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NOTE

Highly Dispersed, Nonsupported Molybdenum Sulfides

The use of fixed-bed reactors for the hydrotreatment of heavy petroleum is limited by deactivation of supported catalysts. The predominant mechanism of deactivation consists of the decrease of accessibility of the active surface, mainly due to the blocking of the porous structure by metallic and carbonaceous species. An alternative to the use of supported catalysts for the processing of highly contaminated feeds is the addition of dispersed catalysts which may be discarded along with the ultimate residue where nonreactive metallic and coke-like species concentrate. Considerations concerning operating cost and the volume of unconverted residue impose that these additives are used at a low concentration level, thus they must possess a high intrinsic activity. This is the first criterion for active phase selection, and molybdenum sulfide may be chosen for its high activity and relatively acceptable cost. Secondly, the active phase once generated must exhibit a large, accessible, and stable surface area. Highly dispersed solids are generally unstable and tend to sinter under the normal conditions of hydrotreatment reactions. As a consequence, efforts have been dedicated to the preservation of the state of dispersion of finely divided catalysts particles. One of the most attractive solutions, which has reached the demonstration stage, consists in generating a carbonaceous matter, together with the active phase, which prevents particles agglomeration. This constitutes the basis for the M-coke process which has been extensively described (1). In this process, an oil soluble organometallic compound is added to the feed. During the initial stage of reaction, the decomposition of this additive generates a finely divided metallic sulfide whose dispersion is preserved owing to the high content of Conradson carbon of the feed. Molybdenum naphthenate is one of the most commonly proposed precursors, and its activity has been studied, for hydrotreatment (2), for coal hydroliquefaction (3) for coprocessing (4), or for heavy oils conversion (5). However, the mechanism of generation of molybdenum sulfide is still obscure, since the presence of coal or petroleum residues impedes any characterization of the resulting sulfide as a function of operating conditions. The present work was undertaken in order to get some insight into the process of generation of molybdenum sulfide from an oil soluble precursor, under experimental conditions reflecting hydroconversion: presence of a liquid solvent, temperature range between 570 and 620 K, high hydrogen pressure (3 to 6 MPa), and presence of sulfur compounds. The resulting solids were characterized by X-ray diffraction and porous structure evaluation. The catalytic activity for hydrodesulfurization of thiophene has been measured and compared with the activity of a nonsupported molybdenum sulfide obtained by aqueous phase precipitation.

Molybdenum naphthenate (containing 6 wt% Mo) was used as the precursor. Synthesis were conducted either in the presence of *n*-hexadecane or 1-methylnaphthalene as the hydrocarbon medium. Sulfiding reagents were carbon disulfide, dimethyl disulfide, and sulfur. The reactants (50 g solvent, 8 g molybdenum naphthenate, and a quantity of sulfiding reagent providing a threefold excess of sulfur, with respect to stoichiometric MoS_2) were introduced in a 250-cc autoclave equipped with a magnetically driven impeller. The reaction vessel was pressurized under 5 MPa hydrogen and heated at $6\ K \cdot min^{-1}$ up to 573 or 623 K for 1 h. The resulting solids were separated by filtration, washed with toluene, vacuum dried for 5 h at 373 K, and desorbed at 673 K under vacuum for 2 h before subsequent characterizations.

A sample of unsupported molybdenum sulfide was obtained by decomposition of ammonium thiomolybdate. This compound was formed by addition of ammonium sulfide to an aqueous solution of ammonium heptamolybdate. It was further decomposed to molybdenum sulfide under hydrogen sulfide (15 vol% in hydrogen) at $10\ K \cdot min^{-1}$ up to 673 K for 4 h. The corresponding solid is referred to as aqueous MoS_2.

Elemental analysis for carbon and hydrogen was obtained through combustion and quantitative evaluation of CO_2 and H_2O, respectively. Molybdenum content in reaction medium was determined, after dilution in xylene, by plasma torch atomic emission spectroscopy. The detection limit is 0.1 ppm.

X-ray diffraction spectra were obtained with a Siemens D500 diffractometer, using the $CuK\alpha 1$ line. Acquisition was performed in the range 5–80°(θ).

