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The influence of reducing and sulfiding conditions on the properties of unsupported MoS_2-based catalysts

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ABSTRACT

Unsupported MoS_2 catalysts were obtained from the decomposition of ammonium tetrathiomolybdate (ATM) at variable temperatures (400–700 °C) and under different gas compositions, from pure H_2S to pure H_2. The catalysts were further studied in the non-promoted state or promoted by Ni and Co. Catalytic activity and selectivity were studied in the model reaction of thiophene hydrodesulfurization (HDS). Surface areas, crystalline phase and particle size distributions were determined by Brunauer–Emmet–Teller (BET), X-ray diffraction (XRD) and transmission electron microscopy (TEM), respectively. A comparison of average values calculated from these techniques has enabled the understanding of the morphology of the solids. The catalysts were characterized before and after catalytic tests by X-ray photoelectron spectroscopy (XPS), laser Raman spectroscopy (LRS) and temperature-programmed reduction (TPR).

Comparison of catalytic activity trends with the results of the characterizations show that over-stoichiometric sulfur, present in the fresh catalysts in the form of edge-located S_2^{2-} species, plays a key role for the activity of unsupported MoS_2 and for its ability to be promoted. Direct hydrogenation (HYD) of thiophene to butane occurs presumably with the participation of –SH groups, produced from the opening of S–S bridges by hydrogen. Whatever the gas atmosphere, any treatment leading to the removal of over-stoichiometric sulfur leads to a decrease in HYD selectivity. Thus, very similar catalytic properties were observed for MoS_2 annealed at 700 °C in pure H_2, H_2S or N_2 gases. Ni and Co introduced by means of reflux with acetylacetonates, gave identical promotion trends for all the MoS_2 samples. The solids treated in pure H_2S could not take up promoter atoms at the edges, whereas for the H_2-reduced samples high promotion levels were achieved. The degree of stacking does not seem to have a significant impact on the thiophene HDS activity and selectivity of the unsupported MoS_2 catalysts.

1. Introduction

Transition metal sulfide (TMS) hydrotreating catalysts, used to produce clean motor fuels, are one of the most important industrial catalytic systems [1–3]. Many studies have dealt with the understanding of the genesis and functioning of the TMS catalysts, and particularly of Ni(Co)–Mo mixed sulfides. The main progress in the comprehension of TMS catalysts has been achieved due to the work by Topsøe and colleagues in which an edge-decorated CoMoS phase model has been suggested [4,5]. Later, the results of scanning tunnelling microscopy (STM) allowed confirming the existence of earlier proposed structures [6,7]. Considerable effort has been directed toward atomistic theory models of the catalytically active TMS phases [8–10]. The MoS_2 edge energies and geometry of species as a function of composition were extensively studied [11]. Current models consider the differences between crystallographically distinct MoS_2 slabs terminations, (namely metal M $(1\,0\,\bar{1}\,0)$ and sulfur S $(\bar{1}\,0\,1\,0)$ edges) as a key point for the understanding of catalytic activity and promotion trends [12]. The nature of the exposed edges is expected to depend on the treatment conditions [13].

Despite considerable progress in the field, several important questions are still unresolved. Thus, since the formulation of the rim-edge model by Daage and Chianelli [14], no clarity has been achieved regarding the relationship between the HYD/HDS selectivity and MoS_2 slabs stacking [15–18]. The number of structurally distinct active centres is also still questionable. One-centre model was proposed by Miller et al. [19] for supported CoMoS systems. However, the DDS and HYD activity do not change in step after incorporating Co into Mo sulfide, suggesting that there are at least two types of centres [20]. One of the most basic still unanswered questions is the exact nature of hydrogen activation by MoS_2 particles. Spectroscopic studies of supported and unsupported sulfides have proven the existence of surface disulfide S_2^{2-} species [21,22] and SH groups [23–25] but not for Mo–H species, which would result from H_2 dissociation on the sulfide edges. Recent papers by Polyakov et al. demonstrate the presence of some

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hydrogen-containing species on the surface of unsupported overstoichiometric MoS_{2+x}, able to hydrogenate olefins in the absence of H_2 [26,27]. Farag et al. observed that the HYD reaction on MoS_2 is promoted by H_2S [28]. These findings have no direct interpretation within the framework of existing models.

Low valence sulfur (S_2^{2-}) species located on the MoS_2 edges were supposed earlier to be involved in H_2 activation [29]. In our recent work [30,31] evidence for homolytic low-temperature H_2 dissociation on S–S bridges has been presented for the amorphous sulfides CoSOH and MoS_3. An effect of hydrogen interaction with S_2^{2-} groups on the catalytic performance seems to be a plausible hypothesis. Therefore, the goal of the present work is to contribute to the understanding of key properties of the MoS_2 catalysts by studying well characterized unsupported catalysts with variable stoichiometry. First, the properties of non-promoted MoS_2 are reported, and then promotion with Co and Ni is briefly considered.

2. Experimental

2.1. Catalysts preparation

High-purity ammonium heptamolybdate and ammonium sulfide were purchased from Sigma–Aldrich. Ammonium tetrathiomolybdate, $(NH_4)MoS_4$, (ATM) was obtained by the addition at ambient temperature of 15 g of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ to 200 mL of a 20 wt% solution of $(NH_4)_2S$, upon stirring. The mixture was stirred for several hours, and then kept in a refrigerator for one week. Dark red crystals precipitated, which were filtered, washed with cold ethanol, dried, and stored under nitrogen.

