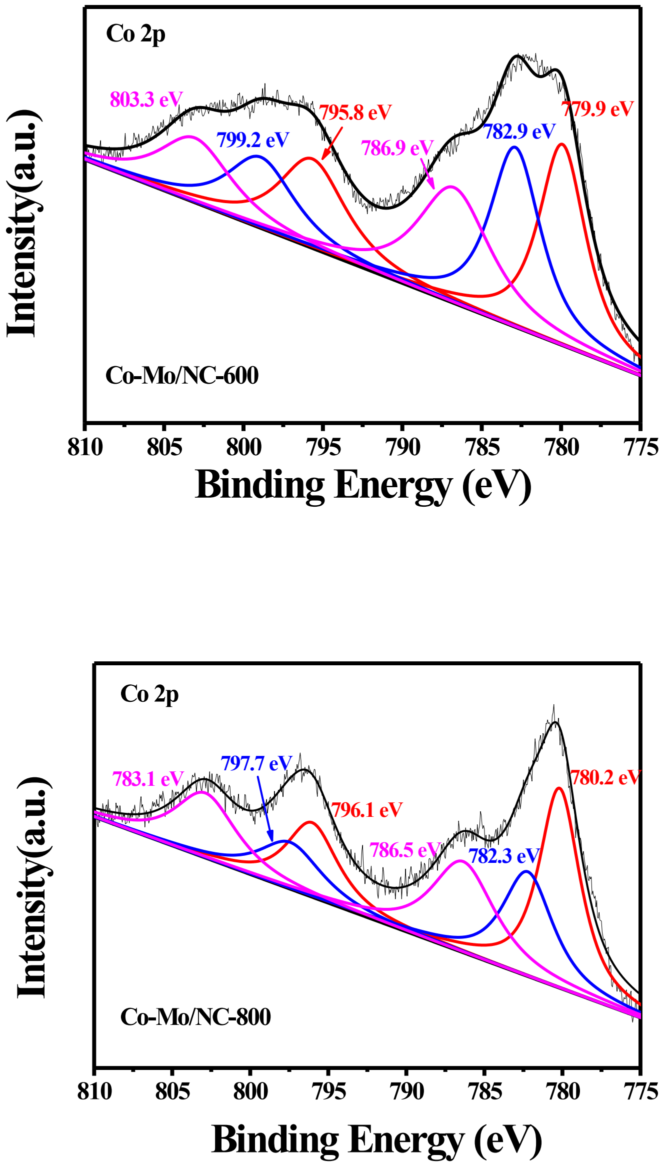
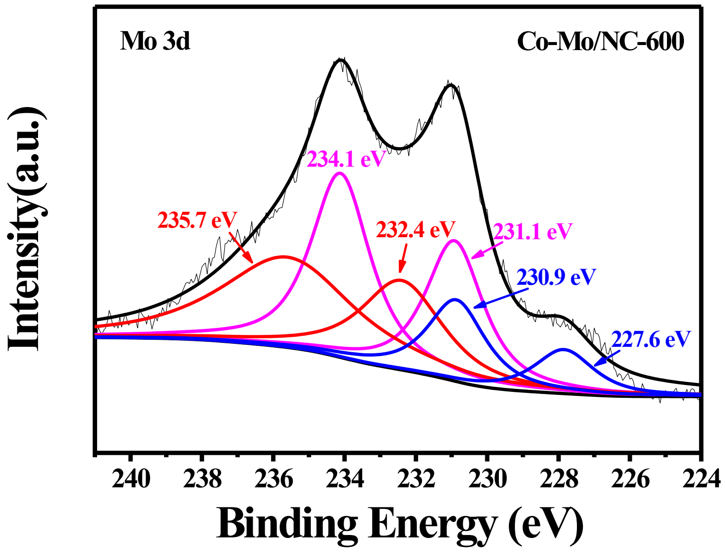


Figure S4. XPS spectra of Co 2p in the Co-Mo/NC-600 and Co-Mo/NC-800 catalysts.



