

Synthesis, characterization and cyclohexene hydrogenation activity of high surface area molybdenum disulfide catalysts

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An ammonium tetrathiomolybdate (ATTM) catalyst precursor is synthesized and then thermally decomposed at different temperatures in N₂ or H₂ atmosphere. Characterization of the resulting compounds by powder X-ray diffraction (XRD) and surface area analysis indicates the formation of MoS₂-2H with a surface area of 5–9 m²/g. When ATTM is treated with cetyltrimethylammonium chloride and then decomposed in N₂ at 723 K, the resulting material has a surface area nearing 200 m²/g. If treatment also includes hydrazine, the surface area of the resulting MoS₂-2H reaches 215 m²/g. Analysis by XRD and electron microscopy shows a noticeable dispersion in the layers of the resulting MoS₂. The catalytic activity of the materials is tested in a batch reactor for cyclohexene hydrogenation, where the highest activity sulfides are those obtained by thermal decomposition of the chemically treated precursors in N₂.

KEY WORDS: high surface area MoS₂; hydrogenation; cyclohexene.

1. Introduction

The field of solid state chemistry has produced numerous studies on the optical, electrical, electrochemical and catalytic properties of transition metal sulfides (TMS). In general, TMS with layered structures exhibit similar catalytic behavior in hydrotreating reactions [1]. While some preparation methods yield highly crystalline, low surface area compounds [2,3], others lead to materials with poor crystallinity and greater surface area, along with appreciable catalytic activity. Such methods include co-maceration [4], precipitation [5, 6], and thiosalt decomposition [7]. In the search for new catalysts, some *in situ* methods have been developed which yield high surface area sulfides. The introduction of alkyl ammonium thiometallate precursors, for example, has produced compounds with greater surface areas than earlier generations of sulfide catalysts [8,9]. The synthesis of MoS₂ by a hydrothermal route also leads to the formation of a highly dispersed compound. Thus, the decomposition of ATTM in water under 20 bar N₂ or H₂S atmosphere has been studied at 15 min intervals for up to 4 h and at different temperatures in the region of 473–573 K, yielding catalysts with areas between 50 and 95 m²/g [10].

Increasing attention has been paid to the role of carbon in the stability of MoS₂ and RuS₂ catalysts, with some studies suggesting that the active phase of

these compounds involves a high surface area MoS₂-_xC_x compound. The first claims of the importance of carbon in these catalysts are made with regard to the synthesis of RuS_{2-x}C_x compounds, where carbon atoms substituting surface sulfur atoms were detected [8,9]. Catalysts obtained from carbon-containing salts of the type (NR₄)₂MoS₄ (where R = alkyl group) have greater catalytic activities than those obtained from the ammonium thiomolybdate salt [8,11–13]. Studies also indicate a noticeable increase in the surface area of the catalyst obtained from carbon-containing ammonium thiosalts, like in the case of MoS_{2-x}C_x which has a surface area of 152 m²/g when prepared from an ethylene-diamine thiosalt, and a surface area of 243 m²/g when prepared from a tetrabutyl ammonium salt [12,14].

Prior synthesis of this type of catalyst has been done *in situ* by decomposing ATTM in a reactor containing sulfur and H₂ [10]. In a recent study, *in situ* catalysts are found to yield greater surface areas than those prepared by conventional *ex situ* thiosalt decomposition, where the thiosalt is treated with a mixture of H₂S/H₂ at 673 K for 4 h [15].

A recent proposal takes aqueous solutions of ATTM, then adds reducing agents such as hydrazine (HZN) or hydroxylamine and in some cases a surfactant agent like cetyl-trimethylammonium chloride (CTAC), to produce molybdenum sulfides with surface area as high as 211 m²/g [16].

In this work, the effect of using non-stoichiometric quantity of CTAC and/or HZN to treat ATTM

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precursors in a variation of the above method is studied, looking to improve catalytic activity for the hydrogenation of cyclohexene, a reaction that is little studied in connection with TMS catalysts compared to HDS.

