Synthesis of methyl mercaptan on mesoporous alumina prepared with hydroxysafflor yellow A as template：the synergistic effect of potassium and molybdenum

Chuang Peng [a, d, 1], Dong Zeng [a, 1], Jianjun Li [c], Shuai Peng [a], Jun Xiong [a], Weiming Wang [a, *], Yingming Chen [b], Hong Liu [b], Hao Liu [e], Rui Qin [b, *]

[a] Hubei Key Laboratory of Biomass Fibers and Eco-Dyeing & Finishing, Wuhan Textile University, Wuhan, 430200, Hubei, PR China

[b] College of Resource and Environmental Science, South-central University for Nationalities, Wuhan 430074, PR China

[c] College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, Fujian, PR China

[d] College of materials science and chemical engineering, Harbin Engineering University, Harbin, 150001, China

[e] State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan, 430074, China

* Corresponding Authors: wangweiming1212@163.com (Weiming Wang), qinrui@mail.scuec.edu.cn (Rui Qin)

3. Experimental Section

3.1 Mesoporous Al_2O_3 Preparation

16.3g hydroxysafflor yellow A (HSYA) was weighed in a conical bottle, 250ml distilled water was added, and 20.0g Al $(NO_3)_3 \cdot 9H_2O$ was added after stirring at room temperature for 0.5h. After stirring evenly, the pH value of the solution was adjusted to 4.8, oscillated at room temperature for 8h, aged for 3h and then filtered. After fully washing the filter cake with distilled water, the filter cake was dried in a vacuum drying box at 60 ℃ for 24 h, and then the mesoporous Al_2O_3 was obtained by aerobic roasting at 600 ℃.

3.2 Catalyst Preparation

The catalyst was prepared by the double co-impregnation method using mesoporous Al_2O_3 prepared above as the support. The metered ammonium molybdate $[(NH_4)_6Mo_7O_{24} \cdot 4H_2O]$ was dissolved in the metered deionized water, and the metered K_2CO_3 was slowly added to the ammonium molybdate solution according to n (K): n

(Mo) = 2: 1, then the support Al_2O_3 was impregnated for 12 hours, dried at 100 ℃ and calcined at 400 ℃ for 3 hours, and the catalyst was recorded as K-Mo/Al. The metered ammonium molybdate was dissolved in the metered deionized water, and then the support Al_2O_3 was impregnated in it. The other preparation conditions were the same as K-Mo/Al, and the obtained catalyst was marked as Mo/Al. Similarly, the support Al_2O_3 was impregnated in the metered K_2CO_3 solution and the catalyst was obtained by drying and calcining, which was recorded as K/Al.

3.3 Catalyst Activity Test

The activity evaluation of the catalysts was carried out in a fixed-bed micro-reactor and the loading amount of the catalysts was 2 ml. The catalyst is not pre-sulfurization before the reaction, but only the inert gas N_2 is used to purge the pipeline. When the temperature rises to the reaction temperature, the raw material CS_2 is pumped into the reactor by a double-plunger micro-metering pump (gasified before entering the catalyst bed), and then the scavenging N_2 is switched to H_2 to react in the catalyst bed. The reaction conditions are as follows: reaction temperature 260-380 ℃, reaction pressure 0.3 MPa. The reaction atmosphere was detected online by gas chromatography equipped with TCD, and the tail gas was absorbed by high-concentration alkali solution. The test result of catalyst activity at a certain temperature point is the average value of many times measured results at that temperature.

3.4 Catalyst Characterization

N_2 adsorption-desorption was carried out on the automatic physical and chemical adsorption tester Micromeritics Tristar 3000. Before the test, the samples (100 mg) were vacuum treated at 120 ℃ for 1 h, and then pretreated at 300 ℃ for 3 h to remove moisture and impurities in the sample. The X-ray diffraction (XRD) was measured on the Panalytical X'Pert Pro X-ray powder diffractometer of Philips Co., Ltd., using Cu Kα as the radiation source ($\lambda = 0.15406$ nm), the working voltage is 40 kV, the scanning current is 30 mA, the scanning range is 10~90°, the scanning step is 0.0167° and the time of each step is 10 s.

