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Cyclohexene hydrogenation with molybdenum disulfide catalysts prepared by *ex situ* decomposition of ammonium thiomolybdate-cetyltrimethylammonium thiomolybdate mixtures

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Abstract

Ammonium tetrathiomolybdate (ATTM) is treated with cetyltrimethylammonium chloride (CTAC) using several ATTM/CTAC ratios. Reaction of ATTM with the limiting reagent CTAC gives the carbon-containing compound cetyltrimethylammonium tetrathio-molybdate (CTAT), resulting in different ATTM–CTAT mixtures or precursors which are then decomposed in N_2 at 723 K, yielding mesoporous samples with surface areas of over 260 m^2/g. Analysis by XRD and electron microscopy correspond to a well dispersed MoS_2–2H phase. The activity of the catalysts is tested in a batch reactor for cyclohexene hydrogenation, where those prepared from ATTM–CTAT precursors are up to seven times more active than the catalyst obtained by thermal decomposition of pure ATTM. The enhanced catalytic activity of these catalysts is attributed to a sulfide phase containing structural carbon.

Keywords: High-surface area MoS_2; Hydrogenation; Cyclohexene; Cetyltrimethylammonium chloride

1. Introduction

The use of transition metal sulfide (TMS) catalysts in oil refinery hydrotreating has helped reduce the toxic SOx and NOx atmospheric emissions of internal combustion engines for several decades. Hydrotreating catalysis involves a variety of reactions, among them, hydrodesulfurization (HDS), hydrodenitrogenation, hydrodeoxygenation, and hydrogenation [1–4].

Several methods are used to prepare sulfide catalysts: sulfidation of coprecipitated oxides [5,6] comaceration [7,8], homogeneous sulfide precipitation [9], ceramic method [10], impregnated thiosalt decomposition [11], all of which yield compounds with surface areas in the order of 5–50 m^2/g.

Tetraalkylammonium thiometallates have been synthesized by the metathesis reaction between ammonium tetrathiomolybdate with tetraalkylammonium chlorides [12] or tetraalkylammonium hydroxides using acetonitrile as a solvent [13]. Transition metal sulfide precursors $(NR_4)_2MS_4$, where R=H, CH_3, or C_4H_9 (alkyl group) and M=Mo or W, were prepared by reacting ammonium tetrathiomolybdate with the corresponding tetraalkylammonium bromide in an aqueous medium, followed by *in situ* decomposition [14,15].

The *in situ* decomposition of tetraalkylammonium thiomolybdates yields molybdenum sulfide catalysts with high-surface area and improved catalytic properties in the HDS of dibenzothiophene. This behavior has been associated with the presence of carbon in substitution of sulfur atoms, generating systems like $MoS_{2-x}C_x$ [16]. In the synthesis of ruthenium sulfides carbon content has also been observed according to the formula: $RuS_{2-x}C_x$ [17,18]. Greater excess of sulfur in Ru and Mo sulfide catalysts with general formula MS_{2+x} as been found to yield a greater carbon content $MoS_{2-x}C_x$ after HDS in organic solvents [19]. On the other hand, researchers have found that metal sulfides supported on carbon show a much greater activity than the same sulfides when supported in alumina [20,21].

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Highly dispersed molybdenum sulfides have recently been produced from precursors obtained by treating aqueous ATTM with CTAC and reducing agents like hydroxylamine sulfate or hydrazine hydrate [22], resulting in surface areas of up to 211 m^2/g. In recent work [23], the treatment of ATTM using an ATTM/CTAC ratio (1/0.2) gives precursors that yield MoS_2 catalysts with similar surface areas.

This work studies the properties of MoS_2 catalysts obtained from the thermal decomposition of precursors resulting from ATTM treated with different quantities of CTAC (ATTM/CTAC molar ratio = 2.5–0.5) including the evaluation of their catalytic activity for the model cyclohexene hydrogenation.

2. Experimental

2.1. Preparation of molybdenum sulfide precursors (MSP)

Untreated $(NH_4)_2MoS_4$, the molybdenum sulfide precursor MSP1, was prepared according to the method described by Berhault [24] which requires adding $(NH_4)S$, 42.5% in aqueous solution to $(NH_4)_6[Mo_7O_{24}]_4\cdot H_2O$ diluted in a minimum amount of water to produce a dark red crystalline precipitate.

