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Preparation of MoS_2 catalysts by in situ decomposition of tetraalkylammonium thiomolybdates

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Abstract

Molybdenum tetraalkylammonium thiosalts were used as precursors for the in situ formation of MoS_2 catalysts for dibenzothiophene hydrodesulfurization. The influence of the chemical composition of precursors $(R_4N)_2MoS_4$ with $R=H^+$, CH_3^+ or $C_4H_9^+$ and mechanical pressing of precursors on the composition and activity of prepared catalysts was investigated. The change of cation from proton to methyl- and to butylammonium increased the surface area and HDS activity of MoS_2 catalysts. Extremely high surface area surpassing 200 m^2/g was obtained for catalysts formed from tetrabutylammonium thiomolybdate. Significant difference was observed for pattern of thermal decomposition of alkylammonium thiosalts compared to ammonium ones. Unusual sponge-like morphology by reason of appearance of secondary porosity was observed in the case of tetrabutylammonium precursors. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Unsupported HDS catalyst based on MoS_2 can be prepared ex situ by decomposition of ammonium thiosalts under typical sulfiding conditions, such as hydrogen sulfide in hydrogen gas mixtures and temperatures around 673 K [1]. A method of in situ activation has been developed [2], where catalyst precursor salts, along with sulfur-containing organic compounds in a hydrocarbon solution, are pressurized with hydrogen and heated to 623 K, eventually yielding active metal sulfides. Thus, the in situ preparation of highly active MoS_2 catalysts was disclosed to involve ammonium- and several alkylammonium thiosalts, including tetramethyl-, tetraethyl- and tetrabutylammonium salts. Catalysts prepared in this way from ammonium thiomolybdate (ATM) contain certain amounts of carbon, and are described with the general formula $MoS_{2-y}C_z$, where $0.01 \leq y \leq 0.5$ and $0.01 \leq z \leq 3.0$ [2]. These catalysts exhibit improved activity for the HDS of dibenzothiophene (DBT), compared to catalysts prepared by other methods.

The role of carbon in the formulation of those HDS catalysts is not completely obvious, but it is possible that carbon, at least partly, is included in the arrangement of active sites. It was recently shown that molybdenum carbide has high activity in hydropro-

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cessing reactions. Produced by carburizing of alumina-supported ammonium molybdate in a CH_4/H_2 reactant stream Mo_2C/Al_2O_3 showed three times higher activity in HDS process than MoS_2/Al_2O_3 catalyst [3].

Molybdenum disulfide can also be produced by thermal decomposition from thiosalts or oxythiosalts. Naumann et al. [4] substituted ammonium ions in ammonium thiomolybdate and received compounds with a general formula $B_2MoO_xS_{4-x}$, where B is an alkylammonium ion or cyclic amine, containing one or more N atoms, and $0 \leq x \leq 2$. Their decomposition takes place preferably in the range 673–773 K; the most common use for these catalysts is in nickel or cobalt promoted forms, for catalyzing hydrogenation or hydrotreating reaction.

It was shown [5], that mechanical activation of ATM precursor leads to more active catalysts. Mechanochemical activation of solids is known to affect the activity of solids by generating of defects in the volume [6]. These defects change the behavior of the in situ catalysts and materials with varied properties were produced.

The aims of this work are to investigate the influence of thiosalts composition along with mechanical activation of precursors on the process of in situ formation of molybdenum disulfide catalysts. Exchange of ammonium cations with the more bulky methyl- and butylammonium cations was expected to influence the in situ reaction and produce modified materials. Tetramethylammonium thiomolybdate (TMATM) and tetrabutylammonium thiomolybdate (TBATM) in as synthesized and mechanically activated forms were selected as the precursors for preparation of catalysts. The microstructure and textural characterization, side by side with catalytic activity measurements, of in situ prepared molybdenum disulfide catalysts from these precursors are reported. The properties of these samples will be compared with the properties of the catalysts prepared from the ATM precursor [5].

