



REVIEW

Studies on Unsupported Nano-MoS₂ Catalyst

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Unsupported MoS₂ hydrodesulfurization (HDS) catalysts shall be concerned for they are sulfided when used without adding toxic sulfur compounds and have ultra-high capacity to hydrodesulfurization. This paper reviewed the progress of the unsupported nano MoS₂ catalysts, including the preparation, characterization and desulfurization mechanism.

Keywords: MoS₂, Unsupported catalysts, hydrotreating desulfurization.

INTRODUCTION

With increasingly serious environmental pollution, the demand of sulfur content in fuel oil is more and more strict, in order to meet the objective requirement, we should continue to improve the existing desulfurization process and catalysts, to explore more efficient, economic and environment friendly diesel desulfurization methods. Among the existing various kinds of diesel desulfurization technologies, hydrogenation desulfurization technology is more mature, more thorough research on reaction mechanism, so it is still the mainstream of the production of ultra-low sulphur diesel. The traditional hydrodesulfurization process can meet the requirements of low sulfur diesel, but the reaction conditions are harsh and equipment investment is large, operation cost and the cost of desulfurization are high. At the same time, the hydrodesulfurization is difficult to achieve ultra-deep desulfurization and the effect of desulfurization is not ideal for thiophene derivatives in diesel which have complex structure, large space steric hindrance. At present, main methods of improving treatment effect of hydrodesulfurization are to improve the existing catalysts and to develop new catalysts¹.

The effective supported amount of the active metals of traditional supported catalysts by constraints of specific surface area and pore volume is difficult to increase dramatically, improving the activity of catalyst is limited. So the desulfurization depth of gasoline and diesel of traditional supported catalysts will not meet the requirement of clean fuel. Unsupported catalysts have higher active component content, have more ability of hydrogenation desulfurization, denitrogenation and aromatics saturation, therefore people are devoted to develop unsupported catalysts used in the production of clean fuel.

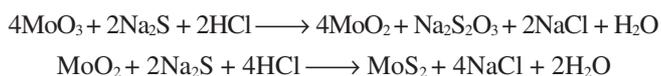
So far, the study on unsupported catalysts is mainly metal phosphide, metal carbon (nitrogen) compound and metal sulfide²⁻⁷.

There is no need to add poisonous sulfur compounds in unsupported metal sulfide catalysts for the sulfidizing of catalyst. Its application process is relatively simple and there is high hydrogenation desulfurization ability to meet the World Fuel Regulations on the requirements of Ultraclean Diesel. Therefore, unsupported metal sulfides catalysts are being focused. The following reviews describes the preparation of unsupported nano-MoS₂ catalyst.

Preparation technologies: Generally common synthesis methods of molybdenum sulfide powder include molybdenum oxide (MoO₃) sulfide method, solution reaction method, solid thermal decomposition method (OFHIP), ultrasonic chemical degradation method, hydrothermal synthesis method, *etc.* The molybdenum sulfide catalysts can be characterized by X-ray diffraction (XRD), N₂ physical adsorption in low temperature (BET), the infrared (FT-IR) and laser Raman (Raman), scanning electron microscopy (SEM), transmission electron microscopy (TEM), high resolution transmission electron microscopy (HRTEM) and energy dispersive X-ray spectroscopy (EDS) on their compositions, structure, surface properties and micro-structure.

Preparation of MoS₂ by molybdenum oxide (MoO₃) sulfide method: Li *et al.*⁸ synthesized MoS₂ in one step with molybdenum oxide as raw material. Under the condition of 200-300 °C, molybdenum oxide mix sodium sulfide in a 1:3 Mo/S atomic ratio, add 0.4 mol/L HCl solution and CH₃CH₂ONa or NH₄Cl organic compounds, then high purity molybdenum sulfide obtained. Due to costs of raw material are relatively high and the output is too little, so not suitable

for commercial production. The reaction mechanism is as follows:



In this method, the preparation of precursor molybdenum trioxide is particularly important. The followings mainly introduce hydrothermal crystallization synthesis of MoO_3 .

