

Supporting Information for:

Ultra-deep oxidative desulfurization of fuel with H₂O₂ catalyzed by molybdenum oxide supported on alumina modified by Ca²⁺

Wei Jin, Yongsheng Tian, Guanghui Wang, Danlin Zeng, Qian Xu, Jiawei Cui

Hubei Key Laboratory of Coal Conversion and New Carbon Material, School of Chemistry and Chemical Engineering, Wuhan University of Science and Technology, Wuhan 430081, Hubei, China

Contents

1. **Fig.1.** FT-IR spectra of MoO₃ (a), Al₂O₃ (b) and Ca/MoO₃/Al₂O₃ (c).
2. **Fig.2.** X-ray diffractions of ammonium molybdate (a), Al₂O₃ (b) and Ca/MoO₃/Al₂O₃ (c).
3. **Fig.3.** Pore structure parameters of Ca/MoO₃/Al₂O₃. (a) Adsorption desorption isotherm; (b) Pore size distribution.
4. **Fig.4.** XPS spectra of Ca/MoO₃/Al₂O₃:(a) Survey, (b) Mo 3d, (c) Ca 2p and MoO₃/Al₂O₃:(a) Survey, (d) Mo 3d.

Fig. 1 shows the FT-IR spectra of MoO₃ (a), Al₂O₃ (b), and Ca/MoO₃/Al₂O₃ (c). The characteristic peaks observed in the FT-IR spectrum of MoO₃ at 988, 878 and 634 cm⁻¹ were attributed to the fundamental vibrational modes of Mo=O.¹ The dominion band at 821 cm⁻¹ is associated with the vibration of Mo-O-Mo bridging

bonds.¹ For the Ca/MoO₃/Al₂O₃ (c), owing to the overlap of the characteristic peaks of MoO₃ with that of the Al₂O₃ appeared at 740 and 640 cm⁻¹ (Al-O bands),² the bands of MoO₃ were not observed after the immobilization of MoO₃ on the support. It suggested that MoO₃ was highly dispersed on the Al₂O₃ support.

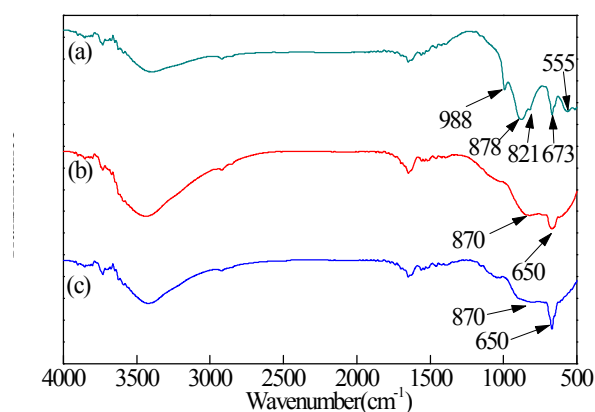


Fig.1. FT-IR spectra of MoO₃ (a), Al₂O₃ (b) and Ca/MoO₃/Al₂O₃ (c).

Fig. 2 shows the powder X-ray diffractions of ammonium molybdate(a), Al₂O₃(b), and Ca/MoO₃/Al₂O₃(c). As shown in Fig. 2, The characteristic peaks of ammonium molybdate at $2\theta = 13.0^\circ$, 23.2° , 25.6° , 27.2° , 34.3° , 39.1° , 46.5° , 50.1° , 53.7° and 60.4° emerged, which belonged to the characteristic peaks of the MoO₃ unit.³ For Ca/MoO₃/Al₂O₃, no crystal diffraction peaks of MoO₃ were found, which indicates that MoO₃ clusters are highly dispersed on the surface of Al₂O₃. XRD analysis confirms that the catalyst Ca/MoO₃/Al₂O₃ structure is an amorphous phase because of no characteristic diffraction peaks.

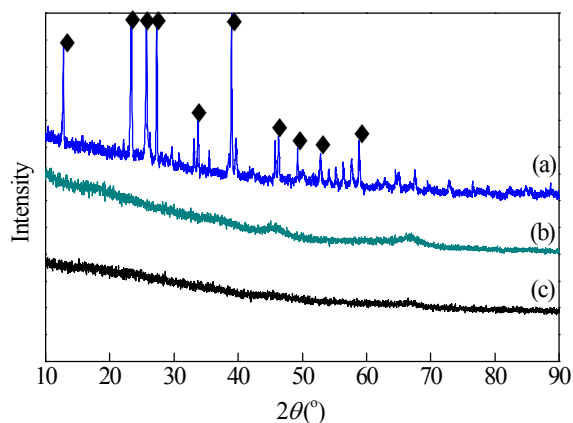


Fig.2. X-ray diffractions of ammonium molybdate (a), Al_2O_3 (b) and $\text{Ca}/\text{MoO}_3/\text{Al}_2\text{O}_3$ (c).

