

HIGHLY ACTIVATED MoS_2 AND CoMoS UNSUPPORTED CATALYSTS FOR UPGRADING LIGHT CYCLED OIL

Ying Zheng*, Haiping Zhang and Hongfei Lin

UNB Hydroprocessing Laboratory
Department of Chemical Engineering
University of New Brunswick
Fredericton, NB
Canada, E3C 1H6

Summary

MoS_2 and CoMoS unsupported catalysts were synthesized through an economic hydrothermal approach. Commercially available MoO_3 and $\text{Co}(\text{NO}_3)_3$ were used as the precursors for the catalyst synthesis. Under subcritical water condition, a highly dispersed nanosized MoS_2 and CoMoS catalysts with high surface area and high crystalline were synthesized. The catalysts were applied to hydrotreat light cycled oil. The hydrodesulfurization activities of both catalysts are high and CoMoS is slightly better than MoS_2 . The catalysts were characterized using a variety of characterization techniques.

Keywords

unsupported catalyst, $\text{MoS}_2/\text{CoMoS}$, light cycled oil, hydrotreating

Introduction

Molybdenum (Mo) sulfide catalysts have been extensively used in petroleum hydroprocessing for several decades. MoS_2 supported on $\gamma\text{-Al}_2\text{O}_3$ and promoted by Co or Ni are widely used^[1, 2]. Deposition of coke and metals on supported MoS_2 catalysts results in rapid deactivation in commercial plants. One approach to limiting the catalyst deactivation is to perform the reaction in slurry hydrocracking reactors using unsupported Catalyst^[3]. Unsupported MoS_2 catalyst commonly has low surface area, which deteriorates its activity in hydroprocessing and hydrotreating petroleum oil. In this work, nanosized MoS_2 , CoMoS unsupported catalysts with high surface area were synthesized using hydrothermal approach.

Experimental

The unsupported Mo based sulfide catalysts were synthesized using hydrothermal method^[4]. MoO_3 was purchased from Strem Chemicals, $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ was purchased from ACROS Organics. $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ and HCl were purchased from Fisher Scientific. Mix MoO_3 , $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ and HCl and put the mixture into autoclave and react at 320°C for 2 hours. When cobalt is involved, keep MoO_3 constant, and add $\text{Co}(\text{NO}_3)_2$ making Co : (Mo+Co)=43% by moles. After 2 hours, the synthesized unsupported catalyst was washed with distilled water and spray-dried with ethanol.

The synthesized catalysts were used to hydrotreat light cycled oil in a 1L autoclave. Catalyst and light cycled oil at a ratio of 1:200 by mass were charged to the 1L autoclave reactor. The reaction took place at 375°C under 1400 psi for 8h.

Results and Discussion

The physical properties of unsupported Mo based sulfide catalysts are shown in Table 1.

Table 1 Composition and properties of fresh unsupported Mo based sulfide catalysts

Catalyst	Synthesis Temperature	Surface area (m ² /g)
$\text{MoS}_2(1)$	200°C	85
$\text{MoS}_2(2)$	270°C	218
$\text{MoS}_2(3)$	320°C	156
CoMoS	320°C	62.39

Three unsupported MoS_2 catalysts were synthesized at different temperature, ranging from 200°C to 320°C . The greatest surface area (218 m²/g) is obtained at 270°C . When the synthesis temperature rises up to 320°C , the surface area reduces significantly. When the Co promoter is added, a further reduction in surface area is observed.