The characterization of H_2-TPR and CO_2/NH_3-TPD was carried out on the automatic chemisorption instrument Altamira Instruments AMI-300 equipped with a TCD detector, and the amount of catalyst used in each experiment was 100 mg. For the H_2-TPR experiment, the samples were pretreated in Ar atmosphere (30 ml/min) at 300 ℃

for 0.5 h to remove moisture and impurities, then decreased to room temperature, switched to 10% H_2/Ar (Volume Fraction) reducing gas purging for 0.5 h, and finally increased to 900 ℃ at the rate of 10 ℃/min. For CO_2/NH_3-TPD experiment, taking CO_2-TPD as an example, the samples were pretreated in 30 ml/min Ar atmosphere at 300 ℃ for 1 h, the temperature dropped to 30 ℃, then switched to 30 ml/min 10%CO_2/Ar (Volume Fraction) atmosphere for adsorption, then switched to Ar atmosphere (30 ml/min) for 10 min, and finally increased to 800 ℃ at the rate of 10 ℃/min.

The pyridine adsorption IR test of the samples was carried out on Nicolet Nexus FTIR 6700 infrared spectrometer. About 40 mg samples were pressed into slices and placed in the center of the in-situ pool heating zone. The samples were first treated in vacuum at 400 ℃ for 0.5 h and then cooled to 250 ℃, 150 ℃, 100 ℃, 50 ℃ to take the corresponding background spectrum. Adsorption of pyridine at 50 ℃ for 60 s, stay in 10 min, continue to vacuum, after stabilization, take the spectrum and deduct the background spectrum, then sequentially temperature up to 100 ℃, 150 ℃, 250 ℃, take the spectrum and deduct the corresponding background spectrum.

The test of X-ray photoelectron spectroscopy (XPS) was carried out on the PHI-Quantum 2000 electron spectrometer. The instrument radiation source uses an Al target with a Monochromator, using Al Kα (hν = 1486.6 eV) as the radiation source, the vacuum of the analysis chamber is better than 1×10^{-7} Pa, and the binding energy of C1s (284.6 eV) is used as the internal standard. The XPS spectra were fitted by Multipak V6.1 software.

