

Preparation and Desulfurization of Unsupported Nano-MoS₂ Catalyst

YUQIN ZHU* and HAIRUI ZHANG

School of Chemistry & Chemical Engineering, Xian Shiyou University, Xi'an, P.R. China

*Corresponding author: Fax: +86 29 68905893; Tel: +86 13032965049; E-mail: zhuyq@xsyu.edu.cn

Received: 11 July 2015;

Accepted: 13 August 2015;

Published online: 5 December 2015;

AJC-17677

Nano-sized unsupported MoS₂ catalysts for hydro-desulphurization of diesel oil were synthesized by a hydrothermal reduction and characterized. The influence of synthetic temperature on the growth morphology, specific surface areas, mean particle sizes of MoS₂ catalysts and desulfurization performance were investigated. The MoS₂ fibers showed lots of defects and they were easily bended, which increased the number of active sites on the catalyst. Under the reactive conditions of 360 °C, 6.0 MPa, 600 ratio of hydrogen to oil (volume ratio) and 2 h⁻¹ of volumetric space velocity in a fixed bed reactor, the desulfurization rate to the straight run diesel was about 98.23 %, that is, the total amount of sulfur by 565 µg/g fell to 10 µg/g, which met the requirements for the hydrodesulphurization of diesel oil.

Keywords: Unsupported nano-MoS₂ catalyst, Hydrodesulphurization, Hydrothermal reduction.

INTRODUCTION

With the increasing concern on energy saving and environmental protection in recent years, the sulfur content of fuel oils used in motor vehicles is becoming lower and lower and most of the developed countries have used super-low sulfur gasoline and diesel fuels. The sulfur content of China's vehicle emissions is also gradually meeting the third type standard of the pertinent World Fuel Regulations [1]. So far, the main productive technology of clean gasoline and diesel fuels in the petrochemical industry remains hydro-treatment catalysis whose kernel is hydrogenation catalyst. Compared with the traditionally supported catalysts, which have been used for the desulfurization of gasoline and diesel fuels, unsupported catalysts have higher catalytic activity and larger specific surface area, therefore, research effort is increasingly devoted to the development of unsupported catalysts.

So far the research on unsupported catalysts mainly encompasses metal phosphides, metal carbon compounds and metal sulfides [2-15]. Generally, active components of non-sulfide hydro-treatment catalysts are oxides, these hydro-treatment catalysts will have higher activity when active components exist as sulfides. Therefore non-sulfide hydro-treatment catalysts must be pre-sulphurized before used. While there is no need to add toxic sulfur compounds to unsupported metal sulfide catalysts, the application process is relatively simple, so the metal sulfide catalysts form the basis for the principal development direction of hydrogenation catalysts.

The study on the preparation technology of unsupported metal sulfide catalysts and desulfurization property is still insufficient. In this paper, nano-sized unsupported MoS₂ catalysts for the desulfurization of diesel oil were synthesized by a hydrothermal reduction, their characterization, the influence of synthetic temperature on the growth morphology of MoS₂ catalysts and desulfurization performance were investigated. These will lay certain theory foundation for the industrial application of MoS₂ catalysts.

EXPERIMENTAL

The hydrothermal reduction was used to prepare MoO₃, the precursor of MoS₂ catalyst, the nano-MoS₂ catalyst was then synthesized by a hydrothermal deoxidization. Materials for the hydrothermal reduction to prepare MoO₃ (MoO₃-Hy) and for hydrothermal deoxidization to synthesize MoS₂ are shown in Tables 1 and 2, respectively. Four types of nano-MoS₂ catalysts (denoted by MoS₂-A, MoS₂-A₂, MoS₂-A₃ and MoS₂-B) were made with hydrothermal deoxidization; their ratios of raw materials and reaction conditions are shown in Table-3.