2. Experimental

2.1. Preparation of ATTM

The precursor thiosalt ATTM, $(\text{NH}_4)_2\text{MoS}_4$, is prepared according to the method described by Berhault *et al.* [17]. A weight of 4 g of ammonium heptamolybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Fluka, 99.0%) is dissolved in 20 mL of water. To this solution is added 38.4 mL of concentrated ammonium sulfide (Aldrich, 20%). The mixture is heated at 333 K for 1 h then cooled in an ice bath for 3 h to induce crystallization. Crystals are separated by filtration, washed with isopropyl alcohol and left to dry at room temperature. The resulting ATTM is then kept in N_2 atmosphere to avoid oxidation. The purity of ATTM is confirmed by XRD.

2.2. Thermal decomposition of ATTM in the presence of a gas

After grinding, 1.0 g of ATTM is placed in a porcelain boat, which is then introduced in the alumina tube of a tubular furnace with a H_2 or N_2 gas flow. Temperature is increased to 723 K using a 10 K/min heating rate, then kept constant for 2 h. At the end the furnace is allowed to cool to 473 K. Immediately after, gas flow is cut and the system is allowed to cool to ambient temperature. Finally, the sample is kept in N_2 atmosphere.

2.3. Molybdenum sulfide catalyst precursor modified with HZN

Since ATTM, HZN and CTAC are sensitive to an oxidizing environment, preparations are done in a N_2 atmosphere glove box. A weight of 2.8 g ATTM is dissolved in 100 mL of water. Elsewhere, 2 mL of HZN (N_2H_4 , Aldrich 35%) are dissolved in 100 mL of water. Both solutions are then mixed together. The mixture is placed in a flask fitted with a condenser, then heated in an oil bath to 333 K for 6 h with constant stirring. The resulting precipitate is filtered, washed with water, dried at 348 K and kept in N_2 atmosphere.

2.4. Molybdenum sulfide catalyst precursor modified with CTAC

Working in a glove box, a weight of 2.8 g ATTM is dissolved in 100 mL of water, then 20 mL of CTAC 0.1 M (from Aldrich, 25%) are added. The resulting mixture thus contains a non-stoichiometric rate of CTAC/ATTM (0.20 mol/mol) which is placed in a flask and the rest of the procedure is the same as in section 2.3.

2.5. Molybdenum sulfide catalyst precursor modified with HZN and CTAC

A weight of 2.8 g ATTM is dissolved in 100 mL of water, to which is added a solution consisting of 2 mL HZN (35%) in 100 mL of water, then finally adding 20.0 mL of CTAC 0.1 M. The mixture is placed in a flask and the rest of the procedure is the same as in section 2.3.

3. Characterization of samples

The BET specific surface area of the solid catalyst samples is measured with a Micromeritics Gemini 2060 surface area analyzer using N_2 as adsorbate gas and a sample mass of 0.2–0.3 g. Diffraction patterns are obtained by powder XRD diffraction with a Philips X'Pert analytical diffractometer using $\text{CuK}\alpha$ radiation. High resolution electron microscopy employs a JEOL 2010 transmission electron microscope; samples are suspended in isopropanol, deposited on holey carbon-coated copper grids and air-dried.

4. Catalytic activity

Catalytic activity for cyclohexene hydrogenation is tested in a high pressure 300 mL Parr reactor by placing 20 mL of cyclohexene with 0.3 g of catalyst. The reactor is purged of residual air, pressurized with H_2 to 35.91 KPa (750 psi) then heated to the reaction temperature of 523 K in about 10 min. A stirring rate of 50 rpm is used. The advance of the reaction is monitored by GC using samples taken every 15 min during the first hour, then every 30 min for the next 4 h. Reduction of sample volume $\leq 5\%$. Catalytic activity is expressed in terms of percentage conversion of cyclohexene and initial reaction rates.

5. Gas chromatography

Samples obtained from the reactor are analyzed using a Hewlett-Packard 5890 gas chromatograph with FID detector. A low polarity J&W DB624 capillary column, 30 m long, 0.53 mm diameter, 3.0 μm thick liquid phase is employed. Column temperature is 373 K, using a N_2 carrier gas flow of 3 mL/min and a split rate of 1:10.

6. Results and discussion

6.1. ATTM decomposition

The surface areas of the products of thermal decomposition of ATTM at different temperatures and in different gas environments are found to be in the range of 5–10 m^2/g , as shown in table 1. Changes are attributed to a varying degree of crystallite sintering.