2. Experimental

2.1. Precursor preparation

The syntheses of tetraalkylammonium salts $(R_4N)_2$-MoS_4 have been reported by J. MacDonald et al. [7]. In the present work, an improved version of this method was used. TMATM and TBATM thiosalts were prepared at room temperature from aqueous solutions of and quaternary ammonium halides $(R_4N)X$, where $R = CH_3^+$ or $(CH_2)_3CH_3^+$ and X=Cl or Br with yields approximately 80%. The details of synthetic procedure are reported separately [8].

Tetraalkylammonium salts used as catalyst precursors were prepared in both powder and pressed forms. The powder forms of the precursors are the thiosalts without mechanical pressing. The pressed forms were obtained by uniaxial pressing of the thiosalts to 427 MPa for 5 min in a stainless steel die. Samples are identified as abbreviation of thiosalt-precursor followed by assignation -P for powder or -427 for pressed samples, respectively. The pellets of pressed precursors were crushed in a mortar before placing them inside the reactor.

2.2. Catalytic activity

The HDS of DBT was carried out in a Parr Model 4522 high pressure batch reactor. The catalyst precursor (2.0 g), along with the reaction mixture (5 vol % of DBT in decaline), was placed in the reactor, then pressurized to 3.1 MPa with hydrogen and heated to 623 K with a heating rate of 10 K/min. When the working temperature was reached, sampling for chromatographic analysis was performed to determine conversion vs. time dependence. The reaction ran for about 5 h. Reaction products were analyzed using a Varian 350 gas chromatograph with a 2.0 m 1/8 in packed column containing OV-17 as separating phase.

2.3. Catalyst characterization

Characterization of catalysts was performed on samples obtained in situ and recovered after the catalytic tests. The samples were separated from the reaction system by filtration, washed with isopropanol to remove residual hydrocarbons and dried under vacuum before analysis.

Catalyst morphology was studied with a Jeol 5300 scanning electron microscope. Samples were placed on the sample holder using graphite paint. Several fields were analyzed at different magnifications to recognize the prevalent features.

The surface composition of the catalysts was determined with a Perkin Elmer PHI 595 scanning Auger electron spectrometer. Measurements were made on the original surface. The relative atomic ratios for molybdenum, sulfur and carbon at the surface were calculated for all samples.

Specific surface areas were determined with a Gemini 2060 from Micromeritics by nitrogen adsorption at 77 K using the BET isotherm. Samples were degassed under flowing argon at 473 K for 2 h before nitrogen adsorption.

The thermogravimetric analysis of thiosalts was made on a Stanton Redcroft DTA-TGA, model STA-80, under dry nitrogen flow, from 293 to 1073 K, with a heating rate of 10 K/min.

3. Results

3.1. Surface area

Fig. 1 shows the results of surface area measurements of the catalysts used in this study. The surface area of ATM-P catalyst [5] ranges in 75–80 m^2/g, that is in general higher than those found in previous studies; 39–43 m^2/g [9], 8–41 m^2/g [10], 9–64 m^2/g, 9–40 m^2/g [11], 10–100 m^2/g [12].

The uniaxial compressing of precursors at 427 MPa generated an increase of surface area of all catalysts for approximately 10% (Fig. 1). In contrast, chemical composition of precursors significantly influenced surface area. The relative range of surface area as a function of the precursors was: TBATM>TMATM>-ATM for both forms of catalysts (Fig. 1). It increased by a factor of 2 and 3 for TMATM and TBATM respectively, indicating that bulkiness of R_4N^+ cations plays a decisive role on defining texture of catalysts. As a result, surface area of catalysts reaches values, typical for industrial catalysts [13].

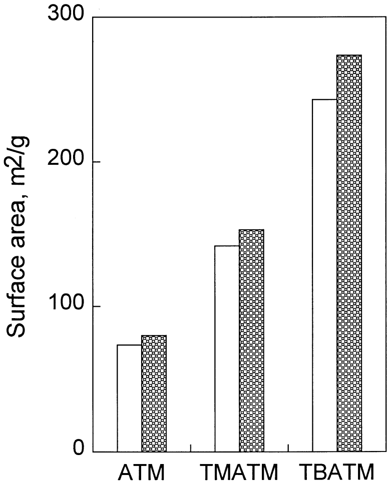

Fig. 1. Surface area of catalysts derived from powder (non-filled columns) and pressed (filled columns) precursors.

