Experimental Study on Unsupported Nano-MoS₂ Catalyst

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Six kinds of unsupported MoS₂ hydrodesulfurization catalysts for ultra low-sulfur diesel oil and the precursor of MoS₂ catalyst, nano-sized MoO₃, were synthesized with a novel hydrothermal reduction method. The influence of the synthetic methods, the precursor (MoO₃) of MoS₂ catalyst, the concentration of reactants and the pH values on the growth morphology of MoS₂ were systematically investigated and thoroughly analyzed. The MoS₂ fibers showed lots of defects and they were easily bended, which increased the number of active sites on the catalyst and easily met the requirements for the deep hydrotreating desulfurization of diesel oil.

Key Words: Unsupported nano-MoS₂ catalyst, Hydrotreating desulfurization, Hydrothermal reduction, Diesel oil.

INTRODUCTION

With the increasing concern on energy saving and environmental protection in recent years, more and more developed countries have accelerated the implementation of compulsory super-low sulfur gasoline and diesel fuels policy. China will also adopt the third type standard of World Fuel Regulations[1] as soon as possible. Although various production technologies of clean gasoline and diesel fuels are emerging, the hydrotreating catalysis still plays the key role in the petrochemical industry. Conventional supported catalysts, which have been used for the desulfurization of gasoline and diesel fuels, can not meet the requirements of the World Fuel Regulations[1]. Therefore people are devoted to develop unsupported catalysts used to produce clean fuel. Thus far, the research on unsupported catalysts mainly includes metal phosphides, metal carbon compounds and metal sulfides[2-9]. Generally, active components of nonsulfide hydrotreating catalysts are oxides. According to experience and theoretical research, the hydrotreating catalysts have higher activity when active components exist as sulfides. Therefore nonsulfide hydrotreating catalysts must be pre-sulfurized before used. The sulfidizing is that the active components of catalysts react with hydrogen sulfide at a given temperature in order to change oxides into sulfides.

There is no need to add poisonous sulfur compounds in unsupported metal sulfide catalysts for the sulfidizing of catalysts, which makes its application process relatively simple. So the metal sulfide catalysts become the hot topic of hydrogenation catalysts. To our best of knowledge, there is no information in the literature about the preparation technology of unsupported metal sulfide catalysts and the influence of reaction conditions on their structure and characteristics. In this work, nano-sized unsupported MoS₂ catalysts for the deep desulfurization of diesel oil were synthesized mainly by the way of hydrothermal reduction and the influence of synthetic methods, the precursor (MoO₃) of MoS₂ catalyst, the concentration of reactants and pH values on the growth morphology of MoS₂ catalysts was systematically investigated and thoroughly analyzed.

EXPERIMENTAL

Based on the analysis of present preparation methods of catalysts, the hydrothermal reduction was used to prepare MoO₃, the precursor of MoS₂ catalyst and the nano-MoS₂ catalyst was synthesized by the hydrothermal deoxidization which was compared with the method of high temperature hydrogen sulphurization.

Materials of the hydrothermal reduction to prepare MoO₃ (MoO₃-Hy), of high temperature hydrogen sulphurization to produce MoS₂ (MoS₂-D) and of hydrothermal deoxidization to synthesize MoS₂ are shown in Tables 1-3, respectively. Five kinds of nano-MoS₂ catalysts, *i.e.*, MoS₂-A, MoS₂-A2, MoS₂-A3, MoS₂-B and MoS₂-C were made with hydrothermal deoxidization; their ratios of raw materials and reaction conditions are shown in Table-4.

