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

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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.\textsuperscript{1} For the Ca/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} (c), owing to the overlap of the characteristic peaks of MoO\textsubscript{3} with that of the Al\textsubscript{2}O\textsubscript{3} appeared at 740 and 640 cm\textsuperscript{-1} (Al-O bands),\textsuperscript{2} the bands of MoO\textsubscript{3} were not observed after the immobilization of MoO\textsubscript{3} on the support. It suggested that MoO\textsubscript{3} was highly dispersed on the Al\textsubscript{2}O\textsubscript{3} support.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{FT-IR spectra of MoO\textsubscript{3} (a), Al\textsubscript{2}O\textsubscript{3} (b) and Ca/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} (c).}
\end{figure}

Fig. 2 shows the powder X-ray diffractions of ammonium molybdate(a), Al\textsubscript{2}O\textsubscript{3}(b), and Ca/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}(c). As shown in Fig. 2, The characteristic peaks of ammonium molybdate at 2\theta= 13.0°, 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 MoO\textsubscript{3} unit.\textsuperscript{3} For Ca/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3}, no crystal diffraction peaks of MoO\textsubscript{3} were found, which indicates that MoO\textsubscript{3} clusters are highly dispersed on the surface of Al\textsubscript{2}O\textsubscript{3}. XRD analysis confirms that the catalyst Ca/MoO\textsubscript{3}/Al\textsubscript{2}O\textsubscript{3} structure is an amorphous phase because of no characteristic diffraction peaks.
Fig.2. X-ray diffractions of ammonium molybdate (a), Al₂O₃ (b) and Ca/MoO₃/Al₂O₃ (c).

The N₂ adsorption desorption isotherm (a) and pore size distribution (b) of Ca/MoO₃/Al₂O₃ are showed in Fig.3. Based on the taxonomy, the adsorption isotherm of Ca/MoO₃/Al₂O₃ exhibit type IV isotherms using IUPAC, revealing that the catalysts are characteristic of mesoporous materials. The adsorption isotherm data were processed by the BET and BJH theoretical models. The pore size distribution of Ca/MoO₃/Al₂O₃ was concentrated at the average pore diameter of 8.00 nm, the specific surface area was 151.09 m²/g, and the total pore volume was 0.302 cm³/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/MoO$_3$/Al$_2$O$_3$. (a) Adsorption desorption isotherm; (b) Pore size distribution.

Fig. 4 shows the XPS spectra of Ca/MoO$_3$/Al$_2$O$_3$ and MoO$_3$/Al$_2$O$_3$. From Fig. 4 (a), the comparison showed that the XPS spectra of Ca/MoO$_3$/Al$_2$O$_3$ had gained a new Ca $2p$ characteristic peak than MoO$_3$/Al$_2$O$_3$. It indicated that the presence of Ca in the catalyst Ca/MoO$_3$/Al$_2$O$_3$. Fig. 4(b) and (d) present the Mo $3d$ spectrum of Ca/MoO$_3$/Al$_2$O$_3$ and MoO$_3$/Al$_2$O$_3$. The appearance of two signals at 233.7 eV (233.0 eV) and 236.9 eV (236.2 eV) for Mo $3d_{5/2}$ and Mo $3d_{3/2}$ respectively. Based on the researches of García-Gutiérrez, the absorption peak at 232.7 eV corresponded to Mo
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/MoO_3/Al_2O_3 catalyst was increased by 0.7 eV with MoO_3/Al_2O_3 (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 H_2O_2, and thereby increase the activity of desulfurization. Fig. 4 (c) presents the Ca 2p spectrum of Ca/MoO_3/Al_2O_3. 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 Ca^{2+}.
Fig.4. XPS spectra of Ca/MoO$_3$/Al$_2$O$_3$: (a) Survey, (b) Mo 3$d$, (c) Ca 2$p$ and MoO$_3$/Al$_2$O$_3$: (a) Survey, (d) Mo 3$d$.

References