Elizondo-Villarreal⁹ added dropwise a 4 M solution of HCl to a saturated solution of sodium molybdate. The mixture is placed in a Teflon-lined autoclave and left at 423 K for 6 h, α - MoO_3 was prepared after filtered and dried.

Song-Jimei *et al.*¹⁰ prepared films of orthorhombic phase α - MoO_3 under low temperature using chemical precipitation-hydrothermal method. The morphology, structure and composition of product were characterized by XRD, FT-IR, XPS and SEM.

Wang-Wendi, *et al.*¹¹ synthesized α - MoO_3 nano-fibers with high yield by using of acidified hydrothermal molybdate solution through regulating the nitric acid concentration. The morphology and structure were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). The results show that when the nitric acid concentration was more than 6.73 mol/L, orthorhombic phase α - MoO_3 nano-fiber can be prepared with diameter size in 50-400 nm, along the growth of the [001] direction. When the nitrate concentration was about 2.6 mol/L, the products were needle-like hexagonal phase MoO_3 . With increasing concentration of nitric acid, the products were transmitted from the hexagonal phase MoO_3 to Orthorhombic phase MoO_3 .

High temperature decomposition method: High temperature decomposition method is that molybdenum disulfide is decomposed from ammonium tetrathiomolybdate or molybdenum sulfide using thermal decomposition or other high-energy physics means, generally need to inert gas protection.

Farag *et al.*¹² synthesized MoS_2 catalyst by means of heating ammonium tetrathiomolybdate and 4,6-DMDBT as precursor while 10 % (v/v) $\text{H}_2\text{S}/\text{H}_2$ gas mixture was allowed to flow at 350-425 °C. The specific surface area of MoS_2 is 54-70 m^2/g ; If added a small amount of water in the reaction, the specific surface area of MoS_2 is 288-335 m^2/g .

Siadati *et al.*¹³ obtained homogeneous molybdenum sulfide using the above method, which has 3.5 nm diameter, 270 m^2/g specific surface area at 300 °C, hydrogen pressure of 6.9-55.2 bar, its morphology shown in Fig. 1.

Hydrothermal synthesis method: Hydrothermal method refers to an effective method of producing a high pressure environment in the reaction system and processing of inorganic synthesis and materials preparation in the special airtight reactor (autoclave), using aqueous solution or organic solvent as reaction system, by heating a reaction system to a critical temperature (or close to critical temperature). Among them, the reaction temperature, reaction pressure and the acidity of the reaction mixture is key factors of product attributes, it can produce kinds of nano MoS_2 ¹⁴⁻¹⁸ by changing these factors, in general, the higher the reaction temperature, the higher reaction pressure, the better crystalline state of product can be obtained.

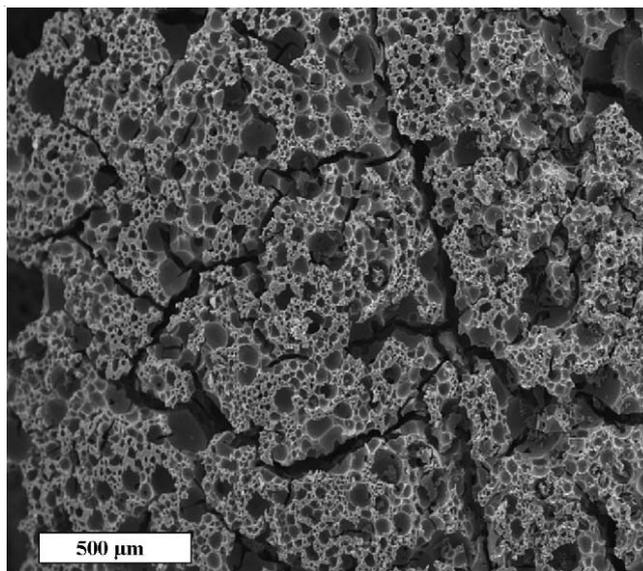
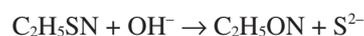