3.2. Scanning electron microscopy

Fig. 2(a) and (c) are images of TMATM catalysts. The catalysts are irregular rounded particles with sizes ranging between 5 and 15 µm. The pressed catalyst have small aggregates on the surface of particles suggesting that pressing of TMATM precursor caused segregation.

Fig. 2(b) and (d) show micrographs of TBATM catalysts. Particles have pronounced sponge-like morphology with complicated porous system. The pressing modifies the apparent pore size distribution. Presence of well-developed porous system coincides with very high value of specific surface area for TBATM samples (Fig. 1).

3.3. Catalytic activity

Table 1 shows the initial rate constants calculated from the slope of plots of DBT conversion vs. reaction time, assuming zero order, as suggested elsewhere

Table 1
Specific surface areas, initial rate constants for HDS and surface composition (normalized to Mo) of in situ prepared molybdenum sulfide catalysts

Sample	*k* (specific) (10^{-6} mol/l g s)	Surface composition	
		S/Mo	C/Mo
ATM-P	4.5	5.0	1.5
TMATM-P	4.7	4.0	1.2
TBATM-P	6.1	4.2	1.6
ATM-350	5.1	4.7	1.5
ATM-700	4.4	3.7	2.0
TMATM-427	3.5	4.2	1.6
TBATM-427	5.6	4.0	1.4

Data for ATM taken from [5].

