Preparation and Characterization of an Unsupported Nano-MoS₂ Catalyst

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Nano-sized unsupported MoS₂ hydrodesulphurization catalysts were synthesized using a novel and mainly hydrothermal, reduction method. The structures of the catalysts, their specific surface areas, mean particle sizes and micro-morphologies were characterized and analyzed. It was the first time that MoS₂ with a specific surface area of as high as 412 m² g⁻¹ area was obtained successfully. Most of the MoS₂ had the shape of stacked platelets (slab < 8), which were between 30 and 40 nm long and 2.0 to 3.5 nm in diameter. It was found that the MoS₂ fibres were readily-flexed and contained many defects, which increased the number of active sites on the catalyst: thus they were easily able to meet the requirements of deep hydro-treatment type desulphurization of diesel oil.

Key Words: MoS₂, Unsupported catalyst, Hydro-treatment desulphurization, Diesel oil.

INTRODUCTION

With the energy savings and environmental protection requirements being strictly regulated in recent years, developed countries have accelerated the uptake of super-low sulphur gasoline and diesel fuels for their vehicles. The sulphur content of China's vehicle emissions is also gradually meeting the third type standard of the pertinent World Fuel Regulations¹. Although various techniques of clean gasoline and diesel fuel production are emerging, the main one in the petrochemical industry remains hydro-treatment catalysis. Traditionally supported catalysts, which have been used for the desulphurization of gasoline and diesel fuels, cannot meet the requirements of the World Fuel Regulations. Therefore research effort is increasingly devoted to the development of unsupported catalysts. Thus far, the research on unsupported catalysts mainly encompasses: metal phosphides, metal carbon compounds and metal sulphides²⁻⁹. Generally, active components of non-sulphide hydro-treatment catalysts are oxides. According to experience and theoretical research, these hydro-treatment catalysts have higher activity when active components exist as sulphides. Therefore non-sulphide hydro-treatment catalysts must be pre-sulphurized before use. The process ensures that the active components of the catalyst react with hydrogen sulphide at a given temperature and thereby change oxides into sulphides.

There is no need to add toxic sulphur compounds to unsupported metal sulphide catalyst; the application process is

relatively simple and the metal sulphide catalyst forms the basis for the principal development direction of hydrogenation catalysts.

In this paper, nano-sized unsupported MoS₂ catalysts for the deep desulphurization of diesel oil were characterized and synthesized by a hydrothermal reduction method and a high temperature hydrogen sulphide deoxidization method.

EXPERIMENTAL

The hydrothermal reduction was used to prepare MoO₃, the forming body of the MoS₂ catalyst: the nano-MoS₂ catalyst is then synthesized by hydrothermal deoxidization which is subsequently compared with high-temperature hydrogen sulphurization.

Materials for the hydrothermal reduction based preparation of MoO₃(MoO₃-Hy), of high-temperature hydrogen sulphurization to produce MoS₂(MoS₂-D) and of hydrothermal deoxidization to synthesise MoS₂ are shown in Tables 1-3, respectively. Five types of nano-MoS₂ catalysts (denoted by MoS₂-A, MoS₂-A2, MoS₂-A3, MoS₂-B and MoS₂-C) were produced by hydrothermal deoxidization.

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

Material	Specification (%)
Hydrochloric acid	37
Sodium molybdate	≥ 99.5

TABLE-2
MATERIALS FOR THE PREPARATION OF MoS₂ BY
HYDROGEN SULPHURATION

Material	Specification (%)
Hydrochloric acid	37
Sodium hydroxide	98
Hydrogen	99.99
Sodium sulphide nonahydrate	≥ 98
Nitrogen	99.99
Sodium molybdate	≥ 99.5

TABLE-3
MATERIALS FOR THE PREPARATION OF
MoS₂ BY HYDROTHERMAL DEOXIDISATION

Material	Specification (%)
Hydrochloric acid	37
Nitrogen	99.99
Alcohol	95
MoO ₃	≥ 99.5
Sodium sulphidenonahydrate	≥ 98

Preparation methods

Hydrothermal reduction for the preparation of MoO₃:

The mixture of sodium molybdate and hydrochloric acid (state proportions here) was placed in the centre of a reactor and heated from ambient temperature to 150 °C at an appropriate rate. The reaction temperature was maintained for 6 h and then the reactor's inner core was rapidly removed and cooled to 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 obtained.

