Catalysis Today 250 (2015) 66–71

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

MoS_2 catalysts derived from *n*-methylenediammonium thiomolybdates during HDS of DBT

L. Romero[a], M. Del Valle[a], R. Romero-Rivera[a], G. Alonso[b], M. Ávalos-Borja[b,c], S. Fuentes[b], F. Paraguay-Delgado[d], J. Cruz-Reyes[a,*]

[a] *Facultad de Ciencias Químicas e Ingeniería, Universidad Autónoma de Baja California, Tijuana, BC, Mexico*
[b] *Centro de Nanociencias y Nanotecnología, Universidad Nacional Autónoma de México, C.P 22800 Ensenada, B.C., Mexico*
[c] *Instituto Potosino de Investigación Científica y Tecnológica, División de Materiales Avanzados, San Luis Potosí, SLP, Mexico*
[d] *Centro de Investigación en Materiales Avanzados, hih. Chihuahua, CHIH, Mexico*

ARTICLE INFO

Article history:
Received 3 October 2013
Received in revised form 17 January 2014
Accepted 16 March 2014
Available online 4 April 2014

Keywords:
Hydrodesulfurization
MoS_2 catalysts
Methylenediammonium
Carbon
In situ-activated

ABSTRACT

Carbon-containing MoS_2 catalysts with specific surface areas of up to 32.4 m^2/g are prepared in situ from ethylenediammonium thiomolybdate (EtDaT, $n = 2$), 1,4-butane-diammonium thiomolybdate (BuDaT, $n = 4$), 1,6-hexanediammonium thiomolybdate (HeDa, $n = 6$), and 1,8-octanediammonium thiomolybdate (OcDaT, $n = 8$), where BuDaT and OcDaT are novel precursors. The *n*-methylenediammonium thiomolybdates are prepared by reacting ammonium thiomolybdate (ATM) with ethylenediamine, 1,4-butanediamine, 1,6-hexane-diamine and 1,8-octanediamine, respectively, in an aqueous medium containing NH_4Cl. Catalysts, as characterized by XRD and TEM, present a well-dispersed 2H-MoS_2 phase. For the hydrodesulfurization (HDS) of dibenzothiophene (DBT), their first order rate constants, *k*, are more than two times higher than that of the reference catalyst (32.0×10^{-7} mol/g·s) derived from carbon-free ATM, with the MS-HeD catalyst being the most active $k = 86.3 \times 10^{-7}$ mol/g·s.

1. Introduction

Hydrodesulfurization (HDS) is a hydrotreatment process that reduces the sulfur content in crude oils. Since the early 20th century several transition metal sulfide (TMS) have been used as catalysts for this purpose [1], as well as molybdenum carbide [2] and phosphine carbide [3] in more recent times. MoS_2 catalysts are commonly used in HDS reactions during the refinement of crude oil and can be synthesized by sulfidation of co-precipitated oxides [4,5], comaceration [6,7], homogeneous sulfide precipitation [8,9], ceramic method [10] and impregnated thiosalt decomposition [11–14]. Tetraalkylammonium thiometallates, $(NR_4)_2MS_4$, where R = alkyl, and M = Mo or W, have been synthesized by the metathesis reaction between ammonium thiometallate and tetraalkylammonium chlorides [15] or tetraalkylammonium hydroxides using acetonitrile as solvent [16]. These thiometallates have since been used as sulfide catalyst precursors (R = H, methyl, *n*-butyl, *n*-pentyl, *n*-hexyl, *n*-heptyl and M = Mo or W) when prepared by reacting ammonium thiomolybdate or thiotungstate with the corresponding tetraalkylammonium bromide in an aqueous medium [17,18].