Preparation methods

Hydrothermal reduction for the preparation of MoO₃: The mixture of sodium molybdate and hydrochloric acid in certain proportion was put into the inner of a reactor and it

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

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

TABLE-2
MATERIALS OF HYDROGEN SULPHURIZATION
FOR THE PREPARATION OF MoS₂

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

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

Materials	Specification (%)
Hydrochloric acid	37
Nitrogen	99.99
Alcohol	95
MoO₃	≥ 99.5
Sodium sulphide nonahydrate	≥ 98

TABLE-4
CONDITIONS OF HYDROTHERMAL DEOXIDIZATION
FOR THE PREPARATION OF MoS₂

Samples	Ratios of materials	Reaction conditions
MOS₂-A	MoO₃-Hy : sodium sulphide nonahydrate : hydrochloric acid = 0.72g : 11.07g : 60 mL (0.4 M)	200 ℃, 12 h
MOS₂-A2	MoO₃-Hy: sodium sulphide nonahydrate: hydrochloric acid = 0.90g : 13.84g : 60 mL (0.4 M)	250 ℃, 12 h
MOS₂-A3	MoO₃-Hy: sodium sulphide nonahydrate : hydrochloric acid = 0.90 g: 13.84g : 60 mL (0.4 M)	270 ℃, 12 h
MOS₂-B	MoO₃-Hy: sodium sulphide nonahydrate : hydrochloric acid = 1.44 g: 22.14 g : 60 mL (0.4 M)	250 ℃, 12 h
MOS₂-C	MoO₃ from market : sodium sulphide nonahydrate : hydrochloric acid = 1.44 g : 22.14g : 60 mL (0.4 M)	250 ℃, 2 h

was heated from the ambient temperature to 150 ℃ at an appropriate temperature-rising speed. The reaction temperature (150 ℃) was kept for 6 h, then the inner was taken out from the reactor hastily and cooled down at the ambient temperature to terminate the hydrothermal reaction. Deionized water was added to the solution to remove sodium ions by high speed centrifugation. Finally the precipitant was put into an oven for several hours and some pale blue MoO₃ with high purity was obtained.

High temperature hydrogen sulfuration for the synthesis of MoS₂: Sodium sulfide nonahydrate from a dropping funnel was added into a three-necked flask containing hydrochloric acid and hydrogen and nitrogen were added into the three-necked flask in order to produce H₂S gas. Then water vapour was removed from H₂S gas in a two-necked flask filled with SiO₂ desiccant. MoO₃ reacted with H₂S gas for 2 h at a high temperature in a muffle furnace, the draining gas was recycled by NaOH solution at the same time. Keep adding H₂, N₂ and H₂S in the muffle furnace until the temperature decreased to ambient temperature. Finally the product was put in a drying oven with N₂ protection.

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 ℃ at an appropriate heating speed. The temperature was kept for 6 h in order that the reactants reacted completely. Then the inner was taken out from the reactor hastily to stop the hydrothermal reaction. Deionized water and alcohol were added into the solution of reaction products to remove sodium ions in the solution by high speed centrifugation. The washed and filtrated black product was heated in an oil bath of the reactor. Air was pumped to keep it in a vacuum state and nitrogen was added to dry the black product (MoS₂) for 24 h. Finally the obtained MoS₂ powder was preserved in a dryer.

RESULTS AND DISCUSSION

The length and width of MoS₂ (or MoO₃) nanowire stack synthesized by high temperature hydrogen sulfuration and hydrothermal deoxidization are showed in Table-5. The average diameter (103.4 nm) of MoS₂-D produced by high temperature hydrogen sulfuration is smaller than that of its precursor MoO₃ (120.9 nm), maybe due to the shrinkage of MoO₃ volume when it was deoxidized by hydrogen at about 500℃. The main product of MoS₂-D is MoO₂ as shown in Fig. 1(a-b) and its subsidiary product is MoS₂ shown in Fig. 1(c-d). At the edge of MoO₂, there are many small MoS₂ crystals that appear as fibrous layered structure because of MoO₂ reacting with high temperature H₂S gas. However the proportion of nano-MoS₂ is relatively low in the mixture powder of MoS₂-D. Further sulfuration may increase the proportion of MoS₂.