High temperature hydrogen sulphuration for the synthesis of MoS₂: Sodium sulphide nonahydrate was added, from a dropping funnel, to a three-necked flask containing hydrochloric acid: hydrogen and nitrogen were then added to produce H₂S gas. Then water vapour was removed from the gaseous H₂S in a two-necked flask filled with SiO₂ desiccant. The MoO₃ was allowed to react with the gaseous H₂S at a high temperature for 2 h in a muffle furnace, while simultaneously recycling the drained-off gas through an NaOH solution. Continual addition of H₂, N₂ and H₂S to the muffle furnace was undertaken until the temperature had decreased to ambient levels. Finally the product was put in a drying oven with N₂ protection.

Hydrothermal deoxidization for synthesizing MoS₂:

The mixture of MoO₃ granules, sodium sulphide nonahydrate and hydrochloric acid (state the proportions here) was put into the centre of a high-temperature reactor and heated to 250 °C at an appropriate rate. The temperature was maintained for 6 h to ensure that the reactions' completion. The reactor core was then removed rapidly to stop the hydrothermal reaction. Deionized water and alcohol were added to the solution of the reaction products to remove sodium ions in the solution by high-speed centrifugation. The black product was then heated, washed and filtered in the reactor's oil bath. Air was pumped continually to maintain a partial vacuum and nitrogen was added to dry the black product (MoS₂) for 24 h. Finally, the MoS₂ powder arising was preserved in a dryer.

RESULTS AND DISCUSSION

Fig. 1 shows the FT-IR spectra of MoO₃(MoO₃-Hy) produced by hydrothermal reduction, of MoO₂ produced by hydrogen reduction with MoO₃ and of MoS₂-A3 by hydrothermal deoxidization, respectively. Their infrared spectra near 3450, 2356 and 1615 cm⁻¹ have been absorbed to varying degrees, corresponding to the asymmetric stretching vibration of the adsorbed water, asymmetric stretching vibration of carbon dioxide and bending deformation vibration of water. The reason is that the sulphide still contained a small amount of water despite the drying process. There was significant Mo-O infrared absorption of MoO₃ at 580.1, 872.1 and 998.6 cm⁻¹; absorption peaks did not appear for MoO₂ within the measurement range of 4000-400 cm⁻¹, indicating that MoO₂ might not have infrared activity. There was still an absorption peak at 3237.4 cm⁻¹ for MoO₃, which was caused by the symmetric stretching vibration of OH groups of crystalline water in the MoO₃ powder, but there was no evidence of the absorption peak in commercially available MoO₃ powder. Complex infrared absorption of MoS₂-A3 appeared at 466.7, 556.2, 671.8, 928.9 and 1166.5 cm⁻¹ to varying extents. This was basically consistent with the infrared spectra of molybdenum disulphide when produced by ammonium molybdate thermal decomposition⁸, indicating that MoO₃, the basis for the formation of the MoS₂, can be completely turned into MoS₂ under condition using Na₂S and HCl as reactants and solvents in the hydrothermal reduction process.

Fig. 1. Fourier infrared spectra of MoO₃, MoO₂ and MoS₂

Fig. 2 shows laser Raman spectra of MoO₃, MoS₂-A3 and MoS₂-D. 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 literature⁹; the peak's shape, sharpness and signal strength, all indicated a well-crystallized oxide powder.

Fig. 2. Laser Raman spectra of MoO₃, MoS₂-A3 and MoS₂-D

The vibration characteristic peaks of MoS₂-D were basically consistent with Mo-O in MoO₃ except between 377.5 and 465.2 cm⁻¹, this indicated that there were also Mo-O groups in the MoS₂-D. The Mo-O characteristic peak intensity of MoS₂-D was, additionally, higher and more accurate than that of MoO₃, indicating that the crystal growth of Mo-O groups in MoS₂-D was better than in MoO₃. The MoS₂-D was produced by high-temperature hydrogen sulphuration of MoO₃, which may have led to further crystal growth by sintering of the powder during the high-temperature treatment process. There were characteristic peaks of Mo-S groups in molybdenum sulphide between 377.5 and 465.2 cm⁻¹. So there were at least two types of Mo-O and Mo-S groups in the MoS₂-D sample.