Fig. 1. Under the 300 °C, 3.45 MPa, synthesis of MoS_2 by OFHIP technology

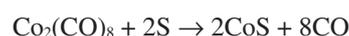
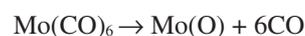
Tian *et al.*^{19,20} obtained nano MoS_2 under lower reaction temperature (200 °C) and shorter reaction time (24 h) by using Hydrothermal synthesis method with $\text{MoO}_3, \text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ and $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$ as the raw material. Xu²¹ obtained MoS_2 suspension by acidifying ammonium tetrathiomolybdate with hydrochloric acid, placed suspension in a Teflon-lined autoclave after filtering, at the same time added iron and hydrochloric acid. The sealed autoclave was slowly heated to 280 °C for 24 h. Once autoclave cooled to room temperature, the product was filtered, washed and dried. Then the MoS_2 nanowires can be obtained with length and diameter of 300-640 nm and 20-40 nm, respectively.

Solvothermal synthesis method: Solvent thermal growth is on the basis of the hydrothermal method, with organic solvent instead of water. He *et al.*²² got molybdenum disulfide with rod-like crystal morphology and its average particle size is about 80 nm under 160 °C with Mo powder and S powder as raw material, ethylene diamine as solvent reaction.

Wei *et al.*²³ added solution of ammonia to a 10^{-4} M solution of ammonium molybdate slowly, then added 1.5 M sodium dithionite and 1.5 M thioacetamide, spherical particles of molybdenum sulfide can be obtained under 180 °C. The catalyst morphology is shown in Fig. 2, the reaction equations are as follows:



Ultrasonic chemical degradation method: Mahajan *et al.*²⁴ synthesized MoS_2 , CoS, CoS- MoS_2 (Mo/Co = 6/1) by use of ultrasonic degradation. The specific method is: 20 mmol $\text{Mo}(\text{CO})_6$ and 42 mmol S or 3 mmol $\text{Co}_2(\text{CO})_8$ and 3 mmol S or 20 mmol $\text{Mo}(\text{CO})_6$, 3 mmol $\text{Co}_2(\text{CO})_8$ and 46 mmol S were added to 60 mL hexadecane solvent and sonicated at 323 K, then obtained 90 % air-stable black particles of $\text{MoS}_2(\text{CoS}$ and CoS-MoS_2). Reaction equations are as follows:



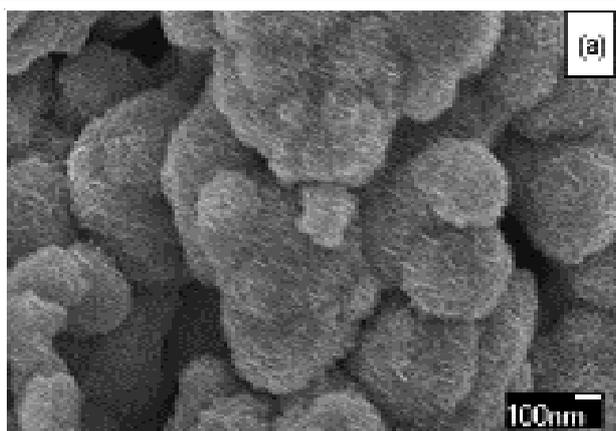


Fig. 2. SEM morphology of MoS₂ synthesized in the aqueous solution

Uzcanga *et al.*²⁵ prepared molybdenum sulfide with sulfur-containing organic. 9 mL CH₃COSH was added dropwise to an aqueous solution of (NH₄)₆Mo₇O₂₄·4H₂O, after ultrasonic degradation CH₃COSH produced a black precipitate, generated H₂S as catalytic hydrogenation vulcanizing agent; Sections of these precipitate were reacted with a stream of H₂S/H₂ in 10 % (vol) at 400 °C for 4 h, molybdenum sulfide with good dispersion obtained, the particle diameter is 0.2-2 μm, the larger surface of the sphere with the smaller particles reunion, shown in Fig. 3.

