Deactivation of MoS_2 catalysts during the HDS of thiophene

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Catalytic properties of unsupported MoS_2 catalysts in the thiophene hydrodesulfurization reaction were determined in the temperature range 623–653 K. The catalysts were prepared by *ex situ* decomposition of ammonium thiomolybdate (ATM) crystals in a mixture of 15% H_2S in H_2 at 673 K. Activity of catalysts decreased very rapidly before reaching a steady state after 15 h on-stream. The thiophene conversion went down from 10–12 to 3–4% in that time. The surface area of the catalysts also decreased during the catalytic reaction from 40–50 to 8–10 m^2/g. Selectivity for hydrodesulfurization, hydrogenation and isomerization reactions was affected distinctly by the deactivation process. By increasing the reaction time, double-bond isomerization increased, hydrogenation of butenes decreased and hydrodesulfurization remained constant. Results indicate that the main cause of activity decay was surface area loss that was due to sintering of MoS_2 crystallites. Selectivity variation indicates that different active sites are involved for the three reactions. A deactivation model involving diminution of active sites located in edge and rim sites of small MoS_2 particles is proposed to explain the variation of product distribution.

Keywords: MoS_2, deactivation, thiophene HDS, sintering

1. Introduction

Upgrading of heavy oil fractions affects catalyst lifetime due to increased deposition of coke and metals as well as severe temperature conditions. During hydrotreating several complex deactivation processes occur and more studies are needed to understand the factors influencing catalysts deactivation.

Industrial hydroprocessing catalysts are deactivated by different mechanisms [1]: (a) sintering of the active phase(s); (b) decomposition of the active phases; (c) covering of the active sites by reactants and/or products; (d) coking; (e) deposition of poisons and/or inhibitors. In hydrotreating operations, coking and metal deposition are the most important causes of deactivation, however, simultaneous aging of the catalysts may also take place due to solid state transformations and sintering of the active species.

During the course of model compound studies, especially with multi-ring compounds, catalysts deactivation with time is invariably observed. This is mainly due to coke deposits and catalyst structural changes. In the hydrodesulfurization (HDS) of thiophene (TP) catalysts lose activity for several hours before achieving a stationary state [2–4].

In order to understand the decay of activity and selectivity observed during initial conditions in the HDS of thiophene, unsupported MoS_2 catalysts, obtained by decomposition of thiosalts, were studied following the catalytic HDS reaction, by X-ray diffraction (XRD), transmission electron microscopy (TEM) and BET nitrogen adsorption. A model of sintering of MoS_2 crystallites is suggested to explain changes in activity and selectivity of catalysts.

2. Experimental

2.1. Precursor preparation

Molybdenum disulfide catalysts were obtained by thermal decomposition of ammonium tetrathiomolybdate crystals (ATM) under a sulfiding atmosphere. The ATM crystals were prepared by precipitation of an ammonium heptamolybdate solution (0.1 M) with hydrogen sulfide [5]. Three precursor samples (ATM-1, ATM-2 and ATM-3) with different crystal sizes were prepared varying the reaction time of the hydrogen sulfide with the solution. Reaction times were 25, 40 and 60 min for the small, medium and large sizes, respectively. To obtain the sulfide catalysts, the precursors were decomposed in a mixture of 15% H_2S in hydrogen at 673 K for 4 h. After cooling to room temperature under the same gas flow, three catalysts named MoS_2-1, MoS_2-2 and MoS_2-3 were obtained. They were flushed and stored under argon for further characterization. All catalytic measurements were performed within 24 h after sulfidation.

2.2. Surface area

Surface areas were measured by the BET method using N_2 as adsorbate, in Digisorb 2600 Micromeritics automatic equipment. Prior to the adsorption process the samples were outgassed under vacuum at 673 K during 2 h.