Table 1

Specific surface areas corresponding to the MoS₂ obtained by thermal decomposition of ATTМ under different conditions

Decomposition temperature (°C)	Gas flow	Surface area (m ² /g)
300	H ₂	10.0
400	H ₂	8.7
450	H ₂	5.5
500	H ₂	5.1
300	N ₂	9.6
400	N ₂	4.2
450	N ₂	9.0
500	N ₂	4.3

Other studies have found surface areas as low as 5.5 m²/g and up to 50 m²/g for the decomposition of ATTМ in the presence of H₂/H₂S [7,15]. Another work using the same conditions for ATTМ thermal decomposition finds that the surface area of 50 m²/g, decreases to 4 m²/g when a temperature of 973 K was applied [18]. These facts show the notable influence of temperature on surface area of catalysts. The catalysts prepared using either a H₂ or N₂ gas environment during the thermal decomposition were found to give surface areas of the same magnitude.

6.2. Decomposition of chemically modified ATTМ

The surface area results of MoS₂ catalysts obtained by modifying ATTМ with HZN and/or CTAC and later decomposing them in N₂ atmosphere at 723 K are reported in table 2. The surface area of the catalyst doubles with the use of HZN and becomes over 20 times greater with the use of the surfactant, suggesting the formation of very small crystallites. Earlier work by Alvarez *et al.* reported that *in situ* catalysts yield greater surface areas than those prepared by conventional *ex situ* thiosalt decomposition, with reported values of 59.9 and 8.0 m²/g for *in situ* and *ex situ* prepared molybdenum sulfide, respectively [15]. The increase in surface area is attributed to the presence of carbon-containing alkyl groups in the structure of (NR₄)₂MeS₄ (R:H or alkyl:Me:Mo or W). In a similar way, the high surface area of the catalysts here obtained from chemically modified precursors is thought to be due to surface structural carbon derived from the surfactant material.

Table 2

Surface areas of the MoS₂ obtained from different precursors by thermal decomposition at 723 K in N₂

Precursor	Surface area (m ² /g)
ATTМ	9
ATTМ + HZN	18
ATTМ + CTAC	195
ATTМ + HZN + CTAC	215

6.3. XRD patterns

The XRD pattern of the pure ATTМ phase in figure 1 consists of sharp peaks, the strongest of which are identified as the (020), (111), (200), (220), (002), (310), (311), (212), (222), (330), and (142) reflections and is in good agreement with the reflections reported for orthorhombic (NH₄)₂MoS₄ (PDF 48-1662). The XRD pattern of the material produced by thermal decomposition of ATTМ + HZN + CTAC in H₂ is shown in figure 2a and is very similar to that of the decomposition product of ATTМ in H₂ shown in figure 2b, except for the reflection at 2θ = 14°. With their broad peaks, the diffraction patterns suggest that both materials are composed of small crystals. The reflections agree with those reported for the structure of poorly crystalline MoS₂-2H [18-20]. The peak at 2θ = 14° corresponds to the layered stacking of the (002) planes. The reflection corresponding to the (100) planes is less intense than in MoS₂-2H crystals and the (103) planes are absent. The attenuated (100) diffraction peak, along with its asymmetric shape, is related to a loss in stacking sequence [20]. From table 1, the fact that the decomposition product of ATTМ in H₂ has a smaller surface area (5.5 m²/g) compared to the one obtained by using N₂ (9 m²/g), along with the resemblance of the XRD spectra, suggest a greater sintering when decomposing in a H₂ atmosphere. It is known that decomposition of the thiosalt at 673 K leads to the formation of MoS₃ and finally MoS₂ at 723 K [7].