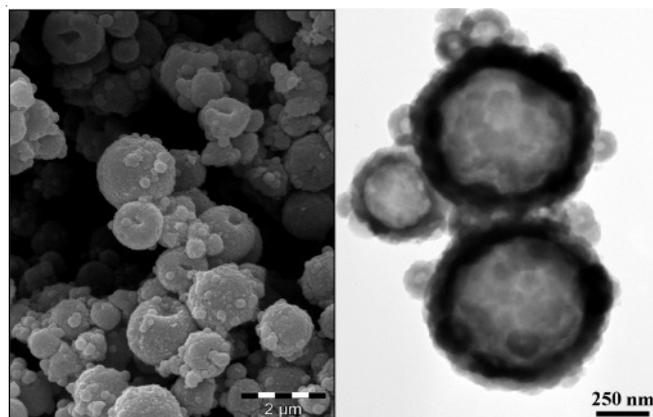


Fig. 3. MoS₂ particles prepared by ultrasonic degradation: scanning electron microscopy, SEM (left); Transmission electron microscopy, TEM (right)

In a word, there are kinds of the preparation method of nano-MoS₂, every preparation method has the advantages and disadvantages, so the decision should be made according to the specific purposes, requirements and the condition of reality. Among them molybdenum oxide (MoO₃) sulfide method has high raw material cost and little production. operation and equipment of high temperature decomposition method are relatively simple in the process of preparation, but the elemental sulfur has serious corrosion on equipment. Hydrothermal synthesis method of nano-MoS₂ is simple and easy to implement, but the product of this method is amorphous state and reunion under lower temperatures. The solvothermal synthesis method has low cost, large product yield and controllable shape, high product purity, can be prepared MoS₂ that can meet different functional requirements, but there is also insufficient,

such as high raw material requirements, long process flow, product easy to reunite, *etc.* Ultrasonic degradation method has large energy consumption, reaction time is long and can only get a small amount of product. In addition to these commonly used method, there are some other special preparation methods, such as electrochemical deposition²⁶, template method²⁷, Y ray method²⁸ and molten salt method²⁹ and so on. Most of these preparation methods attached special preparation conditions and the structure of the product performance is not very outstanding, therefore failed to arouse people's attention.

Desulfurization mechanism of unsupported catalyst:

Hydrodesulfurization of petroleum processing is an important process and it plays an important role for improving the crude oil processing depth, taking use of oil resources rationally, improving product quality, increasing yield of light oil and reducing air pollution. Today's energy consumption trends indicate that crude oil is becoming heavier and worse, while the market for high quality middle distillate demand continues to deepen, so hydrodesulfurization is even more important. Among them, dibenzothiophene as one of the most important and the most difficult to resolve oil of petroleum, solving the problem of sulfur removal of petroleum and getting clean fuel become one of the key research work of hydrodesulfurization. Therefore, the removal research of dibenzothiophene (DBT) and sulfur derivatives generated in the hydrogenation is essential.

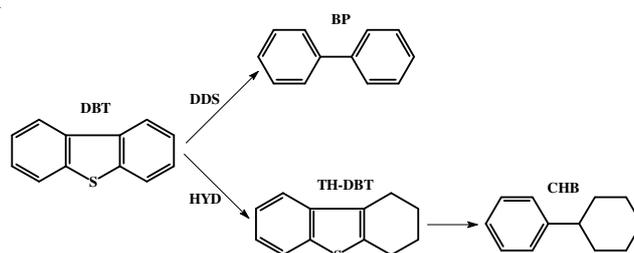


Fig. 4. Hydrodesulfurization of dibenzothiophene pathway

There are two ways of hydrodesulfurization^{30,31} (Fig. 4): the one is obtain biphenyl (BP) by direct desulfurization; the other is the first obtain intermediate tetrahydro-dibenzothiophene (THDBT) by hydrogenation and desulfurization, hydrogenation to generate a large number of cyclohexylbenzene (CHB). Since these two pathways are parallel and competitive, the selectivity (HYD/DDS) is determined by³²:

$$\frac{\text{HYD}}{\text{DDS}} = \frac{([\text{CHB}] + [\text{THDBT}])}{[\text{BP}]}$$