TABLE-5
LENGTH (L) AND WIDTH (D) OF MoS₂ (OR MoO₃)
FIBER SYNTHESIZED BY DIFFERENT METHODS

Samples		Mean value (nm)	Max. value (nm)	Min. value (nm)	Standard deviation (nm)
MoO₃-Hy	D	120.9	322.9	47.1	39.7
	L	2150	5492	464	844
MoS₂-A	D	13	33.7	7.3	3.8
MoS₂-A2	D	2.1	3.3	1	0.5
	L	26.1	72.5	13.5	9.1
MoS₂-A3	D	2.3	4.7	0.9	0.755
	L	31.7	72.4	5.87	12.7
MoS₂-B	D	3.3	7.7	1.2	1
	L	38.2	96	15.3	14.1
MoS₂-C	D	2.2	3.5	0.9	0.6
	L	34.7	56.4	29.3	8.21
MoS₂-D	D	103.4	270.3	52.9	41.5

The transmission electron microscope image of MoS₂-A3 microscopic structure synthesized by hydrothermal deoxidization can be seen from Fig. 2(a). It could be seen that a lot of nanowire stack crystals of MoS₂ are formed with lengths and diameters of 31.7 and 2.3 nm (Table-4), respectively. And
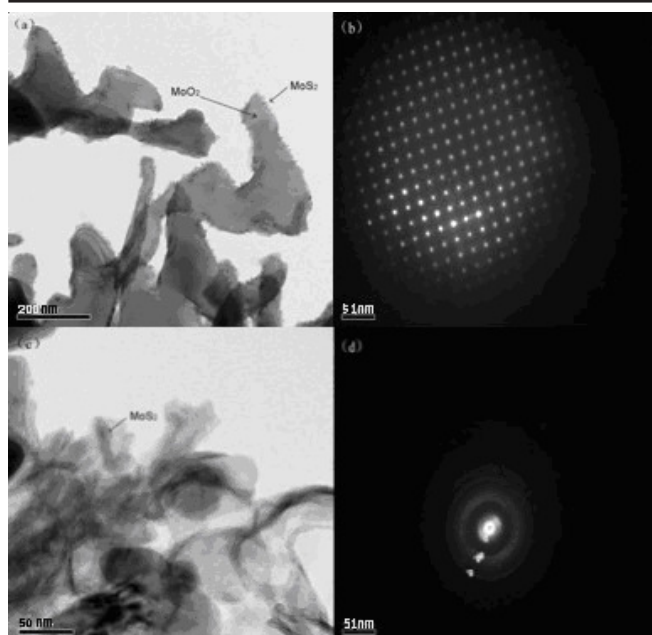
Fig. 1. (a) TEM images of MoO₂ and MoS₂ in MoS₂-D; (b) the electron diffraction pattern of MoO₂ in MoS₂-D; (c) the TEM image of nano-MoS₂ fibrous layered structure in MoS₂-D; (d) the electron diffraction pattern of nano-MoS₂ fiber in MoS₂-D

Fig. 2. (a) TEM image of MoS₂-A3; (b) TEM image of MoS₂-A3; (c) Electron diffraction pattern of MoS₂-A3

nanowire stack crystals of MoS₂ disperse onto the basic plane of the amorphous MoS₂ equably and highly. The growth of nanowire stack along the length is disordered and flexional, which provides the possibility of generating huge disfigurement on MoS₂ fringe.

It can be seen from Fig. 2(b) that MoS₂-A3 nanowire stack is composed of 2 to 7 layers of (002) basal planes. The distance of two lattice fringes is *ca.* 0.62 nm and the value of d corresponding to (002) crystalline planes is 0.6155 nm. It is important that crystalline layer along (002) crystalline planes is flexional. The crystal distortion could promote the formation of a large number of defects and the influence of the number of defects on the activity of the catalyst is significant[10]. The smaller number of stacks increase the quantity of fringe Mo atoms on the MoS₂. These factors mentioned above could contribute to the formation of sulphur vacancies and increase the quantity of active sites in hydrodesulfurization process.

It can be seen that MoS₂ crystal structure is rhombohedra with the space group of P63/mmc from the electron diffraction pattern of MoS₂-A3 shown in Fig. 2(c). The cardinal characteristic of this crystal structure is that it has little effect between (002) crystalline planes in vertical direction of crystal lattice parameter c axes. Therefore, it appears as layered stack and it is easily bended and defects could be brought about. In Table-6

showed that the calculated values of crystalline planes gained from concentric diffraction rings in Fig. 2(c) and their corresponding theoretical values are consistent. The diffraction rings with the close value of d are superposition as showed in Fig. 2(c). This further proves that the microcrystal structure characteristics of MoS₂-A3 are consistent with its TEM images.