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2.3. Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained by means of a Jeol JSM-5300 electron microscope coupled with an electron dispersive X-ray (EDS) unit Kevex Quantum Superdry, for elemental analysis. The powder samples were pressed into wafers. An average of ten different zones and two different samples were calculated for each catalyst before and after reaction. The average error in these measurements was estimated ca. 5 μm. A monocrystal of MoS_2 was used as a reference to perform a quantitative analysis of S and Mo in the catalysts.

2.4. X-ray diffraction

X-ray diffractograms were obtained with a Siemens D-500 unit, using the copper K_α monochromatic radiation. Catalysts were added with α-alumina (25 wt%) before being installed in the sample holder. The peak of alumina was used as an internal reference to determine the variation of the (002) peak width of molybdenum disulfide before and after the reaction test. Particle sizes in the (002) direction were calculated using the following equation:

$$D = \lambda K/\beta \cos\theta, \qquad (1)$$

where $\lambda = 1.54$ Å, $K = 0.9$ and $\beta = B^2 - b^2/B$ (from Klug and Alexander [6]), where B is the half peak width of MoS_2 (sample) and b is the half peak width of α-Al_2O_3 (standard).

2.5. Catalytic activity

The thiophene hydrodesulfurization reaction was carried out in a continuous-flow microreactor under atmospheric pressure with a large excess of hydrogen to avoid carbon deposition. Reactants partial pressure were: thiophene 1700 Pa, hydrogen 1×10^5 Pa. Hydrogen flow rate was maintained at 0.5 ml/s, catalyst weight was 0.1 g. Catalysts were tested in the temperature range 593–623 K. Reaction products were analyzed by gas chromatography using a FID detector. They were separated in a 5 m stainless-steel column containing 10% octane on Porasil maintained at 323 K. At these experimental conditions a continuous deactivation behavior was observed for all catalysts during 15 h on-stream. After that time the steady state was reached. Total conversion was kept lower than 15% by adjusting the gas flow rate or the catalyst weight. Intrinsic rates were calculated using the equation:

$$\text{rate} = (Q/mS_\text{f})C, \qquad (2)$$

where Q is the molar rate of thiophene, m is the weight of catalyst, S_f is the surface area and C is the converted fraction.

3. Results

3.1. Scanning electron microscopy

The morphology of the precursors is shown in figure 1(a). Most frequently observed shapes were hexagonal and rectangular forms. Average crystal dimensions, length (L), width (W), and thickness (T) of the three ATM precursors are shown in table 1. Statistical calculations were performed on over one hundred particles to estimate average values for each sample. Similar values of L and W were found for the three samples, however different values of T were measured among them. Sample ATM-3 was five

(a)

(b)

Figure 1. Scanning micrographs of sample ATM-3: (a) before and (b) after sulfidation.

Table 1
Average crystal dimensions of the ATM precursors.

Sample	L (μm)	W (μm)	T (μm)
ATM-1	307	143	20
ATM-2	360	153	52
ATM-3	407	144	104

Table 2
Surface area of MoS_2 catalysts before and after the catalytic test in the hydrodesulfurization of thiophene.

Catalyst	Initial surface area S_i (m^2/g)	Final surface area S_f (m^2/g)
MoS_2-1	41.0	8.5
MoS_2-2	50.1	9.2
MoS_2-3	50.7	10.5

times thicker than sample ATM-1 and two times more so than sample ATM-2. The change in average sizes led to an average increase of the volume from 0.8 to 6.1×10^6 μm^3. The particle morphology of catalysts was very similar to their respective ATM precursor with no significant change in L, W or T. Nevertheless, porosity was extensively developed in the particles due to the gases (NH_3 and H_2S) evolved during the decomposition process (figure 1(b)).

3.2. Surface area

Surface areas determined by adsorption–desorption of nitrogen are shown in table 2. Surface area values for the catalysts after sulfiding (before reaction) ranged from ca. 40 to 50 m^2/g, which are typical values for molybdenum disulfide obtained by ATM decomposition [7–9]. Surface area measurements performed after the catalytic test revealed that a severe decrease of surface area occurred for all catalysts during the catalytic reaction, in a similar way to that observed by Frety et al. [10]. Surface areas of used catalysts decreased to 8–10 m^2/g.