The in situ decomposition of tetraalkylammonium thiomolybdates, $(NR_4)_2MoS_4$, yields unsupported molybdenum sulfide catalysts with high surface area and improved catalytic properties in the HDS of DBT, which has been associated with the presence of carbon in substitution of sulfur atoms, generating systems like $MoS_{2-x}C_y$ $(0 < y < 1)$ [19]. In the synthesis of ruthenium sulfides, carbon content has also been observed according to the formula: $RuS_{2-x}C_x$ [20,21]. After sulfidation, both Ru and Mo sulfide catalysts present excess sulfur, MS_{2+x} $(0 < x < 0.5)$ [19], and have been found to yield a greater carbon content $MoS_{2-x}C_x$ after HDS in organic solvents [22]. Methylenediammonium thiometallates have also been used as precursors of carbon-containing sulfide catalysts. Thus, the decomposition of ethylene-diammonium thiomolybdate, $[H_3N(CH_2)_2NH_3]MoS_4$, yields a MoS_2 catalyst with a greater surface area and pore volume than the ATM derived catalyst [23]. Recently, Alonso et al. have prepared hexamethylene-diammonium thiometallates (1,6-hexanediammonium thiometallates) from an aqueous system which, when decomposed in situ during the HDS of DBT, produce carbon-containing Mo(W)S_2 catalysts [21].

The present work describes the synthesis of a series of carbon-containing catalyst precursors, *n*-methylenediammonium thiomolydates ($n = 2$, 4, 6, 8), using a modified version of the Coucouvanis aqueous solution method [24,25], where BuDaT and OcDaT are novel precursors, the in situ preparation of MoS_2

---

[*] Corresponding author. Tel.: +664 1272717.
E-mail address: juancruz@uabc.edu.mx (J. Cruz-Reyes).

http://dx.doi.org/10.1016/j.cattod.2014.03.024
0920-5861/

catalysts from these precursors, and their catalytic performance in the HDS of DBT compared to the reference catalyst prepared from ATM.

2. Experimental

2.1. Preparation of ATM, $(NH_4)_2MoS_4$

ATM is prepared according to the method described by Kruss [26], where H_2S gas is bubbled for several hours into a basic solution of ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$) yielding a dark red precipitate. The product is vacuum-filtered, washed with isopropanol and kept in a N_2 atmosphere.

2.2. Preparation of ethylenediammonium, 1,4-butanediammonium, 1,6-hexanediammonium, and 1,8-octanediammonium thiomolybdates

Freshly prepared $(NH_4)_2MoS_4$ (4.0 g, 15.33 mmol) is dissolved in water (40 mL). To this solution is added a second aqueous solution (20 mL), with stirring at 60 °C, containing NH_4Cl (1640 g, 30.66 mmol), and the diamine $H_2N—(CH_2)_n—NH_2$ (15.33 mmol) where $n = 2, 4, 6, 8$ for ethylenediamine, 1,4-butanediamine, 1,6-hexanediamine, and 1,8-octanediamine, respectively. The reaction mixture is kept at 60 °C with stirring for 2 h and then placed in an ice bath for 2 h. The resulting precipitates of ethylenediammonium thiomolybdate (EDaT), 1,4-butanediammonium thiomolybdate (BuDaT), 1,6-hexanediammonium thiomolybdate (HeDaT), and 1,8-octanediammonium thiomolybdate (ODaT) are filtered, washed with cold water and with isopropyl alcohol, then stored in a glass container under a N_2 atmosphere. Precursors are analyzed by FT-IR spectroscopy, presenting peaks at 3285–3425 cm^{-1} (N—H stretching) for the diammonium ion, 2990–2980 cm^{-1} (C—H stretching) for the methylene groups, and at 463–480 cm^{-1} (Mo=S stretching) for the thiomolybdate group.

2.3. In situ preparation of MoS_2 catalysts

Catalysts are obtained by in situ decomposition of the n-methylenediammonium thiomolybdates during the HDS reaction of DBT. The DBT (23.88 mmol), decalin solvent (100 mL), and a sufficient amount of the precursor to obtain 100 mg of catalyst are placed in a 300 mL Parr high pressure reactor. The reactor is pressurized to 3.1 MPa (450 psi) with H_2, heated to 623 K (350 °C) and stirred at 600 rpm for 5 h. Catalysts are recovered by vacuum-filtered, washed with isopropanol and kept in a N_2 atmosphere. The precursors are loaded within an hour of their preparation, to avoid oxidation.