TABLE-6
CALCULATED VALUES AND THEORETICAL VALUES OF d

d (nm)- calculation	d (nm)- theory	h k l
0.616	0.616	0 0 2
0.276	0.274	1 0 0
0.257	0.250	1 0 1
0.216	0.228	1 0 3
–	0.205	0 0 6
0.157	0.158	1 1 0
–	0.154	0 0 8

Effects of the precursor MoO₃ on MoS₂ structure: In this study, two different kinds of MoO₃ powder were adopted as the precursor of MoS₂ catalyst: one was bought from the market, which was used to synthesize MoS₂-C; the other which corresponded to series A and B MoS₂ catalysts (Table-4) was produced by the hydrothermal reduction. Although the nano-MoS₂ catalyst (MoS₂-C) with the micro crystal fibers could be obtained from the commercial MoO₃ powder by the hydrothermal deoxidization [Fig. 3(a-d)], its homogeneity and dispersity were lower than the ones of the MoS₂ catalyst in the series A or the series B. The MoS₂-C was clearly reunited; its united size was as much as 73.8 nm. Some unknown crystals on the MoS₂-C [Fig. 3(a)] were observed, maybe because there were some impurities in the MoO₃ powder from the market. The experimental results showed that the MoS₂ catalyst with microcrystal nanowire stack structure and with equably and highly dispersion using the high purity MoO₃ synthesized by hydrothermal reduction could be obtained.
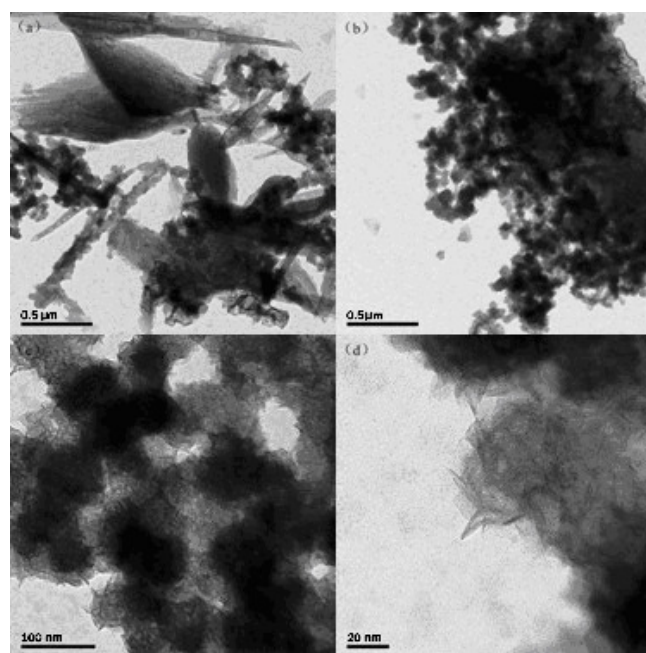

