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Hydrothermal syntheses and catalytic properties of dispersed molybdenum sulfides

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Reactions of ammonium thiomolybdate under mild hydrothermal conditions were studied, and the range of conditions leading to the dispersed MoS_2 product has been determined. The morphology and the catalytic properties of the hydrothermal MoS_2 preparations have been compared with those of reference MoS_2 produced from the thermal decomposition of thiosalts. It has been shown that the length of the slabs and their stacking number of the crystallites of hydrothermal MoS_2 preparations differ considerably from those in the reference sulfides. The morphological differences strongly influence the hydrogenation to hydrodesulfurization activity ratio in these systems.

KEY WORDS: hydrothermal; MoS_2; morphological.

1. Introduction

Molybdenum disulfide (MoS_2) is of considerable interest in several fields such as catalysis, photochemistry or production of lubricating oils. In recent years, a number of works appeared on the preparation of unsupported dispersed molybdenum sulfide catalysts, using thermal decomposition of molecular precursors [1–3]. Earlier we prepared MoS_2 dispersions in aqueous solutions [4,5] or in hydrothermal and solvothermal brines [6]. The use of hydrothermal conditions provides an original synthetic possibility for elaboration of new compounds and for preparation of known substances with particular morphology.

The present work is focused on the study of the products of reactions of $(NH_4)_2MoS_4$ (ATM) precursor under mild hydrothermal conditions. Our goal was to study the products of reaction in reaction mixtures similar to that used previously in [6]. Hydrothermal preparation of MoS_2 with controlled morphology, if accessed by this method, might present considerable interest for catalysis, both in applied and fundamental aspects.

2. Experimental

Hydrothermal preparations were carried out in a stainless steel bomb of 0.25 l volume. To this vessel were added solutions of 2.8 g $(NH_4)_2MoS_4$ (ATM) in 100 ml of water. Reaction was carried out in a nitrogen atmosphere, or under 20 bar of H_2S. In some experiments, 50 ml of $(NH_4)_2S$ solution or 12 g of elementary sulfur was added. The reaction duration varied from 15 min to 4 h and the temperature ranged from 473 to 573 K. Relatively low temperatures and short reaction time were applied in order to obtain high-surface-area materials.

The solids were characterized by X-ray diffraction (XRD), elemental chemical analysis, scanning electron microscopy (SEM), and surface-area measurements. High-resolution transmission electron microscopy (HREM) combined with EDX analysis were done on a JEOL 2010 microscope with an accelerating voltage of 200 keV.

Thiophene hydrodesulfurization (HDS) and tetraline hydrogenation (HYD) were chosen as model reactions for comparison of the catalytic properties. Thiophene HDS was carried out in vapor phase in a fixed-bed microreactor operated in the dynamic mode at 100 kPa of hydrogen (thiophene pressure 2.4 kPa, total flow 6 l/h). The catalyst charge was of $\sim$0.1 g. For the tetralin gas-phase HYD reaction, the range of temperatures studied was 523–573 K, the hydrogen pressure was 4.5 MPa, the tetralin vapor partial pressure was 8.9 kPa and the H_2S pressure was 84 kPa. In all catalytic tests, the specific rate was calculated at 573 K in the steady state after 16 h of stream according to the equation $R = FX/m$, where R is the specific rate ($\mathrm{mol\,g^{-1}\,s^{-1}}$), F is the molar flow rate of the reactant ($\mathrm{mol\,s^{-1}}$), X is the conversion of reactant, and m is the catalyst weight (g). In both catalytic tests the products were analyzed by gas chromatography.

3. Results and discussion

3.1. Products of hydrothermal syntheses

It was found previously [6] that under hydrothermal conditions ATM might be transformed to solids

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Table 1
Conditions of hydrothermal syntheses and the products obtained

Ref.	T (K)	Time (h)	Sulfidizing agent	Phases XRD
493-1-S	493	1	H_2S	$(NH_4)_2Mo_3S_{13}$, (MoS_x)
473-4-S	473	4	H_2S	$(NH_4)_2Mo_3S_{13}$, (MoS_x)
533-4-S	533	4	H_2S	MoS_2
573-4-S	573	4	H_2S	MoS_2
513-F	513	0.2	–	MoS_2
513-F-N	513	0.2	$(NH_4)_2S$	$(NH_4)_2Mo_3S_{13}$
513-1-N	513	1	$(NH_4)_2S$	$(NH_4)_2Mo_3S_{13}$, MoS_2
513-1-N5 [a]	513	1	$(NH_4)_2S$	$(NH_4)_2Mo_3S_{13}$, $(NH_4)_2Mo_2S_{12}$
513-1-S8	513	1	S_8	MoS_2