TABLE-1
MATERIALS FOR THE PREPARATION OF
MoO₃ BY HYDROTHERMAL REDUCTION

Materials	Specification (%)
Hydrochloric acid	37.0
Sodium molybdate	≥ 99.5

TABLE-3
CONDITIONS OF HYDROTHERMAL DEOXIDIZATION FOR THE PREPARATION OF MoS₂

Samples	Ratios of materials	Reaction conditions
MoS ₂ -A	MoO ₃ : sodium sulfide nonahydrate : hydrochloric acid = 0.72 g : 11.07 g : 60 mL (0.4 M)	200 °C, 12 h
MoS ₂ -A2	MoO ₃ : sodium sulfide nonahydrate : hydrochloric acid = 0.90 g : 13.84 g : 60 mL (0.4 M)	250 °C, 12 h
MoS ₂ -A3	MoO ₃ : sodium sulfide nonahydrate : hydrochloric acid = 0.90 g : 13.84 g : 60 mL (0.4 M)	270 °C, 12 h
MoS ₂ -B	MoO ₃ : sodium sulfide nonahydrate : hydrochloric acid = 1.44 g : 22.14 g : 60 mL (0.4 M)	250 °C, 12 h

TABLE-2
MATERIALS FOR THE PREPARATION OF MoS₂ BY HYDROTHERMAL DEOXIDIZATION

Materials	Specification (%)
Hydrochloric acid	37.00
Nitrogen	99.99
Alcohol	95.00
MoO ₃	≥ 99.50
Sodium sulfide nonahydrate	≥ 98.00

Hydrothermal reduction for the preparation of MoO₃:

The mixture of sodium molybdate and hydrochloric acid in certain proportion was placed in the inner of a reactor and it was heated from ambient temperature to 150 °C at an appropriate rate. The reaction temperature (150 °C) was maintained for 6 h and then the reactor's inner was rapidly removed and cooled at the ambient temperature to end the hydrothermal reaction. Deionized water was added to the solution to remove sodium ions by high speed centrifugation. Finally the precipitant was placed in an oven for several hours and a quantity of pale blue high purity MoO₃ was obtained.

Hydrothermal deoxidization for synthesizing MoS₂:

The mixture of MoO₃ granule, sodium sulfide nonahydrate and hydrochloric acid in certain proportion was put into the inner of a high temperature reactor and it was heated to 250 °C at an appropriate heating rate. The temperature was maintained for 6 h to ensure the reaction's completion. The inner was removed rapidly to stop the hydrothermal reaction. Deionized water and alcohol were added to the solution of reaction products to remove sodium ions in the solution by high speed centrifugation. The black product washed and filtrate was then heated in the reactor's oil bath. Air was pumped continually to maintain a vacuum state and nitrogen was added to dry black product (MoS₂) for 24 h. Finally, MoS₂ powder was preserved in a dryer.

RESULTS AND DISCUSSION

Laser Raman analysis: Fig. 1 shows laser Raman spectra of MoO₃ and MoS₂-A3. Mo-O vibration characteristic peaks of MoO₃ (290, 335.7, 667.1, 819.6 and 994.8 cm⁻¹) were completely consistent with reference values in the literature [16], the peak's shape, sharpness and signal strength, all indicated a well-crystallized oxide powder.

The characteristic vibration of MoS₂-A3 only appeared at 380.5, 404.2 and 457.5 cm⁻¹, this was completely consistent with the vibration of MoS₂ reported in the literature [16], indicating that MoS₂-A3 was composed of MoS₂. That is to say, MoO₃ had been completely transformed into MoS₂ through Na₂S and HCl solvent action by hydrothermal reduction treatment above 200 °C. The characteristic peak intensity of

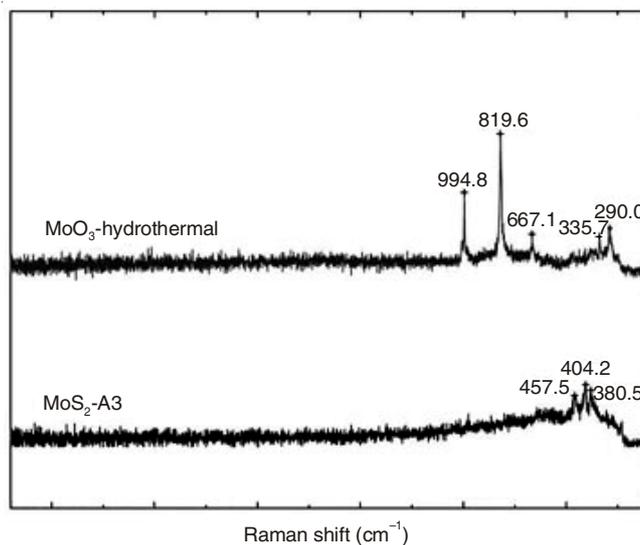


Fig. 1. Laser Raman spectra of MoO₃ and MoS₂-A3

MoS₂-A3 was very low and the peak shape was wider, which may have been caused by two reasons as follows: the powder particles produced by hydrothermal reduction synthesis were extremely fine because of particle effect and the crystallinity of MoS₂-A3 was poor.