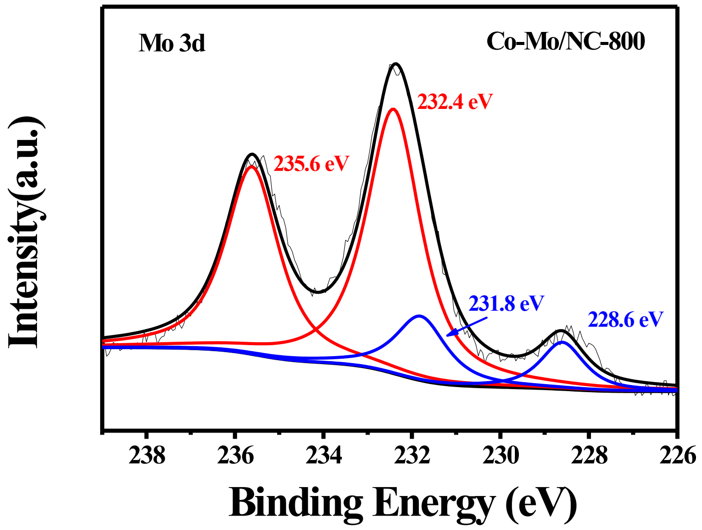


Figure S5. XPS spectra of Mo 3d in the Co-Mo/NC-600 and Co-Mo/NC-800 catalysts.

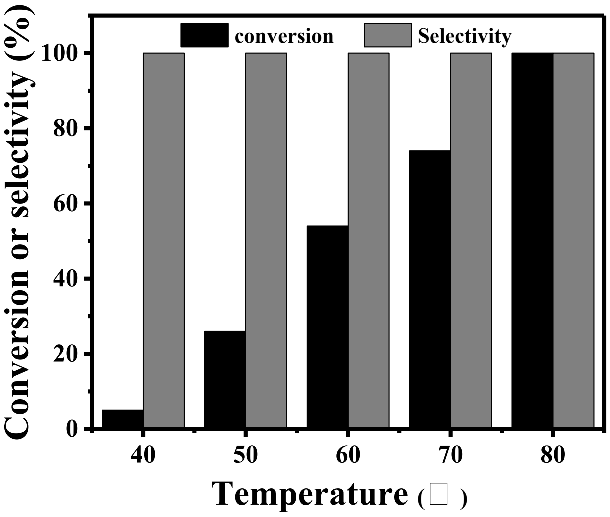


Figure S6. The effect of the reaction temperature on the deoxygenation of diphenyl sulfoxide. [a] Reaction conditions: diphenyl sulfoxide (0.5 mmol), methanol (10 mL), H_2 (10 bar), catalysts (20 mg), 40~80 ^{o}C and 2 h.

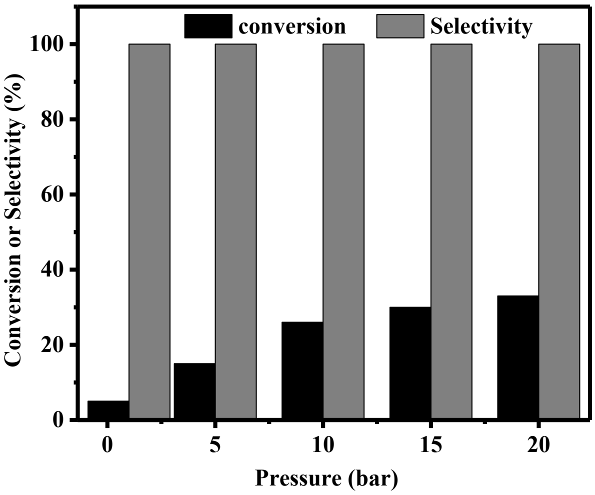
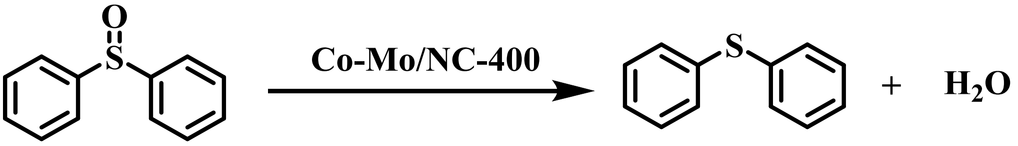


Figure S7. The results of deoxygenation of diphenyl sulfoxide under different hydrogen pressure conditions [a] Reaction conditions: diphenyl sulfoxide (0.5 mmol), methanol (10 mL), H_2 (1~20 bar), catalysts (20 mg), 80 °C and 2 h.