3.3. SEM/EDS

The typical sulfur/molybdenum atomic ratio measured by EDS for the catalyst MoS_2-3 was 2.19 before reaction and 1.81 after reaction, indicating that the elimination of sulfur takes place during the reaction test. This result is similar to that reported by Ledoux et al. [11] in MoS_2 catalysts supported in carbon.

3.4. X-ray diffraction

X-ray diffraction in general gives limited information on poorly crystalline solids such as MoS_2 due to line broadening of the pattern. Variation of the width of the (002) peak permits the calculation of the stacking of layers in the MoS_2 catalyst [12]. In this work to improve measurement of stacking, α-alumina was used as reference to determine the position and width of diffraction lines. Such a procedure was used to observe variations induced by the reaction in the [002] diffraction line (0.615 nm). Figure 4 shows the diffractogram corresponding to the (002) planes for the catalyst MoS_2-3 before and after reaction. An increase in the peak width is observed for the used catalyst, indicating a structure reordering of the MoS_2 crystallites during the reaction. The stacking sizes calculated by line broadening analysis were 3.65 nm (6 layers) and 4.4 nm (7 layers) for the before and after reaction catalysts. The size increase of 0.75 nm between those samples corresponds to the stacking of one additional layer during the catalytic test.

3.5. Catalytic activity

The catalyst deactivation behavior with time on stream is shown in figure 2. A rapid decrease of the activity during 15–16 h is observed before a steady state was reached. Catalysts lost 75–80% of their initial activity during this period. Catalytic activities calculated after 1 h and after 15 h are given in table 3. A slight increase of the specific activity with the thickness of particles is observed, however, when the activity is reported as intrinsic rate (mol/s m^2) all catalysts show about the same activity.

Activation energies obtained from experiments performed in steady conditions at 593–623 K were 20 ± 1 kcal/mol for all samples. These values are considered as standard values for this reaction at the temperature used [13].

The product distribution with time on stream is shown in figure 3. Butane, the product obtained by hydrogenation of butenes, decreased over time, however, both *trans*- and *cis*-butene-2 obtained by double-bond isomerization of butene-1 increased. Finally, butene-1 formed by hydrodesulfurization of thiophene remained constant over the same period. All catalysts showed the same selectivity pattern.

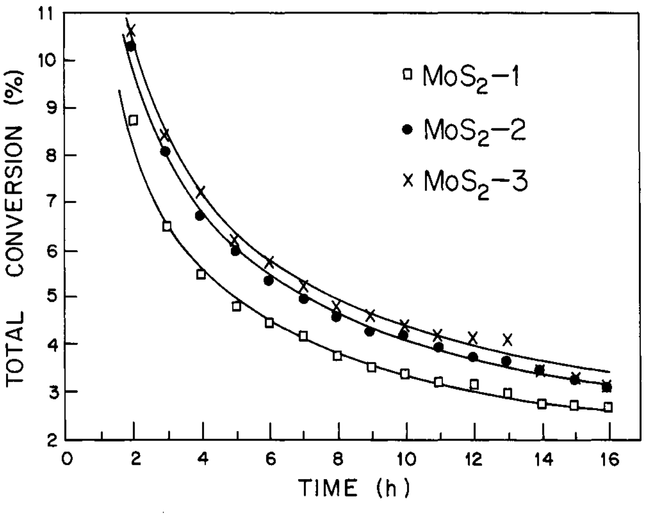

Figure 2. Deactivation of catalysts with time on stream.

Table 3
Specific and intrinsic rates for HDS of thiophene at 623 K: (a) initial rates (after 1 h) and (b) final rates (after 15 h).