Catalytic activity of the isolated solids was determined in the reaction of hydrodesulfurization (HDS) of thiophene, at 623 K, under atmospheric pressure of hydrogen. The partial pressure of thiophene was 2.4 kPa. The reactor and experimental conditions are described in Ref. (6). The influence of hydrogen sulfide upon conversion and initial deactivation is complex: increasing partial pressure causes the observed conversion to decrease, but activity is more stable. In

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TABLE 1

Specific Surface Area and Specific Catalytic Activity in the Reaction of Thiophene Hydrodesulfurization of Unsupported Molybdenum Sulfides

Solid	Solvent	Sulfiding agent	Initial BET area ($m^2\ g^{-1}$)	HDS activity 10^{-8} mol · $g^{-1}\ s^{-1}$	BET area after reaction
MD	1-Methylnaphthalene	Dimethyl disulfide	240	180	238
MC	1-Methylnaphthalene	Carbon disulfide	290	185	282
MS	1-Methylnaphthalene	Sulfur	240	280	240
HD	*n*-Hexadecane	Dimethyl disulfide	500	300	485
HC	*n*-Hexadecane	Carbon disulfide	480	300	472
HS	*n*-Hexadecane	Sulfur	300	380	295
Aqueous	Water	Hydrogen sulfide	35	50	12

order to obtain comparative values for catalytic activity, measurements were performed without addition of hydrogen sulfide, at 10% thiophene conversion level. After an observed initial 5 h deactivation period, activity is measured after 15 h on stream.

Under the considered reaction conditions in hydrocarbon medium, molybdenum naphthenate is quantitatively converted in molybdenum sulfide, as evidenced by the absence of detectable molybdenum in the remaining liquid. The elemental analysis indicates an atomic ratio $S/Mo = 2$. A variable amount of a carbonaceous phase is detected in the solids. It accounts for 6 to 8 wt% of the total solids and is not significantly affected by the nature of the hydrocarbon medium, nor is it by changes in the sulfiding reagent. The H/C ratio of this coke like phase varies between 0.6 to 0.8 and reflects its condensed aromatic nature.

The textural properties constitute the most remarkable feature of these solids. BET surface area of some representative samples are collected in Table 1. Molybdenum sulfides prepared in a liquid hydrocarbon medium exhibit specific surface areas as high as 500 $m^2\ g^{-1}$. The highest surfaces are obtained when preparation is performed in *n*-hexadecane, as compared to 1-methylnaphthalene. Sulfur, as a sulfiding agent, produces solids with lower surface area. In contrast with molybdenum sulfides produced in a hydrocarbon medium, aqueous medium synthesis yields a solid whose surface is about 10 times smaller.

Nitrogen adsorption isotherms reveal considerable differences between these two kinds of solids (Fig. 1). Molybdenum sulfide generated from naphthenate displays a typical type IV isotherm, indicative of a mesoporous structure, while a type I isotherm is obtained with the solid precipitated from aqueous solution. The *t*-transforms of the corresponding adsorption isotherms illustrate this disparity (Fig. 2).

In addition to these contrasted textural patterns, the distinction of crystallographic properties of these two kinds of preparations is illustrated by X-ray diffraction diagrams presented in Fig. 3. Both solids exhibit an ill-defined crystal structure, typically observed in dispersed, supported solids. The line corresponding to a diffraction angle 15° (2θ), attributed to the 002 plan and reflecting the stacking of MoS_2 layers, is absent in the diffraction pattern of

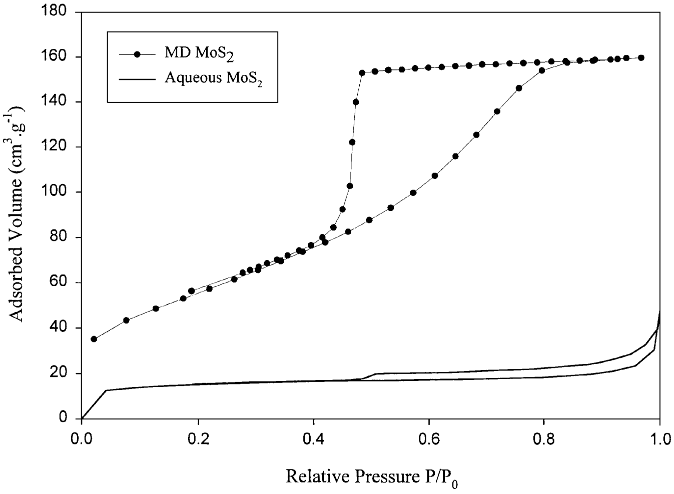

FIG. 1. Adsorption isotherms for aqueous MoS_2 and MD MoS_2 samples.