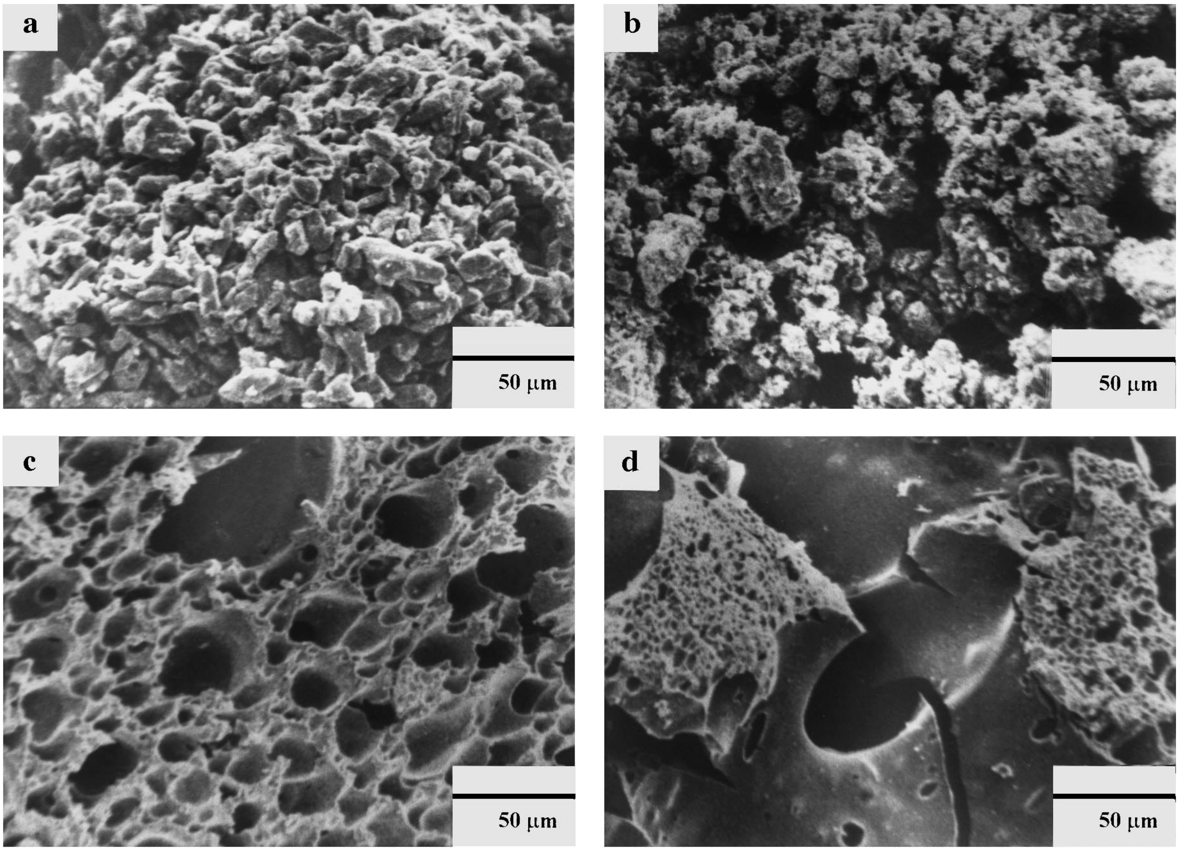

Fig. 2. SEM micrographs of catalysts derived from powder (a, b) and pressed (c, d) precursors: TMATM (a, c) and TBATM (b, d).

[14]. Data for ATM catalysts from [5] are included for comparison.

Specific rate constant increases with the size of precursor cation R_4N^+ for powder form of catalysts, while for pressed ones it changes in the range TBATM>ATM>TMATM.

3.4. Auger electron spectroscopy (AES)

Table 1 shows the S/Mo and C/Mo atomic ratio measured for all catalysts. These values were determined on the original surface, following in situ reaction test. It must be noted that AES gives an S/Mo ratio of four for MoS_2 single crystal instead of two [15]. This is due to: (a) the layer structure of MoS_2 where the four nearest surface layers show an S/Mo ratio of three, and (b) the fact that electron escape distances decrease exponentially with depth, which requires the use of attenuated intensity factors for inner layers. For this reason the reference value for monocrystalline MoS_2 measured by AES is four.

The S/Mo ratio of the surface of catalyst derived from tetraalkylammonium thiomolybdates are, in contrast to ammonium thiomolybdate catalyst, very close to the reference value indicating good stability of the surface.

The C/Mo ratio for most catalysts is approximately 1.5 (Table 1). It indicates that carbon remained at the catalyst surface.

3.5. Thermal analysis

Thermogravimetric (TGA) and differential thermal analyses (DTA) were used to characterize the thermal decomposition of tetramethyl- and tetrabutylammonium thiosalts. Decomposition of tetramethylammonium thiomolybdate appears to take place in one endothermic step. There is no influence of initial

Table 2
Temperature of initial (T_1) and final (T_2) points of weight loss, and weight changes (Δw) of tetramethylammonium precursors during thermal decomposition

	TMATM-P	TMATM-427
T_1 (K)	503	503
T_2 (K)	531	527
Δw, wt.% (exp)	56.1	56.0
Δw, wt.% (theor), assuming residual as MoS_2	57.8	57.8

pressurizing on this process. Both pressed and non-pressed precursors show the same pattern of thermal decomposition (Table 2). Values of weight loss are a little smaller than theoretical ones, assuming the MoS_2 formation. It should be noted that in situ formation of catalyst and TGA experiments are carried out in different atmospheres.

Thermal decomposition of tetrabutylammonium thiomolybdate is much more complicated. Two steps of weight loss are observed for TBATM. Decomposition of precursor depends on initial pressurizing (Table 3). It seems that final products of thermal decomposition in dry nitrogen correspond to MoS_{3+x} for TBATM-P and MoS_{2+x} for TBATM-427 (Table 3). The puzzling behavior of this compound matches very complicated secondary structure of catalyst particles, as it is shown by SEM (see Fig. 2). Further investigation of the details of thermal decomposition of tetrabutylammonium thiosalts is necessary, but this research is beyond the scope of the present work.