Catalyst	Specific initial rates ($\times 10^{-7}$ mol/s g)	Final rates Specific ($\times 10^{-7}$ mol/s g)	Final rates Intrinsic ($\times 10^{-8}$ mol/s m^2)
MoS_2-1	5.25	1.06	1.24
MoS_2-2	6.55	1.33	1.44
MoS_2-3	7.40	1.51	1.42

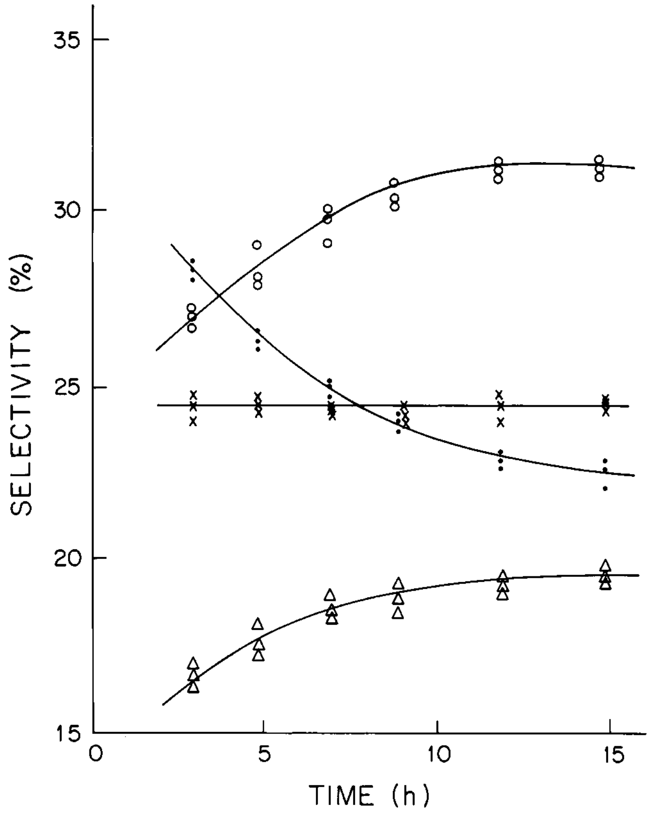

Figure 3. Evolution of selectivities for hydrogenation and hydrodesulfurization with time on stream: (○) *trans*-2-butene, (△) *cis*-2-butene, (×) 1-butene and (•) butane.

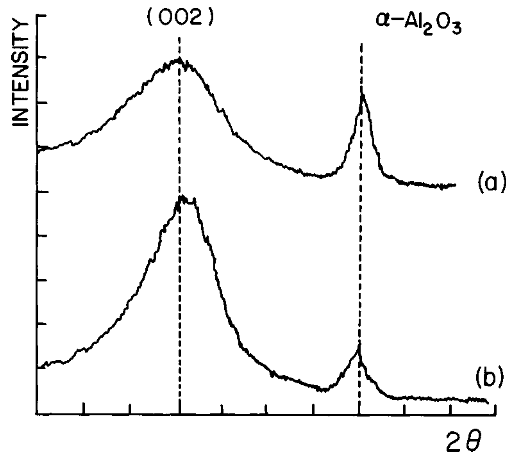

Figure 4. Diffraction pattern of the (002) line of sample MoS_2-3 (reference α-Al_2O_3): (a) before reaction and (b) after reaction.

4. Discussion

The reaction in which ammonium thiomolybdate is transformed to molybdenum trisulfide and molybdenum disulfide has been known for a long time [14]. The thermal decomposition of ATM gives MoS_2 samples with varying S/Mo ratios depending on the treating atmosphere [15]. It has been reported that the reduction of unsupported ammonium thiomolybdate seems to proceed only to the Mo(IV) stage in contrast to alumina-supported catalysts that can reach lower Mo oxidation state [16]. One of the most significant findings about the decomposition of ATM is that the transformation is topotactic and the c axis of ATM becomes the c axis of MoS_2 [17]. Based on these reports it appeared possible to obtain molybdenum disulfide catalysts with different c/a (edge/basal ratios) starting from ATM crystals with different sizes. As shown in table 1 such a goal was reached, the length and width of the different precursors were approximately the same, but the edge size varied by a factor of five between them (ATM-3 = 5ATM-1). This change in size led to a volume increase about eight times between these samples.