Precursor MSP2 was prepared by dissolving 1.0 g (3.84 mmol) $(NH_4)_2MoS_4$ in water (30 mL) and adding 1.56 mmol CTAC as a 25% aqueous solution (2 mL) and stirring for 1 h at room temperature. The resulting precipitate was isolated by vacuum filtration, and kept under N_2 atmosphere. Precursors MSP3, MSP4, MSP5, MSP6 were prepared in a similar way as MSP2, using 4, 6, 8 and 10 mL of CTAC 25% aqueous solution, respectively, to treat MSP.

2.2. Preparation of molybdenum sulfide catalysts (MSC)

The molybdenum sulfide catalysts were prepared by grinding 1.0 g of each precursor, placing it in a porcelain boat, introducing it in the alumina tube of a tubular furnace with N_2 gas flow, increasing temperature to 723 K (10 K/min heating rate) and then kept constant for 2 h. The furnace was later allowed to cool to 473 K and immediately after, the gas flow was cut and the system was allowed to cool down to room temperature. Finally, the sample was kept under N_2 atmosphere.

2.3. Characterization of samples

Horizontal attenuated total reflectance (HATR) IR spectroscopy was recorded with a Series 1700 Perkin-Elmer FTIR spectrophotometer. The IR sample was ground in an agatha mortar and placed evenly on the HATR device.

Specific surface area was measured with a Quantachrome AUTOSORB-1 by N_2 absorption at 77 K using the BET isotherm and a sample mass of 0.2–0.3 g. Samples were degassed under flowing argon at 473 K for 2 h before N_2 adsorption. The pore size distribution was obtained from the desorption data, following the BJH method. The mean standard deviation for the surface area measurements was about 2%.

The X-ray diffraction patterns of the prepared samples were obtained with a Philips X'Pert analytical diffractometer for powder samples using Cu Kα radiation. Their phases were identified with reference to the database of the International Centre for Diffraction Data.

A Jeol JSM5800 IV scanning electron microscope was used to perform morphology and EDX elemental analysis. Several fields were analyzed at different magnifications in order to recognize the prevalent features. EDX analysis was performed using an eBX-ZAF system, using an MoS_2 reference sample to deconvolute the L lines of S and Mo. Transmission electron microscopy was done on a Philips FEG TECNAI F20 transmission electron microscope operated at 200 kV.

2.4. Catalytic activity

The catalytic activity for cyclohexene hydrogenation was tested in a high-pressure 300 mL Parr reactor by placing 20 mL of cyclohexene with 0.3 g of catalyst. The reactor was purged of residual air, pressurized with H_2 to 35.91 kPa (750 psi) then heated to the reaction temperature of 543 K in about 10 min. A stirring rate of 50 rpm was used. The advance of the reaction was monitored by GC using samples taken every 20 min during the first hour, then every 30 min for the next 4 h. Reduction of sample volume due to sampling was $\leq 5\%$ of total volume. Catalytic function was expressed in terms of % conversion of cyclohexene versus time and from these data, initial reaction rates were calculated for each catalyst.

2.5. Gas chromatography

Samples obtained from the reactor were analyzed using a Hewlett–Packard 6890 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 was employed. Column temperature was 373 K, using a N_2 carrier gas flow of 3 mL/min and a split ratio of 1:10.

3. Results and discussion

3.1. Infrared spectroscopy

Reflectance FT-IR spectral data in the 465–485 cm^{-1} region is presented in Fig. 1 and Table 1. For precursor MSP1 (pure ATTM), a single absorption band is observed around 467 cm^{-1} which is assigned to the Mo–S stretching vibration. This band becomes considerably weaker for the MSP2 sample and is barely visible in the spectra of the remaining samples in the series. Precursor MSP6 (from the stoichiometric reaction between ATTM and CTAC) presents a single absorption band at 477.19 cm^{-1}, which is assigned to the Mo–S stretching vibration of CTAT, in close agreement with the corresponding absorption bands previously reported for other alkylammonium thiomolybdates [25]. For precursors MSP2 through MSP5 a clear displacement of the CTAT absorption band from 476.10 to 477.99 cm^{-1} is observed. This effect has been attributed to solid-state cation–anion interactions between the unreacted ATTM and the CTAT product in the precursor mixtures [26].