Table S1. The effect of reaction solvents on the deoxygenation of diphenyl sulfoxide to diphenyl sulfide



Entry	Solution	Conversion (%)	Yield (%)	Selectivity (%)
1	H_2O	97	94	97
2	Methanol	100	100	100
3	Ethanol	97	96	99
4	*i*-PrOH	93	93	100
5	DMF	69	69	100
6	1,4-dioxane	77	77	100
7	THF	74	74	100
8	Toluene	73	73	100
9	Hexane	45	45	100
10[b]	Methanol	91	91	100

[a] Reaction conditions: diphenyl sulfoxide (0.5 mmol), solvents (10 mL), H_2 (10 bar), catalysts (20 mg), 80 °C and 2 h. [b] Reaction conditions: diphenyl sulfoxide (0.5 mmol), solvents (10 mL), H_2 (10 bar), catalysts (20 mg), 25 °C and 60 h

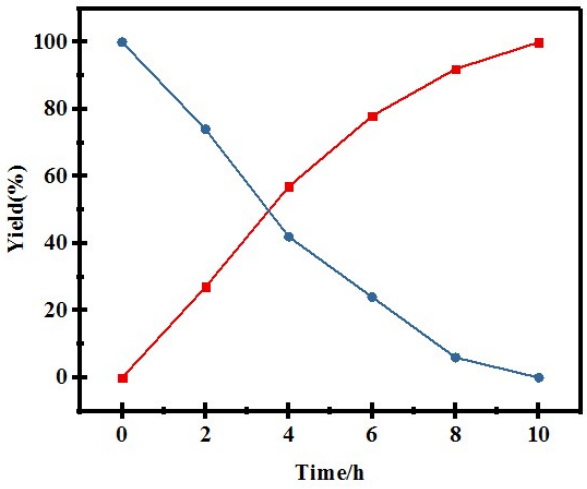


Figure S8. Time course of the product distribution for the reduction of phenyl sulfoxide at 50 °C, (●) unreacted phenyl sulfoxide, (■) phenyl sulfide. [a] Reaction conditions: diphenyl sulfoxide (0.5 mmol), methanol (10 mL), H_2 (10 bar), catalysts (20 mg), 50 °C and 2 h.

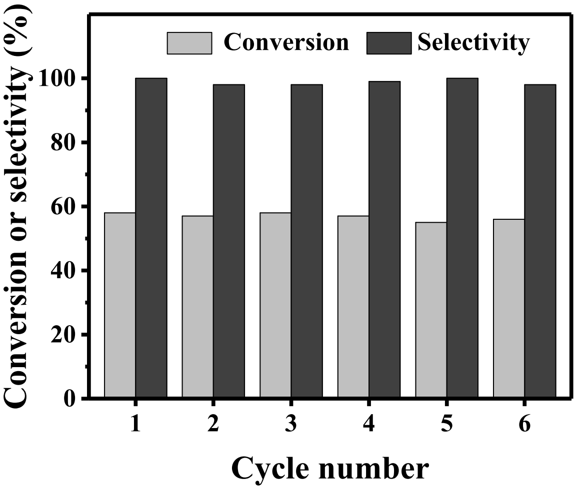


Figure S9. Recycling experiments of the Co-Mo/NC-400 catalyst. Reaction conditions: diphenyl sulfoxide (0.5 mmol), methanol (10 mL), H_2 (10 bar), catalysts (20 mg), 50 ^{o}C and 4 h.