Upon heating these precursors at 673 K for 4 h under 15% hydrogen sulfide on hydrogen, the precursors were converted to molybdenum disulfide particles with the same external morphology of the precursors but with a well developed internal porous structure. No significant modifications of the external dimensions of the molybdenum disulfide particles in reference to the precursors were observed due to this sulfidation treatment. High surface areas measured on these catalysts (40–50 m^2/g) strongly suggest that the main factor contributing to the surface is the internal porous structure. The fact that a change in volume of precursors by a factor about eight was not observed in the surface area confirms that internal porosity provides the main increase in total area.

Dropping of surface area could be assigned to shrink of the porous structure due to sintering. Sintering of the active phase has been observed in $CoMo/Al_2O_3$ catalysts during sulfiding treatments at high temperatures in hydrogen [18,19]. Parham and Merrill reported that the size of MoS_2 crystallites in $CoMo/Al_2O_3$ catalysts increased ca. 1.5 nm between 573 and 673 K under sulfiding conditions [20]. Studies by Knözinger et al. [21] indicate that sintering of MoS_2 particles via lateral growth occurs for sulfided Mo/Al_2O_3 catalysts in hydrogen alone at relatively high temperature (773 K). Other studies have shown that MoS_2 crystallites grow three-dimensionally upon high-temperature sulfiding [22–24].

Surface area decrease during the reaction, as mentioned above, could be due to sintering of MoS_2 crystallites that leads to collapse of the internal porous structure. Sintering of crystallites may proceed by way of two mechanisms: re-stacking and lateral growth. In the first case, crystallites stack on top of each other, through basal planes, increasing the number of layers in the c direction. In the latter case, crystals sinter side by side, through the edge and border planes, increasing the length in the a-axis direction. The re-stacking mechanism decreases exposed basal planes and affects the surface area leaving unaffected the catalytic activity because edge planes remain exposed. Otherwise, lateral growing of crystallites affects the catalytic activity and the selectivity because edge and border planes are being eliminated during the process. Several studies have reported a decrease of catalytic activity by increase of crystallite size. Owing to the driving force for sintering it is believed that both the presence of hydrogen and the temperature are determinant for that process. An increase of temperature increases the mobility of particles, while hydrogen eliminates sulfur atoms from the edge area facilitating the reaction among particles. The relative importance of each process remains to be elucidated in further studies.

Catalytic results showed no marked differences in reaction rate, selectivity or deactivation with time on stream, among the three catalysts, indicating that the active surface was independent of the external morphology of particles. The difference in reaction rates measured after 1 and after 15 h coincides with the difference of surface area before and after reaction, suggesting that direct correlation between those parameters exist and, therefore, active sites are located in the internal microcrystallites. Such results are in agreement with a previous one [7] that showed that there is a direct relationship between catalytic activities and surface areas for unsupported molybdenum disulfide and tungsten disulfide catalysts. In general, no direct correlation between N_2 surface area and catalytic activity is found in metal sulfides [25]. Exceptions are catalysts prepared by the same procedure [7,8].

A recent result reports that the HDS activity of supported MoS_2 is due to top edge sites, more precisely two-vacancy centers at the top edge [26]. A report by Iwata et al. [27] suggests that catalytically active sites exist on the curvature of the basal planes of MoS_2 crystallites. Eijsbouts et al. [28] reported that HDN and HDS activities are proportional to MoS_2 dispersion and that high-activity commercial catalysts have very high MoS_2 dispersions.