[a] The amount of $(NH_4)_2S$ divided by 5.

possessing original properties. In the present work, varying the reaction conditions and the source of sulfur, we followed the composition of the solid products. Different solids were obtained, including non-stoichiometric sulfides MoS_x with x varying from 3 to 6, condensed thiomolybdates $(NH_4)_2Mo_2S_{12}$ and $(NH_4)_2Mo_3S_{13}$ or highly dispersed stoichiometric MoS_2 having anisotropic morphology and specific surface areas of 80–120 m^2/g. The most important results are shown in table 1. The samples are referenced as *XXX-Y-A*, where *X* is the reaction temperature, *Y* is the time of reaction (F means fast, about 0.2 h) and *A* is the sulfidizing agent.

In some cases the products are mixtures of different Mo-containing phases; in other cases pure compounds were obtained. Over 533 K all the preparations yield as a main product molybdenum sulfide, MoS_2. Note that formation of MoS_2 under hydrothermal conditions occurs at lower temperatures than thermal decomposition of the same ATM precursor at atmospheric pressure under nitrogen or hydrogen flow. Indeed, thermal decomposition of thiomolybdates occurs only in the temperature region 573–693 K [7–9]. Moreover, recently the hydrothermal syntheses of MoS_2 from the oxide precursors using various sulfidizing agents have been reported at temperatures even lower than 533 K [10,11]. It seems that MoS_2 is the most stable sulfide compound at these conditions; therefore it is produced whatever the precursors used and the source of sulfur. Using the ATM precursor in which molybdenum is already bound to sulfur, MoS_2 might be prepared hydrothermally at 513 K without the addition of other sulfur-containing compounds (513-F sample). In this case formation of MoS_2 occurs due to decomposition of ATM analogously to that occurring upon thermal treatment, but due to hydrothermal conditions the decomposition temperature is lowered and the morphology of the sulfide strongly changed.

Hydrothermal MoS_2 presents in SEM the agglomerates of anisotropic particles of rather uniform shape and size as depicted in figure 1. Compared with the samples prepared from the thermal decomposition of ATM, the hydrothermal samples have higher surface area and much longer MoS_2 sheets (table 2). The hydrothermally prepared solids have specific surface areas between 80 and 100 m^2/g and are thermally stable, being able to withstand heating in nitrogen to 773 K without considerable loss of the specific surface area. We believe that hydrothermal conditions promote the planar growth of the MoS_2 sheets. As a result, transmission microscopy shows mostly low-energy (002) planes exposed in the hydrothermal samples, explaining therefore the resistivity of their texture to the thermal treatments. Note that the nature of the textural stabilization in this case is different from that reported earlier [1–5], which was due to the persistence of some carbonaceous impurities.

Beside MoS_2, the products often formed in our synthesis are ammonium thiomolybdates. Very pure $(NH_4)_2Mo_3S_{13}$ compound can be obtained rapidly, using ammonium sulfide as a sulfur source, while the Mo precursor might be either ATM or ammonium heptamolybdate. The needle-like and often hollow crystals of $(NH_4)_2Mo_3S_{13}$ are observed in SEM (figure 2). Their heating under nitrogen or hydrogen flow at

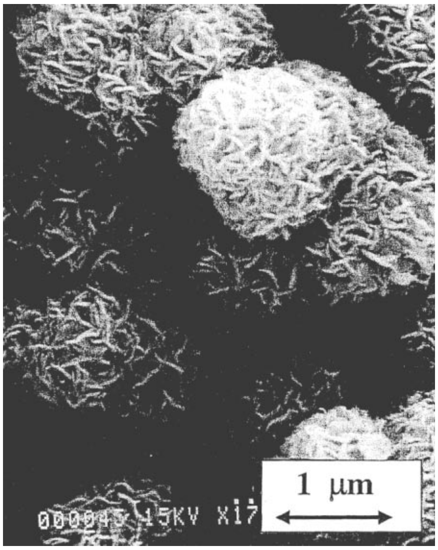

Figure 1. SEM micrograph (×17 000) of the hydrothermally-prepared MoS_2, 513-FSS sample.