Table 3
Temperature of initial (T_1), intermediate (T_2) and final (T_3) points of weight loss, and weight changes (Δw) of tetrabutylammonium precursors during thermal decomposition

	TBATM-P	TBATM-427
T_1 (K)	420	420
T_2 (K)	436	436
$\Delta w_{1\text{–}2}$, wt.% (exp)	34.7	30.5
$\Delta w_{1\text{–}2}$, wt.% (theor)	34.0	32.0
Assuming loss of	Bu_4N^+	$4Bu^+$
T_3 (K)	481	475
$\Delta w_{2\text{–}3}$, wt.% (exp)	36.4	44.9
$\Delta w_{2\text{–}3}$, wt.% (theor)	38.8	45.4
Assuming loss of	Bu_4NS^-	$2Bu_2NH_2S^-$
Δw_{Σ}, wt.% (exp)	71.1	75.4
Residual, wt.% (exp)	28.9	24.6
Residual, wt.% (theor), Assuming residual as		
MoS_3	27.1	27.1
MoS_2	22.6	22.6

4. Discussion

Decomposition of thiosalts is known as a very effective method for the preparation of highly active MoS_2 unsupported or alumina supported catalysts [16,17]. The thermal decomposition of thiosalts to obtain MoS_2 involves elimination of alkylammonium cations to get MoS_3 and, after that, simultaneous reduction of Mo^{6+} to Mo^{4+} and sulfur elimination. The degree to which sulfur is removed and the lattice becomes organized depends on the temperature [18].

The decomposition step of MoS_3 to MoS_2 and MoS_{2+x} transition was investigated using TGA and temperature programmed desorption [19], as well as by electron spin resonance [20]. It was shown [20] that some intermediate metastable phase with composition close to $MoS_{2.6}$ was formed, and a hypothetical new structure was proposed for the composition domain from $MoS_{2.7}$ to $MoS_{2.4}$.

Thermal decomposition of tetraalkylammonium thiosalts under N_2 shows different patterns of decomposition than obtained for ATM [5] both for methyl- and butylammonium precursors (Tables 2 and 3). There are no exothermic peaks in the process of tetraalkylammonium thiosalts decomposition, that corresponds to trisulfide→disulfide transition in the case of ammonium thiosalts decomposition. It means that sulfur is removed as sulfur-organic compounds simultaneously with removing of alkylammonium cations. For TMATM sulfur-rich compounds close to MoS_3 are formed in inert atmosphere of dry nitrogen during DTG measurements.

However, all catalysts, independent of precursor composition and mechanical activation, show high activity once the reaction temperature is reached, indicating that a rapid activation process took place. This can be due to the high hydrogen pressure which favors sulfur elimination through H_2S formation. It is known that amorphous MoS_3 (the first step of ATM decomposition) is very sensitive to the presence of H_2, which lowers the onset of its decomposition [19]. The combination of low temperature of decomposition

(623 K) and high pressure of hydrogen (3.1 MPa) can produce a very disordered MoS_2 structure with large surface area and improved catalytic activity.

During in situ activation in the presence of high pressure of hydrogen the composition of catalysts seems to be closer to MoS_2 (see Table 1). It is known that hydrogen facilitates sulfur elimination. This leads to the appearance of sulfur vacancy ($\square_S$),

$$S^{2-} + H_2 \rightarrow H_2S + \square_S + 2e^-$$

and simultaneous reduction of metal to lower valent state. Catalyst activation also includes interaction of MoS_{2+x} with hydrocarbons and appearance of sulfur-deficient carbon-containing material:

$$MoS_2 + H_{2y}C_z \rightarrow MoS_{2-y}C_z + yH_2S$$

that corresponds to the composition of the final catalysts $MoS_{2-y}C_z$ at the surface, where $0.05 \leq y \leq 0.2$ and $1.0 \leq z \leq 2.0$.

5. Conclusions

The method of in situ activation of MoS_2 starting from tetraalkylammonium thiosalts yields catalysts with enhanced surface area and improved catalytic performance. Applied mechanical pressure affects the surface area by increasing it by ~10%. The rate of reaction rises with the bulkiness of alkyl radical for non-pressed samples. For MoS_2 catalyst, prepared from ATM precursors [5], activity increased with applied pressure, while now for TMATM and TBATM decreases. Modification of the composition of precursor thiosalts leads to a sharp increase of surface area with the bulkiness of R_4N^+ cation, and appearance of sponge-like morphology for butylammonium tetrathiomolybdate precursor.

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