* To whom all correspondence should be addressed

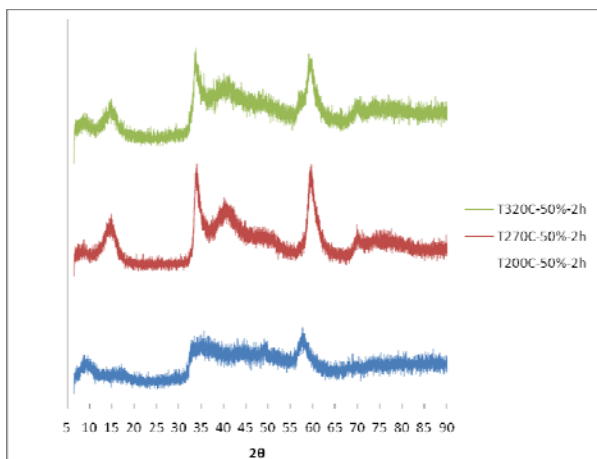


Figure 1 XRD patterns of unsupported MoS₂ catalysts

Figure 1 presents the XRD patterns for the unsupported MoS₂ catalysts synthesized at different temperature. The MoS₂ synthesized at low temperature (200°C) exhibits weak XRD peaks, indicating a very poorly crystalline structure characteristic of the molybdenum disulfide. The XRD patterns also showed that the two catalysts synthesized at relatively high temperatures formed good crystalline.

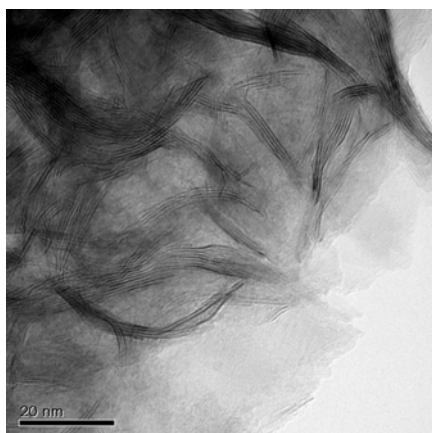


Figure 2 TEM images of MoS₂(3) catalysts

Figure 2 shows the TEM image of MoS₂ catalyst synthesized at 320°C. The black thread-like fringes in Figure 2 correspond to the MoS₂ slabs. Statistical study of the TEM images of all three MoS₂ catalysts suggested that increase in synthesis temperature leads to longer slabs and lower number of layers for one crystal, but higher number of crystallines.

The four catalysts were used to hydrotreat light cycled oil. The property of the light cycled oil is shown in Table 2.

Table 2 The property of the light cycled oil

Sulfur content	Nitrogen content	Density @ 20°C
1.5 wt%	156 ppm	0.96 mg/L

The LCO used in this experiment, characterized by high density, high aromatic content, and high sulfur content, is a typical inferior feedstock for hydrotreatment.

The reaction results are shown in Table 3. Comparing the three MoS₂ catalysts, MoS₂ synthesized at 200°C shows the lowest activity. This is expected since MoS₂(1) has poor crystalline structure. Although MoS₂(2) has the largest surface area, its HDS and HDN activities are significantly lower than MoS₂(3), indicating that surface area is not directly related to the catalyst activity. It is also seen that CoMoS catalyst exhibits much higher HDS and HDN activities than the three MoS₂ catalysts.

Table 3 Hydrotreating results

Catalyst	Density of products @20°C	HDS conversion	HDN conversion
MoS ₂ (1)	0.95	0.44	~ 0
MoS ₂ (2)	0.94	0.62	0.57
MoS ₂ (3)	0.92	0.90	0.95
CoMoS	0.91	0.97	n.d.

References

- (1) Topsoe, H.; Clausen B.S.; Massoth F.E. in: J.R. Anderson, M. Boudart (Eds.), *Catalysis Science and Technology*, vol. 11, Springer, Berlin, 1996, p. 162.
- (2) Ding, L.H.; Zheng Y.; Zhang Z.; Ring Z.; Chen J. *Journal of Catalysis* **2006**, 241, 435.
- (3) Yoosuk, B.; Kim .H.; Song C.; Ngamcharussrivichai C.; Prasassarakich P. *Catalysis Today* **2008**, 103, 14
- (4) Li, W.J.; *Journal of Crystal Growth* **2003**, 250, 418.