Hydrodesulfurization of Dibenzothiophene over Core-Shell Ni/Al$_2$O$_3$@SOD and Mo/Al$_2$O$_3$ Composite Catalyst

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Part 1.

1.1 Preparation of SOD zeolite zeolite precursor suspension

The SOD type zeolite was prepared by mixing a silicate solution (solution A) and an aluminate solution (solution B) in an ice bath. Solution A: 10 g of SiO_2, 9.368 g of sodium hydroxide, and 26.3 g of deionized water were mixed under continuous stirring at 25 °C to get a clear silica solution. Solution B: 5 g of sodium hydroxide was dissolved in 10 g dd deionized water, then 0.54 g aluminum powder was added to the caustic solution to get a clear aluminate solution. Then, solution B was added drop wise to solution A in an ice bath to produce a transparent precursors suspension. Then the precursor suspension was placed in the freeze dryer at - 80 °C (40 Pa) for 24 h to obtain the highly viscous SOD gel.

1.2 Preparation of Mo/Al$_2$O$_3$

The $MoS_2/\gamma-Al_2O_3$ catalyst aqueous solution of ammonium molybdate tetrahydrate. 10 g of the $\gamma-Al_2O_3$ pellets were placed in the ziplock bag including the Mo impregnation solution (Mo: 5.6 wt.%). The ziplock bag was shaked slightly until the $\gamma-Al_2O_3$ pellet (water suction rate: 85%) absorbed the Mo impregnation solution completely. The immersed pellets were air-dried at room temperature for 10 hours, and then transferred to an oven at 120 °C for further drying for 20 hours. Finally, the samples were calcined in air at 500 ºC for 4 h. The supported $Mo/\gamma-Al_2O_3$ catalyst can be obtained. The theoretical loading of Mo on the $\gamma-Al_2O_3$ was 4.5 wt.%.

1.3 Preparation of Pt/Al$_2$O$_3$@SOD

a. Preparation of impregnation solution containing 1.48 wt% Pt (made form chloroplatinic acid);

b. 5 g of $\alpha-Al_2O_3$ was put in a three-necked flask filled with 120 mL deionized water, and 1.69 mL of the Pt solution was added into the soaking solution at room

temperature with stirring for 1 h. Then 1.6 g of urea was added into the soaking solution and the mixing solution was refluxed at 80 °C for 10 h. The cooled support was placed in an oven at 120 °C to dry for 4 h, and then calcined for 4 h at 500 °C to obtain the Pt/Al_2O_3 catalyst with a theoretical loading of 0.5 wt%. The catalyst was ultrasonically washed with deionized water, and dried (120 °C, 4 h) for later use.

c. The $Pt/Al_2O_3@SOD$ catalyst (named PS) was prepared as follows: the Pt/Al_2O_3 catalyst was surface-treated with 5 wt.% NaOH solution at 120 ºC for 2 h, and then washed with ethanol for four times followed by the wrapping of an SOD shell. The precursor suspension was prepared as described in 2.2.1. Then the precursor suspension was placed in the freeze dryer at - 80 °C (40 Pa) for 24 h to obtain the highly viscous SOD gel. The surface-treated Pt/Al_2O_3 was putted in the highly viscous SOD gel, evenly wrapped, and transferred to a Teflon-lined autoclave at 60 ºC for 20 h. After rinsed with deionized water, the product was dried in an oven at 120 ºC for 12 h to obtain the $Pt/Al_2O_3@SOD$ catalyst.

Part 2.

The characterization of MoS_2/Al_2O_3 catalyst.