The N_2 adsorption-desorption isotherm (a) and pore size distribution (b) of $\text{Ca}/\text{MoO}_3/\text{Al}_2\text{O}_3$ are shown in Fig.3. Based on the taxonomy, the adsorption isotherm of $\text{Ca}/\text{MoO}_3/\text{Al}_2\text{O}_3$ exhibits type IV isotherms using IUPAC, revealing that the catalysts are characteristic of mesoporous materials.⁴ The adsorption isotherm data were processed by the BET and BJH theoretical models. The pore size distribution of $\text{Ca}/\text{MoO}_3/\text{Al}_2\text{O}_3$ was concentrated at the average pore diameter of 8.00 nm, the specific surface area was $151.09 \text{ m}^2/\text{g}$, and the total pore volume was $0.302 \text{ cm}^3/\text{g}$. The abundant pores and high pore volume would be favorable to the oxidation reaction because it would assist the adsorption of 4,6-DMDBT, DBT and BT on the catalyst surface.

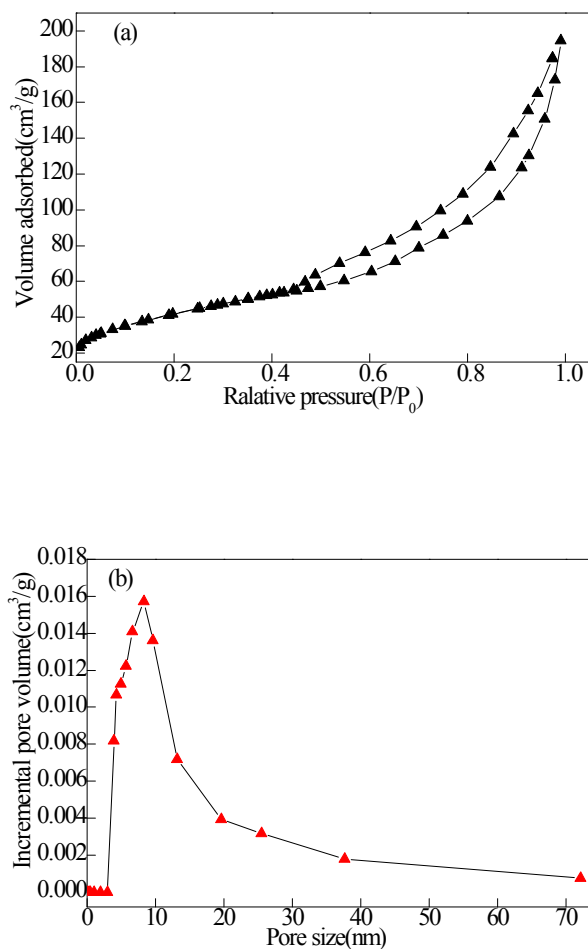
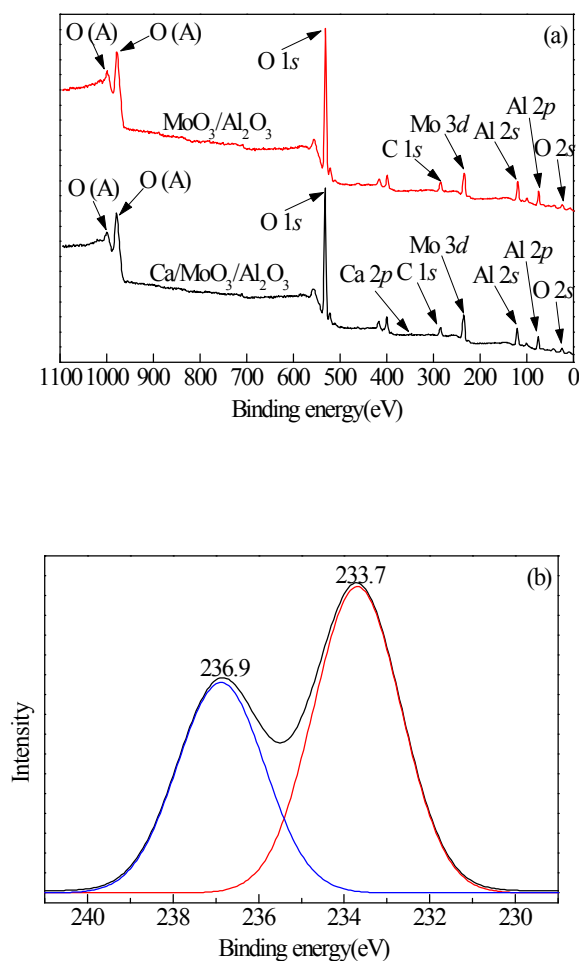


Fig.3. Pore structure parameters of Ca/MoO₃/Al₂O₃. (a) Adsorption-desorption isotherm; (b) Pore size distribution.