The XRD patterns for the catalyst materials obtained by decomposition of modified ATTМ in N₂ are shown in figure 3. Analysis of the nearly identical figure 3a and b, corresponding to the decomposition products of TTMA + HZN + CTAC and TTMA + CTAC, respectively, identifies the (100), (103), (110) and (200)

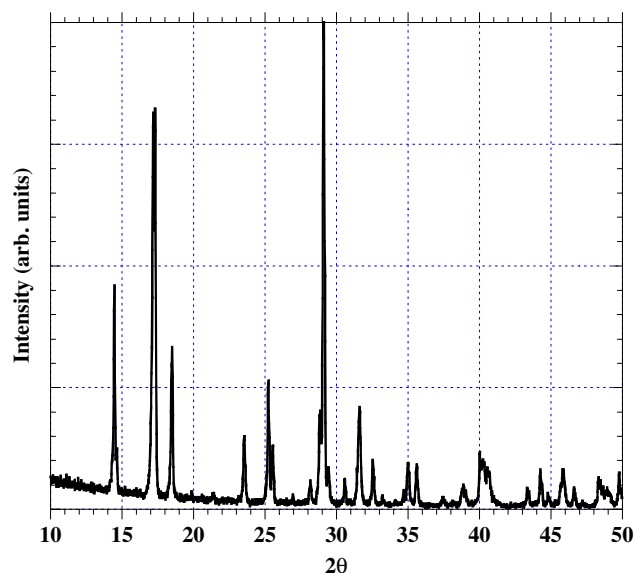


Figure 1. Diffractogram of freshly prepared (NH₄)₂MoS₄.

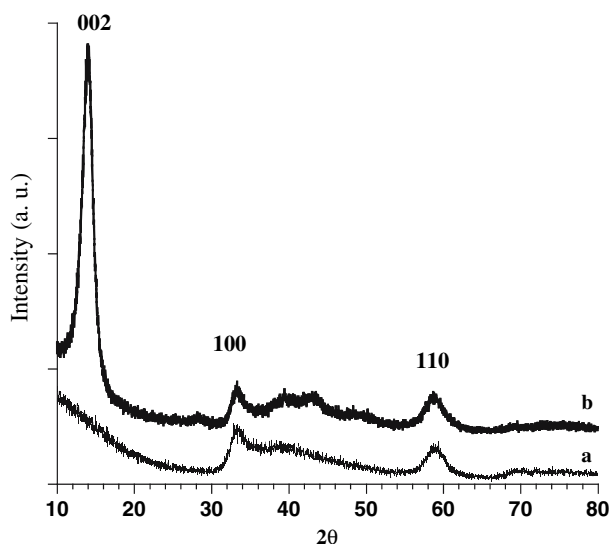


Figure 2. Diffractogram of the MoS_2 obtained by thermal decomposition in H_2 of (a) ATTMM + HZN + CTAC and (b) ATTMM.

reflections of $\text{MoS}_2\text{-2H}$. It is important to note the absence of the reflection corresponding to the (002) family of planes. This suggests the formation of crystallites consisting of only a few atomic layers. The pattern in figure 3c is nearly identical to figure 2b and corresponds to ATTMM decomposed in N_2 .

6.4. Electron microscopy

High resolution electron micrographs of the MoS_2 obtained by thermal decomposition of pure ATTMM and the MoS_2 obtained by thermal decomposition of ATTMM + HZN + CTAC are similar to the one in figure 4. The micrographs show no long range crystal-

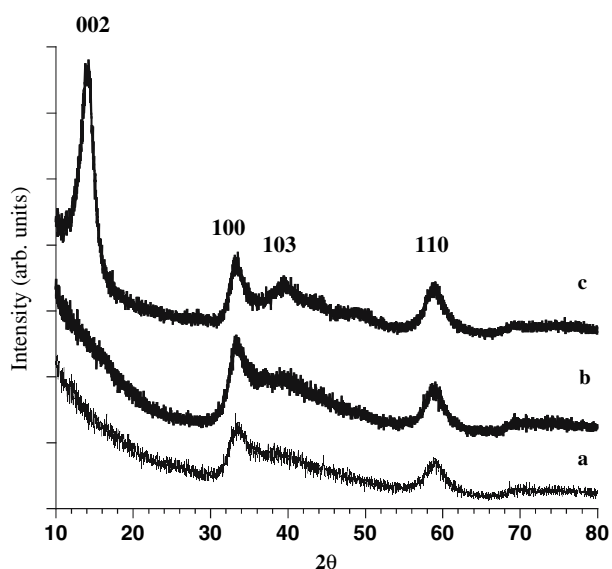


Figure 3. Diffractogram of the MoS_2 obtained by thermal decomposition in N_2 of (a) ATTMM + HZN + CTAC, (b) ATTMM + CTAC, and (c) ATTMM.