2.4. Catalytic activity measurements

The course of the HDS reaction was monitored by gas chromatography with a HP 6890 gas chromatograph using a J&B DB640 capillary column (30 m × 0.32 mm × 0.5 μm). Samples were 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 ≤ 5% of total volume. The identity of the reaction products was confirmed by mass spectrometry with a HP 6890 GC–MS using a HP-5MS capillary column (30 m × 0.25 mm × 0.25 μm). Catalytic activity was expressed in terms of % conversion of DBT vs reaction time, and from this data the reaction rate constant, k', was calculated for each catalyst using the integrated form of the first order rate law

$$-\ln(1-X) = k't$$

where X is the DBT conversion fraction and t is the reaction time in minutes. A plot of $[-\ln(1-X)]$ vs time, optimized by linear regression, gives k' as the slope of the plot. The specific rate constant, k, for the catalyst is then calculated by

$$k = k'(n_{\mathrm{DBT}})\left(\frac{1}{60}\right)\left(\frac{1}{w_{\mathrm{cat}}}\right) = [\mathrm{mol/g/s}]$$

where n_{DBT} is the initial amount of DBT in moles and w_{cat} is the weight of the recovered catalyst in grams. The mean standard deviation for catalytic measurements is about 2.5%.

The HDS of DBT follows two parallel pathways, yielding mainly biphenyl (BP) through the direct desulfurization (DDS) pathway, and cyclohexylbenzene (CHB) and tetrahydrodibenzothiophene (THDBT) through the hydrogenation (HYD) pathway. Other HYD products are cyclohexyl-cyclopentylmethane (CHCPM) and dicyclohexyl (DCH). As generally accepted, the HYD/DDS selectivity is calculated by the equation [27]:

$$\frac{\mathrm{HYD}}{\mathrm{DDS}} = \frac{[\mathrm{CHB}] + [\mathrm{THDBT}]}{[\mathrm{BP}]}$$

2.5. Characterization of catalysts

Characterization of catalysts is performed on samples obtained after the catalytic tests. A FEI Quanta 200 scanning electron microscope coupled with energy dispersive X-ray (EDX) spectroscopy is used to perform morphological and elemental analysis. Specific BET surface area and pore size distribution using the BJH method are determined by nitrogen adsorption with a Quantachrome AUTOSORB-1 analizer. XRD studies are performed using a Phillips X-Pert MPD diffractometer, equipped with a curved graphite monochromator, using Cu $K\alpha$ radiation ($\lambda = 1.54056$ Å) operating at 43 kV and 30 mA. Transmission electron microscopy is done on a FEI Tecnai F30 transmission electron microscope operated at 300 kV.

3. Results and discussion

3.1. Elemental analysis

The S/Mo and C/Mo atomic ratios for the catalyst series are reported in Table 1, where the S/Mo is seen to vary from 1.1 to 2.5 and the C/Mo varies from 0.7 to 3.9. Only the MS-OcDaTM catalyst presents the theoretical S/Mo = 2 ratio. The higher ratio of the MS catalyst may be the result of the heterogeneous characteristics of its surface. There is a significant reduction in the S/Mo rate of the MS-EtDa, MS-BuDa and MS-HeDa catalysts, which in similar cases has been attributed to the replacement of sulfur atoms with carbon atoms in the molybdenum sulfide structure [19]. With regard to the C/Mo ratio, it is found to increase with the size of the hydrocarbon chain of the precursor. Although the ATM precursor has no carbon, the reference MS catalyst has a C/Mo = 0.7, leading some authors to suggest that the carbon comes from the decomposition of the decalin solvent [19,28]

3.2. Surface area and pore size distribution

Surface area and pore volume analysis by N_2 fisisorption are grouped in Table 1. The surface area of the catalysts derived from precursors with $n = 6, 8$ are only 1/3 that of the reference catalyst. While these surface areas are modest compared to those of MoS_2 catalysts derived from tetraalkykammonium thiomolybdates, they are consistent with the SEM results. The surface area reported here is less than that reported for molybdenum sulfide (152 m^2/g) by Chianelli and Pecoraro [23], who use prolonged reaction times to assure a stable active phase. Reduced surface area may attributed