Fig.4 shows the XPS spectra of Ca/MoO₃/Al₂O₃ and MoO₃/Al₂O₃. From Fig. 4 (a), the comparison showed that the XPS spectra of Ca/MoO₃/Al₂O₃ had gained a new Ca 2*p* characteristic peak than MoO₃/Al₂O₃. It indicated that the presence of Ca in the catalyst Ca/MoO₃/Al₂O₃. Fig. 4(b) and (d) present the Mo 3*d* spectrum of Ca/MoO₃/Al₂O₃ and MoO₃/Al₂O₃. The appearance of two signals at 233.7 eV (233.0 eV) and 236.9 eV (236.2 eV) for Mo 3*d*_{5/2} and Mo 3*d*_{3/2} respectively. Based on the researches of García-Gutiérrez,⁵ the absorption peak at 232.7 eV corresponded to Mo

⁶⁺, so it shall serve to illustrate the valence of molybdenum element in the catalysts are +6. The comparison of Fig. 4(b) and (d) showed the binding energy (233.7 eV) of the Mo 3d_{5/2} on the Ca/MoO₃/Al₂O₃ catalyst was increased by 0.7 eV with MoO₃/Al₂O₃ (233.0 eV). The result indicated that the electron cloud density of Mo atoms in the Mo=O bands was increased by Ca-doping, which was beneficial to the good association of H₂O₂, and thereby increase the activity of desulfurization. Fig. 4 (c) presents the Ca 2p spectrum of Ca/MoO₃/Al₂O₃. The appearance of two signals at 347.8 eV and 350.9 eV for Ca 2p_{3/2} and Ca 2p_{1/2} respectively, and these binding energy values corresponded to Ca²⁺.⁶



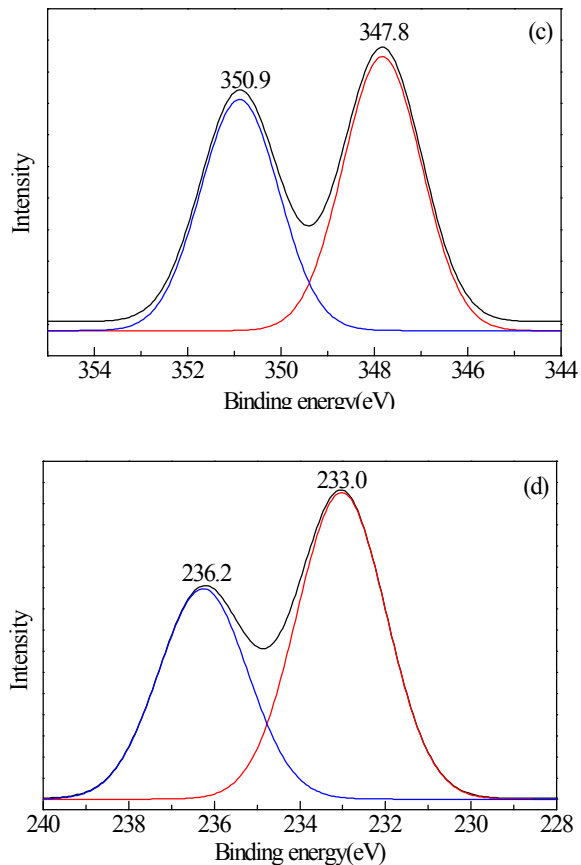


Fig.4. XPS spectra of Ca/MoO₃/Al₂O₃:(a) Survey, (b) Mo 3d, (c) Ca 2p and MoO₃/Al₂O₃:(a) Survey, (d) Mo 3d.

References

- [1] Krishna A G; Ravikumar R V S S N; Kumar T V; et al. Materials Today Proceedings, **2016**, 3(1):54-63.
- [2] Pavlenko V I; Cherkashina N I; Yastrebinskaya A V; et al. World Applied Sciences Journal, **2013**, 25(12):1740-1746.
- [3] Du K; Wei R H; Bai Y N; et al. Advanced Materials Research, **2012**, 554-556:494-497.
- [4] Sing K S W. Pure & Applied Chemistry, **1985**, 57(4):603--619.
- [5] García-Gutiérrez J L; Fuentes G A; Hernández-Terán M E; et al. Applied

Catalysis A General, **2006**, 305(1):15-20.

[6] Eighmy T T; Kinner A E; Shaw E L; et al. Surface Science Spectra, **1999**,
6(3):193-201.