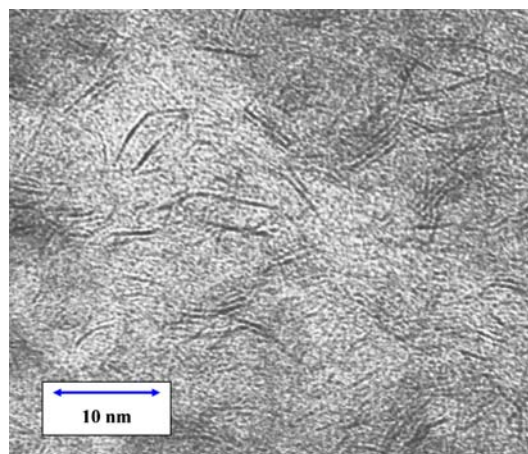


Figure 4. Electron micrograph of the MoS_2 obtained by the thermal decomposition of ATTMM + HZN + CTAC.

line order, but mostly different areas made up of only a few atomic layers with the 0.62 nm interplanar spacing characteristic of the (002) family of $\text{MoS}_2\text{-2H}$ planes. The MoS_2 from modified ATTMM seems to exhibit a greater dispersion than the one from pure MoS_2 .

6.5. Catalytic activity

Hydrogenation activity measurements for catalyst samples are presented in figures 5 and 6. Analysis of the kinetic data by the integration method finds that the hydro-genation reaction closely follows a first-order rate law over the 5 h reaction time, with a correlation factor of over 0.98. The corresponding hydrogenation reaction rates at the initial cyclohexene concentration are then calculated. Since molybdenum disulfides are anisotropic and their activity has no direct relation with their total surface area, catalytic activity is expressed in terms of rates per catalyst weight rather than rates per catalyst

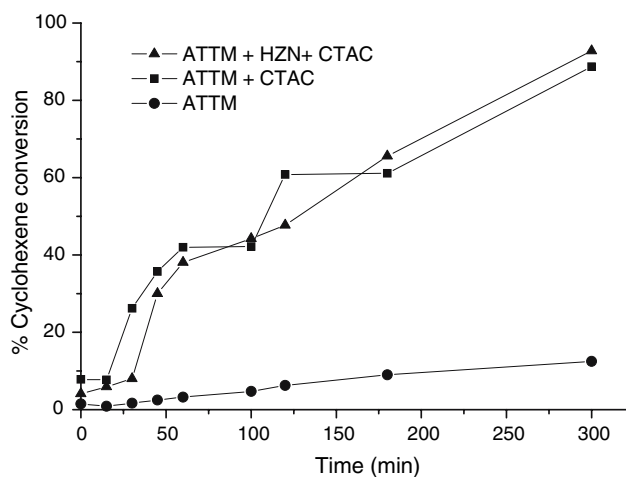


Figure 5. Catalytic activity of the MoS_2 obtained by thermal decomposition of different precursors in H_2 .

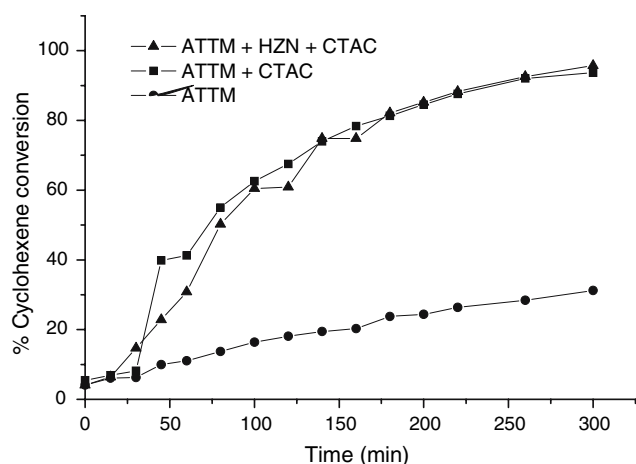


Figure 6. Catalytic activity of the MoS₂ obtained by thermal decomposition of different precursors in N₂.

surface area, as shown in table 3, in order to compare their activity with that of other catalysts reported in the literature. Thus, the initial reaction rates at 523 K for both ATTM-derived catalysts are greater than those found by Ramirez *et al.* for MoS₂/Al₂O₃ catalysts, which are in the order of 8×10^{-6} mol/g_{cat}S at 573 K [21].