Low temperature N₂ physical adsorption: The authors measured the specific surface area of sulfide molybdenum powder by BET method. The results showed that, under low temperature and low concentration ratio conditions, the MoS₂-A produced by hydrothermal reduction had the highest specific surface area (412.3 m²/g). When the synthesis temperature increased to more than 250 °C, the specific surface area of MoS₂ decreased rapidly. The specific surface area of MoS₂-B was 63.8 m²/g at a high concentration ratio, this indicated that a high degree of crystal growth of MoS₂-B powder may have occurred or that there was significant stacking and re-joining of powders. The specific surface area for molybdenum sulfide powder was similar to the reported values [16].

Effects of hydrothermal deoxidization synthesis temperature on structure of MoS₂: Table-4 showed the statistics results of length and width of MoS₂ (or MoO₃) nanowire stack which was synthesized by hydrothermal deoxidization. MoS₂-A, MoS₂-A2 and MoS₂-A3 were MoS₂ powders with synthesis temperature of 200, 250 and 270 °C, respectively. The structure of MoS₂-A was amorphous (Fig. 2a-2c), its average diameter was 13 nm and a small quantity of MoS₂ appeared in the form of nanowire stack crystal (Fig. 2d). The number of stack layers was low and the length of the nanowire stack was short. It showed that the lowest synthesis temperature was not less than 200 °C to gain nanowire stack crystal of MoS₂.

TABLE-4
LENGTH (L) AND WIDTH (D) OF MoS₂ (OR MoO₃) FIBERS

Name		Mean value (nm)	Max value (nm)	Min value (nm)	Standard deviation (nm)
MoO ₃	D	120.9	322.9	47.1	39.7
	L	2150	5492	464	844
MoS ₂ -A	D	13	33.7	7.3	3.8
MoS ₂ -A2	D	2.1	3.3	1	0.5
	L	26.1	72.5	13.5	9.1
MoS ₂ -A3	D	2.3	4.7	0.9	0.755
	L	31.7	72.4	5.87	12.7
MoS ₂ -B	D	3.3	7.7	1.2	1
	L	38.2	96	15.3	14.1

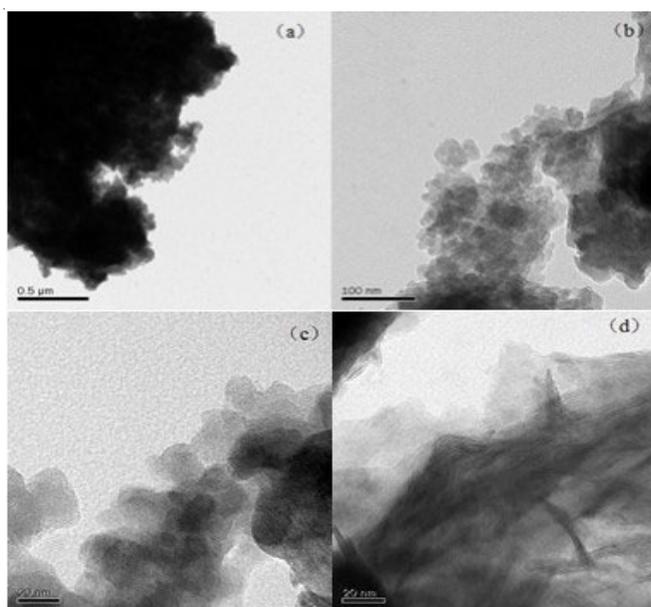


Fig. 2(a)-(d). TEM images of MoS₂-A at 200 °C and 12 h

Fig. 3 is the TEM images of MoS₂-A2 synthesized by hydrothermal deoxidization under the condition of 250 °C and 12 h, which was similar to MoS₂-A3's TEM images synthesized at 270 °C. Nano-crystal stack of MoS₂-A2 dispersed equably and highly without having been united, the average length was 26.1 nm and the diameter was 2.1 nm, all smaller than those of MoS₂-A3, 31.7 nm and 2.3 nm respectively. It showed that