Table 2
Properties of the unsupported sulfide catalysts before and after catalytic tests

Catalyst	Initial S (m^2/g)	After HDS		After HYD		Stacking		Fringe length (nm)
		S (m^2/g)	S/Mo	S (m^2/g)	S/Mo	XRD	TEM	
513-F	86	80	1.7	65	1.9	6	7	47 ± 5
513-1-S	95	92	1.75	71	1.9	–	–	–
Ex-th2	54	16	1.8	19	1.88	–	–	–
Ex-th1	67	22	1.8	36	1.95	4	5	5 ± 1

S is specific surface area. S/Mo is atomic ratio determined by elemental analysis.

673 K produces MoS_2 having the same needle-like morphology. In the narrow range of conditions, ammonium thiodimolybdate $(NH_4)_2Mo_2S_{12}$ was formed, in the form of plate-like crystals. To obtain this compound, the amount of $(NH_4)_2S$ applied should be decreased.

The acid–base properties of the reaction mixture seem to play a determining role. The mixtures containing $(NH_4)_2S$ have basic reaction, pH being between 9 and 10, depending on the amount of ammonium sulfide added. Varying this last amount, pure trimolybdate, of its mixture with dimolybdate was obtained. By contrast, in the cases when H_2S, S_8 or no sulfur compound was added, the mixture after the reaction is weakly acidic (pH 3). In general, basic pH stabilizes $(NH_4)_2Mo_3S_{13}$ compound, whereas softly acidic medium is more favorable for the formation of microcrystalline MoS_2 and amorphous MoS_x sulfides.

3.2. Catalytic properties of the solids

Insight into the catalytic properties of MoS_2 requires consideration of its anisotropic structure. Within one layer, its structure can be viewed as a two-dimensional macromolecule with each Mo ion surrounded by six sulfur anions in a trigonal prismatic arrangement. In this configuration, each sulfur ion is bound to three Mo ions, which results in a weak interaction with the next layer. Though it is generally accepted that the catalytically active CUS centers are localized at the edges of layers [12,13], the role of stacking (number of MoS_2 layers in crystallites) for the catalytic properties is not yet completely clear. In the patches of MoS_2 fringes, two kinds of topologically and energetically unequal CUS molybdenum atoms can be distinguished according to their position in the stacks: those located inside the stacks (called "edge sites"), and those at the outer layers ("rim sites"). According to the "rim–edge" model proposed by Daage and Chianelli [14], rim and edge sites have considerably different hydrogenation and hydrodesulfurization properties. For the reactions of dibenzothiophene, they concluded that HYD occurred exclusively on the rim sites, whereas HDS was obtained on both the rim and the edge sites. Therefore, the effects of structural sensitivity might be observed in these reactions for materials with varying fringe lengths and stacking numbers. Originally, the rim–edge model was based on the properties of the solids obtained from the thermal decomposition of MoS_3 at different temperatures. Using a hydrothermal preparation technique, we provide an alternative way of preparing MoS_2 with varying morphology. Our initial goal was to compare HYD and HDS properties of such systems in terms of the rim–edge model. Such a study of differently prepared unsupported catalysts was undertaken by Iwata *et al.* [15,16] for the reactions of dibenzothiophene HDS and methylnaphthalene HYD. They suggested that in addition to rim and edge sites there are also active inflection points of basal planes. In our work, the properties of hydrothermal MoS_2 are compared with those of the solids obtained from the thermal decomposition of thiosalts. We compare the activities of unsupported sulfides in the gas-phase HDS and HYD reactions of small molecules, which are thiophene and tetralin respectively.

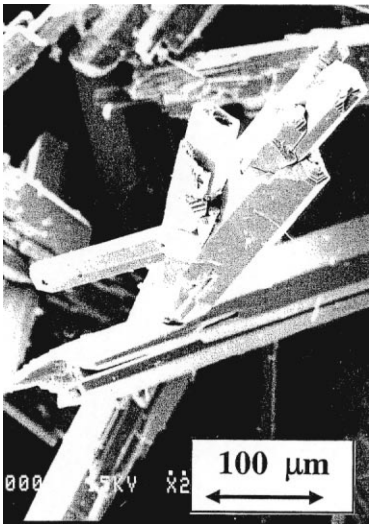

Figure 2. SEM micrograph (×220) of the hydrothermally-prepared $(NH_4)_2Mo_3S_{13}$, 513-1H sample.