Decomposition of ATM was carried out in Pyrex or quartz reactors. A weighted amount of ca. 2 g ATM was placed in a reactor and treated in a gas flow of 60 mL/min of pure H_2, pure H_2S or 15% vol. H_2S/H_2. The temperature was raised at a rate $5^\circ\ min^{-1}$ to a desired value and kept for several hours. During the treatment and the following cooling, the gas composition was kept constant or was varied, and this represents an important point of the experimental procedure. The conditions of preparation are listed in Table 1. Self-explanatory designations of the catalysts are applied whenever possible. For example, the sample sulfided in pure H_2S at 500 °C is named S-500, whereas the solid first sulfided and then treated in pure hydrogen at 400 °C is designated SH-400. A reference MoS_3 amorphous sulfide was obtained by acidification of the ATM aqueous solution, as described in [31].

Promoted catalysts were prepared according to Ref. [32]. In brief, a weighted amount of Ni or Co acetylacetonate complex was dissolved in a minimum amount of methanol while flushed by nitrogen. Then MoS_2 powder was added to the solution in an atomic ratio of Co(Ni)/Mo = 0.4 and then the suspension was heated at the boiling temperature of methanol (65 °C) for 4 h without admission of air. To achieve complete interaction, the mixtures were cooled to room temperature and kept overnight under nitrogen. Afterward, the solids were recovered by filtration and dried under N_2 at room temperature. The catalysts were tested as such or after re-sulfidation with H_2/H_2S at 350 °C for 1 h.

2.2. Characterization and catalytic tests

Temperature-programmed reduction (TPR) was carried out in a quartz reactor. Samples of sulfides (ca. 0.005–0.01 g) were heated under a hydrogen flow ($50\ cm^3/min$) from room temperature to 1050 °C at a rate of $5^\circ\ min^{-1}$. The H_2S evolved in the reduction was detected by means of a HNU photoionization detector equipped with a 10.2 eV UV light source. Other gases were detected by a VG Thermo quadrupole mass-spectrometer. The amount of H_2S released from the solid was quantified after calibration of the detector with a gas mixture of known H_2S content. Temperature-programmed desorption (TPD) was carried out in the same device. The solids were treated in hydrogen at a given temperature, cooled to room temperature and then hydrogen was replaced by a flow of pure argon. After a stabilization period of 0.5–1 h, linear heating was commenced to obtain the TPD traces. The desorbed hydrogen was detected by a mass-spectrometer.

Transmission electron microscopy (TEM) was carried out on a JEOL 2010 device with an accelerating voltage 200 keV. The samples were dispersed in *n*-hexane by ultrasound, and then put onto a holey carbon filament on a copper grid sample holder. In order to protect them from oxidation by air, the samples still covered with liquid hexane were immediately introduced into the vacuum chamber. The analysis of images (slabs stacking and length) was carried out using Digital Micrograph Gatan™ software. The average slab lengths (L) and stacking layer numbers (N) were calculated as the first moments of the respective distributions.

Nitrogen adsorption–desorption isotherms were measured on a Micromeritics ASAP 2010 instrument. Pore size distributions in the mesopores domain were calculated by the Barrett–Joyner–Hallenda (BJH) method. The BJH pore size distributions were calculated from the desorption branch of the isotherms. Prior to measurements the samples were heated in a secondary vacuum at 300 °C for 4 h. The X-ray diffraction (XRD) patterns were obtained on a Bruker diffractometer with Cu Kα emission and identified using standard JCPDS files. Mean particles size was determined using the Scherrer equation. Laser Raman spectra of sulfides were obtained using a LabRam HR spectrometer (Jobin Yvon) equipped with a CCD detector. The exciting line at 514.53 nm of an Ar^+–Kr^+ RM 2018 laser (Spectra Physics) was focused on each point with a 100× objective and a power of ca. 1 mW. To protect them from air, the samples were sealed in Pyrex capillaries under inert atmosphere. X-ray photoelectron spectroscopy (XPS) studies were performed on a VG ESCALAB 200R spectrometer using Al Kα radiation. The XPS spectra of O 1s and S 2p and Mo 3d were recorded and their binding energies (BE) referred to the energy of the C 1s peak (BE 285.0 eV). Quantification of the surface contents of the elements was done using the sensitivity factors provided with the VG software. The metals content in the synthesized solids was determined, after dissolution in a HNO_3/H_2SO_4 mixture, by plasma-coupled atomic emission spectroscopy (AES-ICP). The sulfur and carbon contents were measured with a Strohlein Instruments CS-MAT 5500 analyzer.

Catalytic activities were measured for thiophene HDS at atmospheric pressure in a fixed-bed flow microreactor. In the chosen temperature range, 280–320 °C, the thiophene conversion was below 10% under the conditions used (50 mL/min gas flow, 50–500 mg of catalyst), and the plug-flow reactor model was used to calculate the specific reaction rate, V_s, according to equation

$$V_s = -(F/m)\ln(1-x)$$

where F is the thiophene molar flow (mol/s), m is the catalyst mass (g), and x is the thiophene conversion. To compare the catalysts evolution on a common basis, HDS activity at 300 °C was measured every 1 h for 80 h at different thiophene molar feed rates (3.0 and $1.0\ h^{-1}$) and at two levels of thiophene partial pressure (2.85 and 0.64 kPa).

3. Results and discussion

3.1. Non-promoted MoS_2 catalysts

3.1.1. Properties of MoS_2 solids as a function of treatment conditions

To study MoS_2 catalytic properties as a function of stoichiometry and morphology, simple model systems with a minimal num-