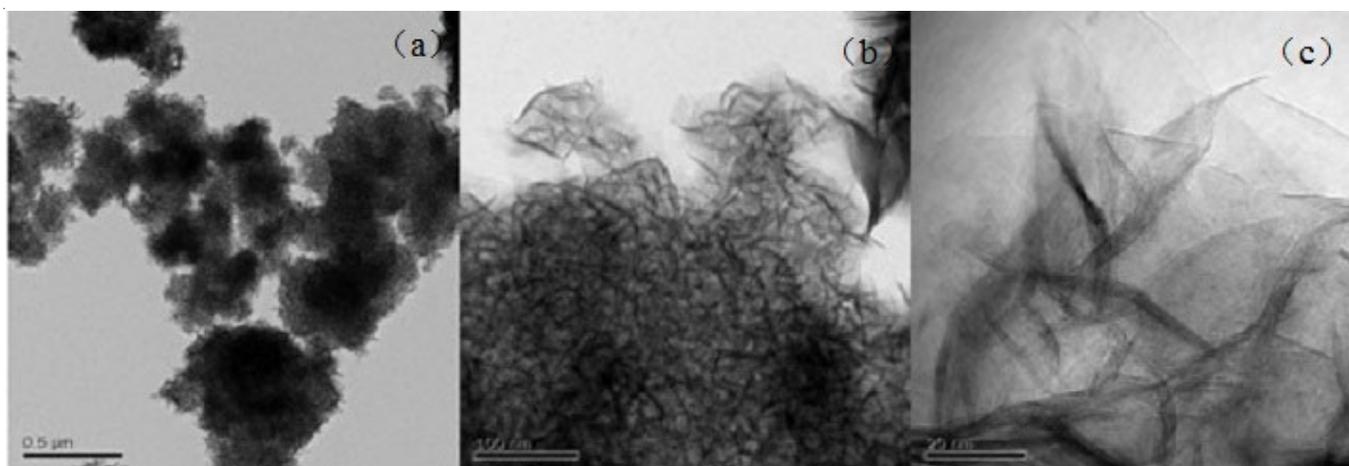


Fig. 3(a)-(c). TEM images of MoS₂-A2 at 250 °C and 12 h

the size of MoS₂ depended on synthesis temperature; the higher synthesis temperature can increase crystal size and improve crystallinity. Because the size of crystal MoS₂ was very small (2-3 nm) and there were plenty of Mo atoms on lattice fringe, so that lots of sulfur vacancies were brought. This is useful to the formation of active sites in catalytic hydrogenation process. Therefore, we can adjust the synthesizing temperature to control the size of the catalyst and to achieve the aim of changing the number of catalyst active sites.

Catalyst's hydrogenation desulfurization performance:

The hydro-desulfurization reaction for straight-run diesel oil occurred in a fixed bed reactor under the following conditions: 2 g of MoS₂ catalyst, 360 °C, 6.0 MPa of hydrogen pressure, 600 ratio of hydrogen to oil (vol.) and 2 h⁻¹ of volumetric space velocity. No. 1, No. 2, No. 3 and No. 4 represent catalyst samples of MoS₂-A2, MoS₂-A3, MoS₂-A and MoS₂-B, respectively.

Influence of synthetic conditions on hydro-desulphurization: Fig. 4 showed that MoS₂-A (No. 3) catalyst had the highest desulfurization rate (98.23 %). Because MoS₂-A catalyst had bigger specific surface area, which was good for active component being dispersed on the surface of catalysts with thin layers or very fine granules, this kind of highly dispersed structure could produce more active center easily. However, too much metal load amount can result in the stacking of edge active component, which reduced the specific surface area and decreased the catalytic effects.