Daage and Chianelli³³ established "rim-edge" model to associating molybdenum sulfide morphology and selectivity of hydrodesulfurization (direct desulfurization), to determining the different active sites. They further proposed two kinds of active site models that existed in different location of edge layer (Fig. 5). One presents in close to the base surface exposed to the reaction environment outside the thin layer "rim sites", occurs hydrogenation reaction and desulfurization reaction simultaneously; Another presents in the basal plane without exposing internal thin layer "edge sites", occurs desulfurization reaction only.

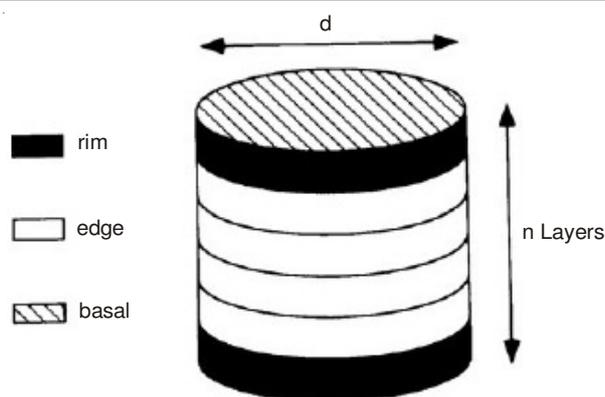


Fig. 5. Simulation model of properties of molybdenum sulfide particle

The relative ratio of rim and the edge can be seen from Fig. 5³³ the simulation model of properties of molybdenum sulfide particle. The model assumes that there are n layers of molybdenum sulfide accumulation with a diameter of d . The relative ratio of rim is: $[r/(r + e)] = 2/n$, r represents the number of rim active sites, e represents the number of edge active sites. The relative ratio only depends on the degree of accumulation of thin layer. According to this model, the single-layer dominant molybdenum sulfide catalyst has higher hydrodesulfurization selectivity than stacking dominant molybdenum sulfide catalyst.

In contrast to the rim-edge model, Hensen *et al.*³⁴ reported that increasing MoS₂ layer stacking increases hydrogenation because of a less hampered planar adsorption of reactants. Similar observations were made for hydrogenolysis in the hydrodesulfurization of dibenzothiophene, whereas hydrogenolysis of thiophene is not a strong function of the number of MoS₂ layers because of perpendicular adsorption through the S atom of thiophene.

Application and research direction in the future: Unsupported catalyst shows high catalytic activity, has very obvious advantages compared to traditional supported hydrofining catalyst, it overturns the concept of carrier and active component of traditional catalyst, it is a leap of the composition and activity of catalyst, it represents the development trend of hydrodesulfurization catalyst. Unsupported hydrotreating catalysts currently in the development stage, industrial applications are very little. NEBULA catalysts are the most representative unsupported hydrotreating catalysts. NEBULA is a registered trademark of ExxonMobil Corporation. NEBULA (new bulk activity) catalyst is a significant patent technique developed mutually by Akzo Nobel, Exxon Mobil and Nippon Ketjen companies, which successfully achieved industrialization in 2001.

There are FH-FS unsupported hydrotreating catalysts developed by Chinese Sinopec Fushun Petrochemical Research Institute. Zhenhai Refining Company is applied in the fuel oil hydrogenation unit currently.

In order to realize the sustainable development of human and the nature, economy and environment, the development of high quality clean diesel fuel production technology still is one of the main problems in the field of oil refining, ultra-low sulfur will be becoming development trend of diesel fuel in

the future. Development of efficient and stable, green and low-cost of diesel desulfurization process is the main direction of research. Further improving activity of the unsupported hydrotreating catalysts, reducing production costs, simplifying preparation process are the next step to work together.

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