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 literature⁹, indicating that the MoS₂-A3 was composed of MoS₂, just as its FT-IR analysis results showed. That is to say, MoO₃ had been completely transformed into MoS₂ through Na₂S and HCl solvent action and hydrothermal reduction treatment above 200 °C. The characteristic peak intensity of 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 being extremely fine because of particle effects and the crystallinity of MoS₂-A3 being poor.

Low temperature N₂ physical adsorption: The authors measured the specific surface area of the sulphide molybdenum powder by low-temperature nitrogen physical adsorption static capacity method (BET method); salient data are shown in Table-4. The results showed that, under low-temperature and low-concentration ratio conditions, that MoS₂-A produced by hydrothermal reduction had the highest specific surface area (412.3 m² g⁻¹). When the synthesis temperature increased to more than 250 °C, the specific surface area of MoS₂-A decreased rapidly. The specific surface area of MoS₂-B was 15.9 m² g⁻¹ 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

TABLE-4 SPECIFIC SURFACE AREAS OF MOLYBDENUM SULPHIDE			
Samples	MoS ₂ -A	MoS ₂ -B	MoS ₂ -C
Specific surface area (m ² g ⁻¹)	412.3	15.9	63.8

of powders and flocs thereof. The specific surface area for the molybdenum sulphide powder was similar to published reference values⁹.

The transmission electron microscopic image of MoS₂-D is shown in Fig. 3. It shows that this MoS₂-D was composed of a large MoO₂ crystal, which was long, fibrous and clavate (*i.e.* greater than 2 μm long and of 103 nm average width). The growth orientation of these crystals was irregular, there were many small, filamentous crystals especially at the edges: these were tiny and their growth orientation lay parallel to the surface normal. These small crystals were shown to be nano-molybdenum sulphide crystals by further electron diffraction analysis. The outer surface of the MoO₂ crystals showed a thin layer presence of MoS₂. The TEM analysis also confirmed that there was more MoS₂ in the MoS₂-D sample. The results were consistent with the aforementioned Raman spectrum analysis.

Fig. 3. TEM image of MoS₂-D

Fig. 4 shows the electron diffraction image of MoO₂ in MoS₂-D. There were many tiny fibres with regular diffraction rings on the surface of the MoO₂ crystal, indicating that the fibrous material was of tiny nano-crystalline form. It was confirmed that these small crystals belonged to the family of orthorhombic hexahedral molybdenum sulphide crystals through the *d*-value analysis of the diffraction ring.

Fig. 5 shows the TEM picture of MoS₂-A3 from where it can be seen that MoS₂-A3 was composed of countless, tiny, fibrous crystals dispersed evenly in an amorphous matrix. The average fibre length was 30 nm and width less than 3 nm. Each bundle of fibres was composed of about 2 to 5 fibres. The TEM image is a transmission image of the crystal in a plane, so these fibres were formed by small MoS₂ crystals which are built-up in layers in a flat panel stacking arrangement. The layered stacking structure was extremely important for catalytic hydrogenation and thus deep desulphurization.

Fig. 4. Electron diffraction image of MoO₂ in MoS₂-D

Fig. 5. Transmission electron micrograph of MoS₂-A3

Conclusion

The high-temperature hydrogen sulphide deoxidization and hydrothermal reduction were two types of more suitable

methods for the synthesis of molybdenum sulphide powder. Infrared spectroscopy, Raman spectroscopy and TEM analysis results showed that the powder obtained from high-temperature hydrogen sulphide deoxidization was a mixture with, mainly, highly crystalline MoO₂ and less crystalline nano-MoS₂. MoS₂ fibres spread and grew to the centre of the MoO₂ crystal surface along the surface normal direction: the particle size was larger and more stacking manifest. Fibrous nano-molybdenum sulphide crystallization with high purity, high dispersivity and a uniform distribution, could be produced by the hydrothermal reduction method. The average fibre length was *ca.* 30 nm, with a width of less than 3 nm as evidenced by the processing of TEM images of the crystallized molybdenum sulphide. The molybdenum sulphide, MoS₂-A, as produced by hydrothermal reduction method, had the highest specific surface area, at up to 412.3 m² g⁻¹.

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