Influence of reaction temperature on hydro-desulphurization: The influence of reaction temperature on the catalyst's hydrogenation desulfurization performance is shown in Fig. 5. The desulfurization rate increased with the reaction temperature, it may reach the maximum value (98.23 %) under 360 °C. This is because the reaction rate is accelerated as the reaction temperature increases. The desulfurization rate changed little when the temperature exceeded 360 °C, which indicated that most of the sulfur-containing compounds of straight run diesel had been basically transformed. Considering the effect of thermodynamics and other indicators of the refining of diesel oil (such as reverse reaction of aromatics saturation, cetane number reduction), the optimum reaction temperature may be at 360 °C.

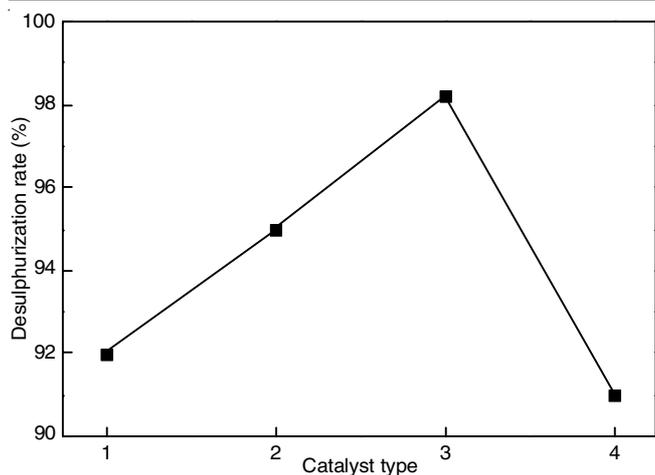


Fig. 4. Influence of synthetic conditions on hydro-desulphurization

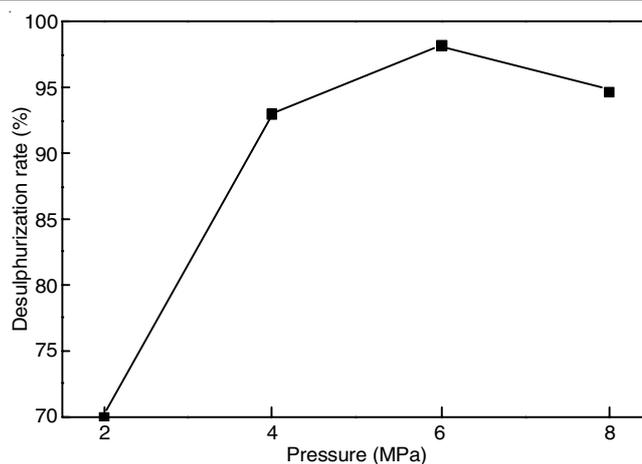


Fig. 6. Influence of reaction pressure on hydro-desulphurization

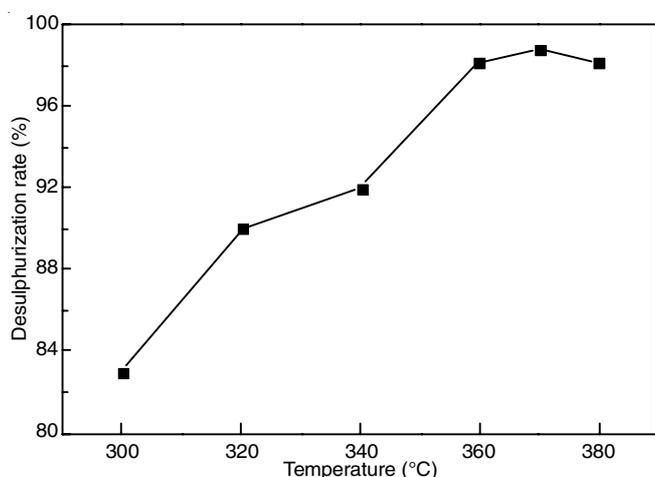


Fig. 5. Influence of reaction temperature on hydro-desulphurization

Influence of reaction pressure on hydro-desulphurization: Fig. 6 showed the influence of reaction pressure on hydro-desulphurization. The desulfurization rate increased with pressure as pressure was less than 6 MPa, it could reach the maximum around 6 MPa and then it decreased with the increasing of pressure when pressure was more than 6 MPa. This is because the number of molecules per unit volume increases with the reaction pressure, which improves the contact probability of molecules of straight-run diesel to the catalyst and enhances the reaction rate at the same time. However, the reactants will be turned into liquid when pressure is increased to a certain value, which will make the hydro-desulphurization become poor. Therefore, the optimum pressure is about 6 MPa.