The γ-Al_2O_3 showed two obvious characteristic peaks at $2\theta= 45.8º$ and $67.0º$ in figure S1a. For the Mo based catalysts (MoS_2/Al_2O_3 and Mo/Al_2O_3), only the peaks represented γ- Al_2O_3 were detected，indicating the low loading content and the uniform dispersion of Mo on γ- Al_2O_3. The lattice characteristics of MoS_2/Al_2O_3 were given by HRTEM. The obvious MoS_2 lamellar structure could be observed in figure S1b, and the structure was mostly double-layered with a layer spacing of 0.6 nm. In addition, through the statistical analysis of multiple HRTEM results, it was found that the layer length of MoS_2 was about 2.7 nm (figure S1c), and the number of stacking layer was mostly among 1-3 (figure S1b). All of the above were attributed to the typical
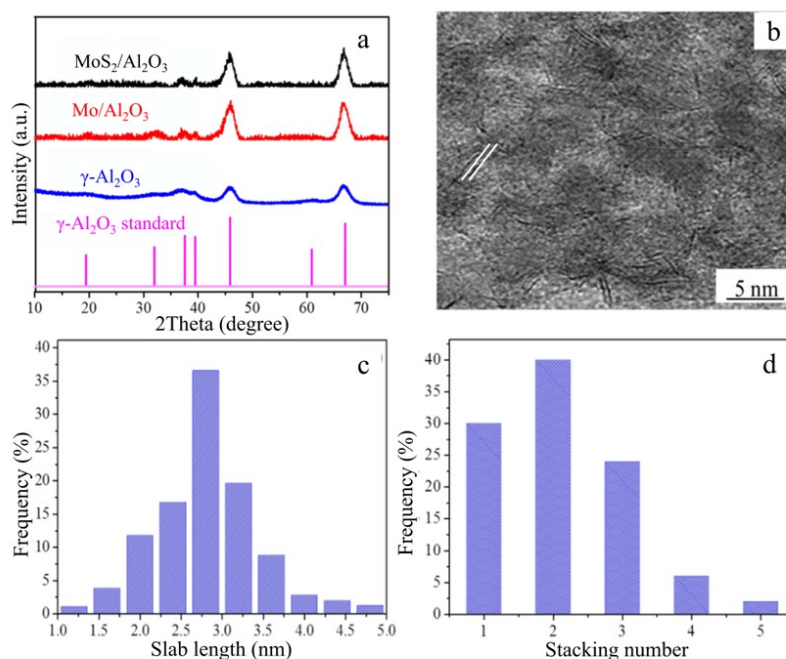
MoS$_2$ characteristics.

Figure S1. XRD patterns (a) of Mo/Al$_2$O$_3$, MoS$_2$/Al$_2$O$_3$, and γ-Al$_2$O$_3$; the HRTEM images of MoS$_2$/Al$_2$O$_3$ (b); the distribution of slab length (c) and stacking number (d) of the MoS$_2$ in MoS$_2$/Al$_2$O$_3$.

The valence state analysis of the sulfided Mo-based catalyst was obtained by XPS. As shown in figure S2, the double peaks appeared at the binding energies of 228.3 eV and 231.8 eV were belonged to Mo^{4+}(IV), which represented MoS$_2$ species [S1, S2]. The peaks at 229.7 eV and 232.8 eV represented Mo^{5+}(V) and illustrated the existence of MoO$_x$S$_y$ species [S1, S2], the poor peak at around 265.0 eV was attributed to the Mo^{6+}(V) (MoO$_3$), and no peaks attributed to MoO$_2$ was detected in the spectrum, indicating that the Mo catalyst were highly sulfurized.
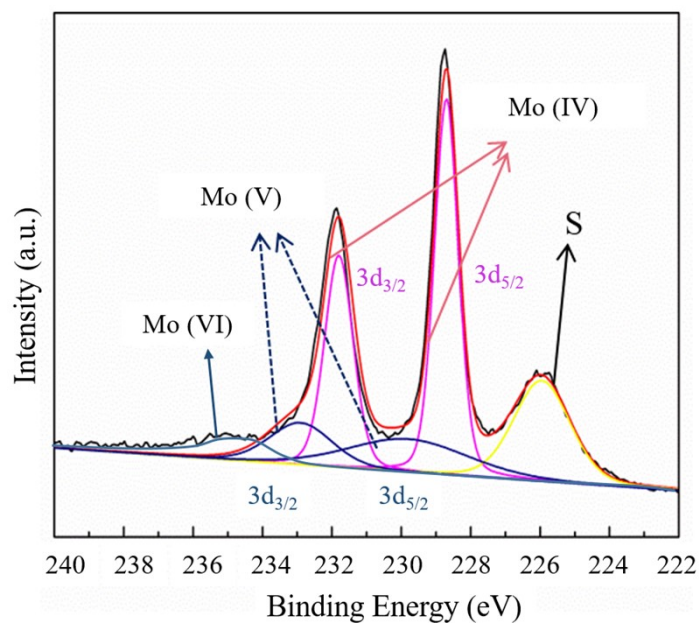
Figure S2. XPS characterization of sulfided Mo-based catalysts

Reference

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[S2] Liu. B, Lei. L, Zhong. W. Effect of hydrogen spillover in selective hydrodesulfurization of FCC gasoline over the CoMo catalyst. Catalysis Today, 2017, 282:214-221.