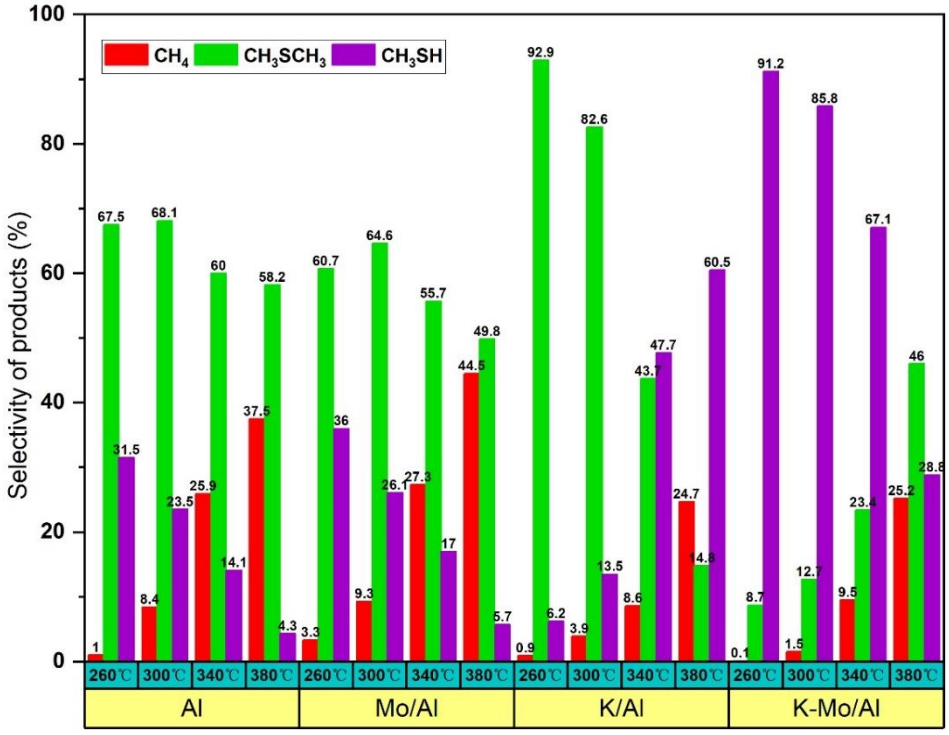

Figure S1. The selectivities toward CH_4, CH_3SCH_3 and CH_3SH as a function of reaction temperature over the Al, Mo/Al, K/Al and K-Mo/Al catalysts. Reaction conditions: P=0.3MPa, $R(CS_2)$ =1.6ml/h, $R(H_2)$ =30ml/min, 2ml of the Catalyst.

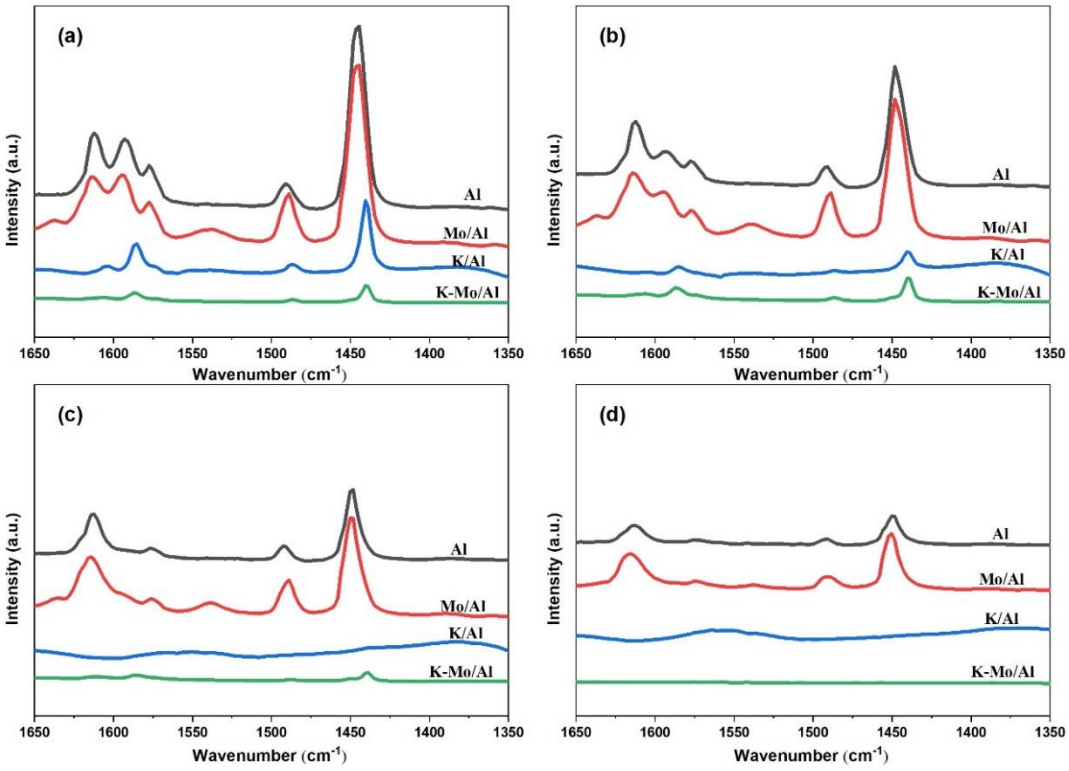

Figure S2. Spectra of pyridine adsorbed on the catalysts at (a) 50℃, (b) 100℃, (c) 150℃, (d) 250℃.