For the catalytic study we used two hydrothermal samples: 513-1-S8, prepared from ATM and elementary sulfur, and 513-F, synthesized from sole ATM by its hydrothermal decomposition. The properties of these two samples are similar: both consist of long stacked patches of well-stacked MoS_2 fringes as in figure 3. The

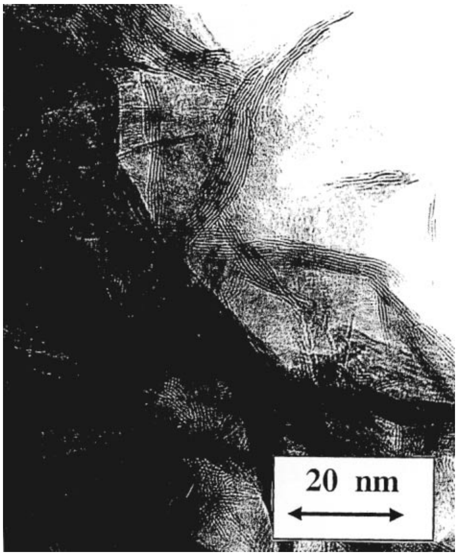

Figure 3. HREM micrograph (×400 000) of the 513-FSS sample after the tetralin HYD catalytic test.

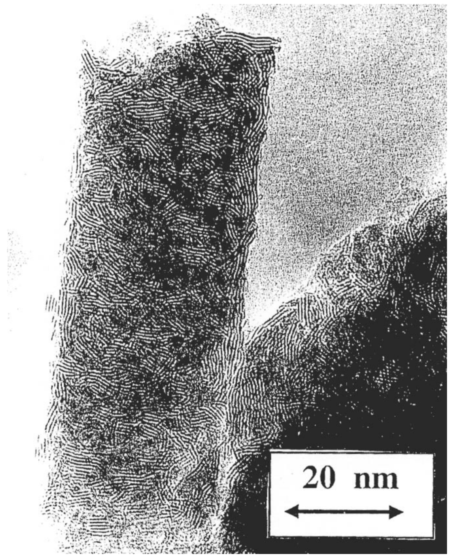

Figure 4. HREM micrograph (×400 000) of the Ex-th2 sample after the tetralin HYD catalytic test.

composition determined prior to catalytic tests, after activation in the H_2S/H_2 flow at 673, was MoS_{2+x}, $x = 0.04$–0.05. In table 2, the morphology of hydrothermal specimens and the reference sulfides is described, as measured by transmission microscopy, analysis of powder X-ray diffraction lines and nitrogen adsorption. The total specific surface area depends on the number of slabs in the MoS_2 crystallites (stacking) and the lateral extent of MoS_2 layers (fringe length).

The two reference samples for comparison were prepared from the decomposition of thiosalts. The first, Ex-th1, is obtained from the decomposition of ATM at 673 K in hydrogen for 4 h. The second, Ex-th2, was prepared from the $(NH_4)_2Mo_2S_{12}$ using the same treatment conditions as for Ex-th1. The samples have similar initial surface areas of 67 and 55 m^2/g respectively, and have the composition MoS_{2+x}, $x = 0.06$–0.07. Both ex-thiomolybdate solids are constituted by shorter fringes with less stacking than the hydrothermal ones (figure 4). Though the correct statistical treatment of HREM images is difficult for the unsupported samples because of stacks overlapping, it seems obvious that the edge sites are relatively more abundant for the hydrothermal samples, whereas the ex-thiosalt solids expose a more important share of the rim sites. The analysis of breadth of the (002) XRD line and estimation of stacking from the HREM images give the same qualitative result, though the absolute values of average stacking numbers somewhat differ (table 2).