Conclusions

Raman spectroscopy and TEM analysis results showed that nano-molybdenum sulphide crystallization with high purity, high dispersivity and a uniform distribution, could be produced by hydrothermal reduction method. The average fibre length was about 30 nm, with a width of less than 3 nm and a stack number of less than 8 as evidenced by the processing of TEM images of the crystallized molybdenum sulphide. The amorphous MoS₂ was obtained that dispersed equably and highly at the synthesis temperature of higher than 200 °C and the average diameter was about 13 nm. Increasing the

synthesis temperature could promote the growth of catalyst and change the catalyst size and distribution, that led to the change of Mo atom quantity on lattice fringe and the quantity of catalyst active sites. Meanwhile, the generation of a huge number of nano-microcrystal MoS₂ fibers could restrain the formation of micro-porosity and make the specific surface area of MoS₂ descend from 420 to 65 m²/g.

Among the catalyst samples prepared, MoS₂-A had the best desulfurization effect. For MoS₂-A, the optimum reaction conditions of hydro-desulphurization were as follow: 360 °C, 6 MPa, 600 ratio of hydrogen to oil (volume ratio), 2 h⁻¹ of volumetric space velocity and the desulfurization rate to straight run diesel was about 98.23 %.

ACKNOWLEDGEMENTS

The authors acknowledged the support of the Scientific Research Program Funded by Shaanxi Provincial Education Department (Program No. 14JK1563).

REFERENCES

- B.H. Liu, G.X. Yao, J. Liao and J. Petrochem, *Ind. Trend.*, **27**, 12 (2001) (in Chinese).
- P. Afanasiev, *J. Catal.*, **269**, 269 (2010).
- N. Liu, *J. Catal.*, **215**, 254 (2003).
- S.T. Oyama, P. Clark, X. Wang, T. Shido, Y. Iwasawa, S. Hayashi, J.M. Ramallo-López and F.G. Requejo, *J. Phys. Chem. B*, **1913**, 106 (2002).
- M.K. Neylon, S.K. Bej, C.A. Bennett and L.T. Thompson, *Appl. Catal. A*, **232**, 13 (2002).
- M. Saito and R.B. Anderson, *J. Catal.*, **63**, 438 (1980).
- S. Ramanathan, C.C. Yu and S.T. Oyama, *J. Catal.*, **173**, 10 (1998).
- B. Yoosuk, C. Song, J.H. Kim, C. Ngamcharussrivichai and P. Prasassarakich, *Catal. Today*, **149**, 52 (2010).
- H. Farag, *Appl. Catal. A*, **331**, 51 (2007).
- A. Olivas, T.A. Zepeda, I. Villalpando and S. Fuentes, *Catal. Commun.*, **9**, 1317 (2008).
- G.H. Jin, J.H. Zhu, H.L. Ju, D. Sun and J.B. Gao, *J. Chem. Ind. Eng.*, **157**, 799 (2006) (in Chinese).
- L.X. Chang, H.B. Yang, W.Y. Fu, J.Z. Zhang, Q.J. Yu, H.Y. Zhu, J.J. Chen, R.H. Wei, Y.M. Sui, X.F. Pang and G.T. Zou, *J. Mater. Res. Bull.*, **43**, 2427 (2008).
- G.A. Camacho-Bragado, J.L. Elechiguerra, A. Olivas, S. Fuentes, D. Galvan and M.J. Yacamán, *J. Catal.*, **234**, 182 (2005).
- Z. Wu, V.M.L. Whiffen, W. Zhu, D. Wang and K.J. Smith, *Catal. Lett.*, **144**, 261 (2014).
- Y.J. Yi, B.S. Zhang, X. Jin, L. Wang, C.T. Williams, G. Xiong, D. Su and C. Liang, *Mol. Catal. A*, **351**, 120 (2011).
- A.A. Tsyganenko, F. Can, A. Travert and F. Maugé, *Appl. Catal. A*, **269**, 189 (2004).