Fig. 3. (a-d) TEM images of MoS₂-C

Effects of concentration of reactants and pH values on MoS$_2$ structure: The TEM images of MoS$_2$-B and MoS$_2$-A2 are shown in Fig. 4, respectively. MoS$_2$-B and MoS$_2$-A2 shared the same reaction temperature (250 ºC), the same reaction time (12 h) and the amount of hydrochloric acid (60 mL). However, the concentration of MoO$_3$ and sodium sulfide nonahydrate for MoS$_2$-B was higher than those for MoS$_2$-A2, *i.e.*, the pH value of MoS$_2$-B was higher than that of MoS$_2$-A2. The ionization equilibrium of H$_2$S tends to increase the number of HS ions (Fig. 5). The pH values are more than 8 at the end of reaction, both acidity and strongly alkaline are not good for the formation of MoS$_2$.
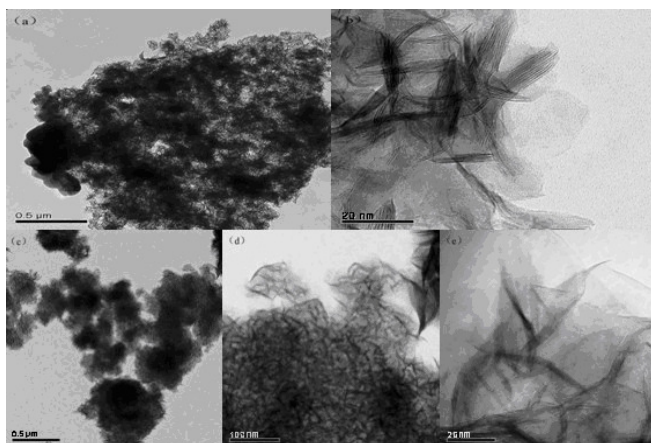

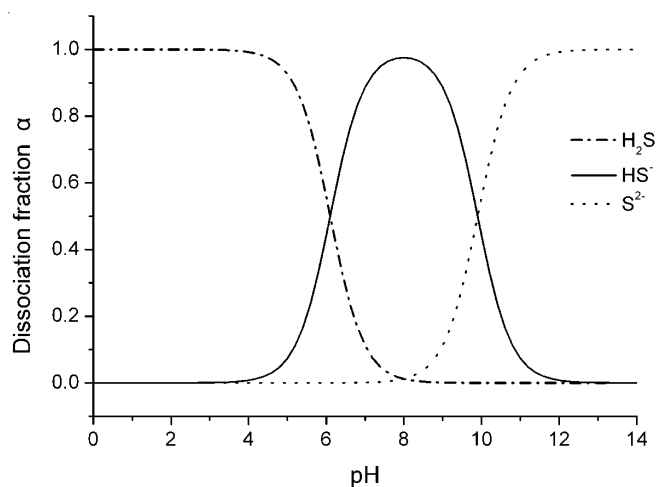Fig. 4. (a-b) TEM images of MoS$_2$-B (c-e) The TEM images of MoS$_2$-A2

Fig. 5. Effect of pH values under 250 ºC on the separation[11] of H$_2$S, HS$^-$ and S^{2-}

Since the reaction speed increases with increasing concentrations of reactants and the concentration of reactants of MoS$_2$-B was higher than those of MoS$_2$-A2, the average length of MoS$_2$-B was 38.2 nm and the diameter was 3.3 nm, both larger than those of MoS$_2$-A2, 26.1 and 2.2 nm (Table-5).

By comparing Fig. 4, it can be found that the number of crystals on MoS$_2$-B is more than that on MoS$_2$-A2, the reunion phenomenon and the overlap of nano-microcrystal fibers are observed on MoS$_2$-B. Therefore, the microcrystal structure could be controlled by changing the concentration and pH values of the reactions.

Conclusion

• The main product MoO$_2$ coated with nano-MoS$_2$ was obtained by high temperature hydrogen sulfuration deoxidization.

• The microcrystal nanowire stack MoS$_2$ was synthesized with equable and high dispersion by hydrothermal deoxidization. The average length of nanowire stack is 30-40 nm, the diameter is 2.0-3.5 nm and the stack number is less than 8. The microcrystal nanowire stack of MoS$_2$ is flexional. There are plenty of defects and many active sites could be gained on catalysts of MoS$_2$, which easily meets the requirements for the hydrotreating ultra-desulfurization of diesel oil.

• The distribution and sizes of MoS$_2$ catalyst could be controlled by different kinds of MoO$_3$ and the precursor of catalyst. The good dispersed equably and highly microcrystal nanowire stack MoS$_2$ can be obtained when taking the high purity MoO$_3$ by hydrothermal reduction.

• The distribution and sizes of nano-MoS$_2$ microcrystal can be effectively changed by the concentration ratio of the precursor of MoS$_2$ catalyst and its pH value. The degree of crystallization, growth and coarsening of nano-MoS$_2$ microcrystal increase with the concentration ratio and the pH value.

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