Compared with the ex-thiomolybdates, the specific activity of hydrothermal MoS_2 is higher in the thiophene HDS but lower in the tetralin HYD, as presented in table 3. The intrinsic activity of hydrothermal samples is always lower, because of their high specific surface area, in which a great contribution of catalytically inactive basal planes is present. However, the share of border (rim or edge) sites for the hydrothermal samples is about 10 times lower than for ex-thiomolybdates. Therefore, the intrinsic activity should be lower for the hydrothermal sulfides by an order of magnitude, which is not the case. The reason for such a discrepancy might be in the different accessibility of catalytic centers for the reacting molecules or in the non-zero activity of curved basal planes, as suggested by Iwata *et al.* [15,16].

As follows from the results of the catalytic study presented in table 3, qualitative differences of catalytic activity exist between hydrothermal and thermal decomposition-derived sulfides which are of the same

Table 3
Reactivity of sulfides in thiophene HDS and tetralin HYD at 573 K

Catalyst	Tetralin HYD		Thiophene HDS		
	V_s (10^{-8} mol/g s)	V_i (10^{-8} mol/m^2 s)	C^0/C^{2-} ratio	V_s (10^{-8} mol/g s)	V_i (10^{-8} mol/m^2 s)
513-FSS	12.2	0.17	0.1	44.6	0.48
513-1S	9.1	0.14	0.09	18.0	0.23
Ex TS 1	28.0	0.78	0.27	13.5	0.61
Ex TS 2	15.7	0.82	0.47	9.0	0.60

V_s is the specific reaction rate. V_i is the intrinsic reaction rate. C^0/C^{2-} is the butane to butene ratio.

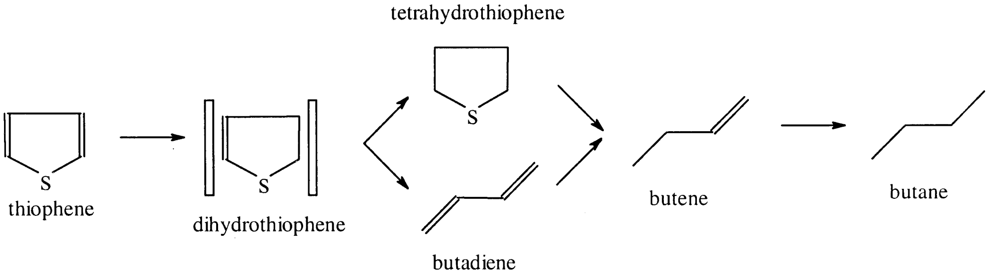

Figure 5. Thiophene HDS reaction network.

kind, for all four preparations studied. The variation in the HYD/HDS activity ratio is remarkable: for the hydrothermally-prepared samples the HDS activity (either specific or intrinsic) is always greater than the HYD activity, whereas for the solids obtained by thermal decomposition the ratio of activities is inverse. In agreement with the HYD/HDS activity ratios observed in two different reactions, the selectivity in the thiophene HDS is also very different at comparable conversions. As follows from its less hydrogenating properties, both hydrothermal samples have at least three times higher butene to butane ratio (table 3). Therefore, without resolving the kinetic equations we may state that the direct HDS pathway without intermediate formation of tetrahydrothiophene (figure 5) prevails in these specimens over the consecutive hydrogenation–HDS route. It seems that this difference depends only on the sulfide morphology, because the initial and measured S/Mo ratios after catalytic tests are very similar for two types of preparation. As for eventual impurities, their influence is unlikely since all the samples were prepared from the decomposition of the same ATM precursor.

4. Conclusions

Hydrothermal synthesis allows one to obtain molybdenum sulfide compounds with original morphology. The reaction temperature and the acidity of the reaction mixture are key parameters, determining the nature of the products obtained. Varying these parameters, pure phases of needle-like $(NH_4)_2Mo_3S_{13}$ of highly dispersed MoS_2 with very long layers have been prepared. They are interesting model solids with which to study the nature of catalytic function in the sulfide systems. The surface areas of hydrothermal MoS_2 solids obtained in this work (about 80–100 m^2/g) are somewhat lower than those of carbon-stabilized samples from previous reports. However, their stability is high and, being free of carbon, they are also free from its influence on the catalytic properties, whatever the latter. Such a set of solids gives a good opportunity to study the structural sensitivity of the HYD and HDS reactions. We see that the HYD/HDS activity ratio was inverted in these experiments as a function of the catalyst morphology. Therefore, control of Mo sulfide catalyst selectivity *via* the change of its morphology is indeed possible.

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