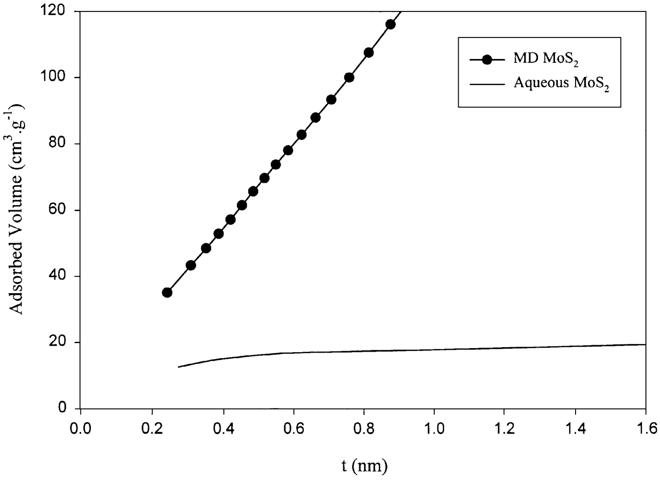

FIG. 2. *t* Transform of aqueous MoS_2 and MD MoS_2.

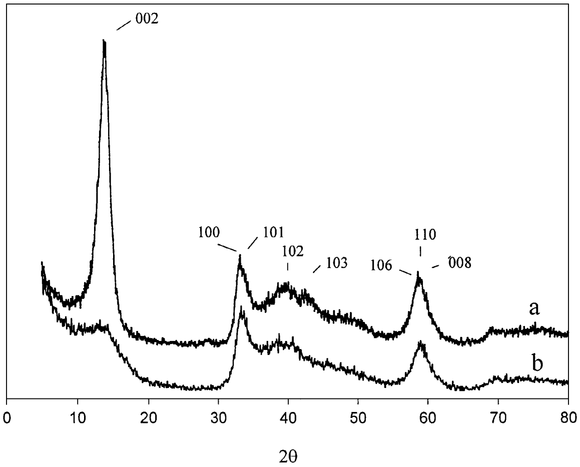

FIG. 3. X-ray diffraction diagrams of unsupported molybdenum sulfides; (a) aqueous MoS_2; (b) MD MoS_2.

ex-naphthenate solids. In the diagram of aqueous precipitated MoS_2, the corresponding line is intense, thus indicating a three-dimensional structure.

The catalytic activity of these solids has been measured in the reaction of hydrodesulfurization of thiophene. Specific activities, expressed per unit weight of catalyst, are collected in Table 1. Aqueous MoS_2 is much less active than the other solids, but no correlation is observed between catalytic activity and specific surface area. The HS solid, which is the most active, possesses a medium range surface area. Similarly, a twofold variation in surface as observed for example between the MS and HD solids, is not associated with a corresponding variation in activity. Surface area determinations, performed after activity measurements, indicate that the textural properties of ex-naphthenate solids are preserved. This outstanding stability contrasts with the dramatic decrease in BET surface area of aqueous MoS_2 whose initial surface is divided by a factor of 3 after 15 h on stream under thiophene HDS reaction conditions.

The original textural properties of these nonsupported molybdenum sulfides, generated through sulfidation of an organic precursor in a hydrocarbon medium, contrast with the relatively low surface area of equivalent solids produced from aqueous solutions. Furthermore, the dispersion state is preserved, as evidenced by the absence of sintering during catalytic activity measurements. Considering the simultaneous presence in the solids of a carbonaceous phase (“coke”), the question of the relative distribution of surface area between the two phases arises. Carbonaceous deposits admittedly have a high specific surface area; however, considering the limited amount of coke which account for a few percent of the considered solids, it must be concluded that, intrinsically, the generated MoS_2 possesses a high specific surface. The role of the coke phase is certainly of paramount importance in the preservation of the dispersed state, as was intuitively proposed in the earlier developments of the M-coke process (1). However, the present work indicates that the previous existence of a carbonaceous substance, such as Conradson carbon residue, is not required for a support effect to be observed.

The genesis of coke in the reacting medium cannot be elucidated by the present results. Methylnaphthalene and hexadecane are not likely to suffer condensation reactions under the considered experimental conditions. It must therefore be concluded that the coke phase originates from the organic molybdenum precursor. Naphthenates are complex mixtures of salts obtained from carboxylic polycyclopentanic structures. Therefore, after decomposition of the organometallic species, various reactions between hydrogen sulfide and oxygenated species may occur. Reactions of carbonyl groups with hydrogen sulfide yields a complex set of products, including cyclic oligomer structures (7). Thus the formation of reticulated compounds originating from naphthenic residues cannot be ruled out during the decomposition of molybdenum naphtenate.

The catalytic activity of these solids is not directly correlated with BET surface area. Since the respective share of surface between molybdenum sulfide and coke is not determined, the actual surface of MoS_2 is unknown. Moreover, variations in coke texture may affect the accessibility of reactants to MoS_2 surface and consequently, catalytic activity may depend upon the coke-molybdenum sulfide interface.

Further work is in progress in order to elucidate the mechanism of coke formation and to characterize the microstructure of these unusual molybdenum sulfides.

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