According to figures 5 and 6, the catalyst obtained by decomposition of the ATTM in H₂ yields a 13% conversion, compared to 33% for the catalyst obtained from the ATTM decomposed in N₂. For samples prepared in N₂, the corresponding reaction rate ratio, $v(\text{ATTM} + \text{HZN} + \text{CTAC}) : v(\text{ATTM} + \text{CTAC})$, is 1.03, while that of the samples prepared in H₂ is 1.10. Thus, the combination of HZN + CTAC seems to contribute little to the enhancement of MoS₂ catalytic activity over CTAC alone. The catalysts derived from ATTM + CTAC in both figures reach over 90% cyclohexene conversion after 5 h, compared to less than 35% for those derived from pure ATTM. The corresponding reaction rate ratio, $v(\text{ATTM} + \text{CTAC}) : v(\text{ATTM})$, is 14 for samples prepared in H₂, and 7 for samples prepared in N₂.

The improvement in activity for the catalyst prepared by decomposition of ATTM in N₂ relative to decomposition in H₂ [$v(\text{ATTM}, \text{N}_2) : v(\text{ATTM}, \text{H}_2)$ is 2.8], is due to a greater amount of active sites responsible for hydrogenation. Decomposing the thiosalt in H₂ may in fact induce the generation of species like Mo(II), which

Table 3

Initial reaction rates (10^5 mol/g_{cat}S) for cyclohexene hydrogenation with MoS₂ catalysts obtained from untreated and treated ATTM

Treatment gas	ATTM	ATTM + CTA	ATTM + HZN + CTA
H ₂	0.54	7.49	8.25
N ₂	1.49	10.21	10.53

is not the case with the decomposition in N₂. In terms of the so called “rim-edge model” used to discuss the hydrodesulfurization (HDS) and hydrogenation behavior of MoS₂ catalysts [22], catalyst microcrystals consist of a stack of n monolayers of diameter d . The top and bottom layers have both border and rim sites, while the middle layers have only border sites; the top and bottom surfaces (basal planes) are inert. According to the “rim-edge” model, desulfurization reactions take place on both rim sites and border sites, while hydrogenation only occurs on rim sites. The greater activity of the catalysts obtained by thiosalt decomposition in N₂ compared to those obtained in H₂ would thus imply a greater number of MoS₂ crystallites having rim sites independent of the number of atomic layers in-between, as suggested by the greater surface area of the catalyst obtained using N₂. In these crystallites the presence of the “rim” is important, since it constitutes the site assigned for hydrogenation.

The hydrogenation activity of the MoS₂ obtained from ATTM treated with CTAC yields about 95% conversion in 5 h, as seen in figure 6. The activity of the MoS₂ obtained by ATTM treated with both HZN and CTAC is only slightly greater than that of the catalyst derived from ATTM + CTAC alone, observing a greater slope at the beginning of the reaction in both cases. The TEM micrograph of the MoS₂ derived from ATTM treated with CTAC, figure 4, shows the typical “rag structure” described by Chianelli [23] for these sulfide catalysts.

7. Conclusions

ATTM treated with CTAC using a 1:0.2 molar ratio ATTM/CTAC yields MoS₂ catalysts with surface areas comparable to those reported in the literature for MoS₂ catalysts obtained using a 1:1 ratio of CTAC/ATTM. In other words, the 1:1 ratio is not critical to attaining high surface areas.

The XRD pattern of the ATTM + CTAC system decomposed in N₂ does not contain the (002) reflection, indicating that the resulting molybdenum sulfide is made of amorphous material or very small crystallites, consistent with an efficient dispersion produced by the tensoactive agent.

The use of the tensoactive agent in the ATTM + CTAC derived catalyst produces a 7-fold increase in the hydrogenation rate constant, compared to that of the ATTM derived catalyst, when the precursors are decomposed in N₂, and a 14-fold increase when precursors are decomposed in H₂.

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