The deactivation behavior with time on stream of molybdenum disulfide catalysts has been related either with sulfur elimination, surface area loss and carbon deposition [10,11]. In the case of sulfur elimination and carbon deposition, thermal treatments under hydrogen–hydrogen disulfide mixtures at high temperature reactivate spent catalysts. In the present work, it was observed that the S/Mo atomic ratio decreased from 2.19 to 1.81 during 15 h of reaction revealing that a loss of sulfur happened during the reaction. Carbon deposited in the catalysts after reaction was undetected by EDS analysis. Rejuvenation experiments in 20% H_2S on H_2 at 673 K for several hours failed to recover catalytic activity, only 20% of the initial activity was recovered after that treatment, indicating that mostly an irreversible deactivation took place. Therefore, it is suggested that the main cause of deactivation with time on stream is the surface area loss. It should be mentioned that sulfur loss could be related with surface area loss, as shown in [15], however, our conditions are quite different from those used in this work.

A further indication of the internal surface modification that occurs during the reaction is provided by the selectivity variation with time on stream (figure 3). The butane selectivity decreasing through time indicates that hydrogenation sites are being lost at a higher rate that the total active area. On the other hand, the isomerization selectivity for *cis*- and *trans*-butene-2 increasing through time suggests that isomerization sites were less sensitive than the total active surface to deactivation. Finally, the hydrodesulfurization sites that give butene-1 decrease at the same time as the total active area decreases, as indicated by the selectivity constancy with time on stream. By assuming, as noted above, that the main cause of deactivation is the surface area loss due to sintering of MoS_2 crystallites, then selectivity changes can be well understood considering a geometrical model where the active sites are located on different planes. Thus, considering that hydrodesulfurization sites are placed on edge sites, as has been reported by Tauster [29], and the fact that butene-1 selectivity decreases parallel to the total surface, it suggests that the mechanism of deactivation effectively can involve a sintering process through the edge planes. This possibility has been mentioned previously on the growth mechanism of radio frequency sputtered molybdenum disulfide films, and is a consequence of the chemical reactivity of the edge planes [30].

The selectivity decrease in hydrogenation may also be explained by assuming that this reaction takes place on corner or rim sites located between basal and edge planes, as suggested by Daage [31]. These sites are more affected than edge sites by the two processes, re-stacking and lateral growth. In the case of double-bond isomerization, the increase in selectivity can only be explained if the active sites for this reaction are located on basal planes which are decreased to a lower rate than the edge sites.

The XRD structure characterization of catalysts before and after reaction showed a change of the average edge size of crystallites as the number of stacked (002) planes increased from 6 to 7. In an earlier work [32] we carried out the microstructure characterization of MoS_2 catalysts by HREM. It was found that the average stacking of layers increased from 5.5 to 7.0 due to the reaction experiment of thiophene HDS. Therefore, both techniques XRD and TEM show a slight increase in the number of stacking layers during the catalytic test. On the other hand, statistics of crystallite length of MoS_2 determined by HREM on similar catalysts showed an augmentation of three times in the average length of the used catalyst [32]. The fact that the length increases by a factor of three, and the number of fringes by one fifth, suggest that the crystallites growth occurred preferentially at the edge surfaces ((100) or (010) planes). Therefore, the microstructure characterization supports the sintering mechanism described above where lateral growth of crystallites prevails in unsupported MoS_2 catalysts during the HDS reaction. Delanney [33] reported a good agreement between the decrease in HDS activity and the decrease of edge area in MoS_2 caused by increase of the sulfiding temperature. The sintering of MoS_2 crystallites observed by XPS and EXAFS has been also found to lower the hydrogenation activity [34].

Very recent studies of Calais et al. [35] reported that crystallite size determination by TPR, HREM and XRD experiments give complementary results.

5. Conclusions

From this study the following conclusions may be drawn:

(a) The textural and catalytic properties of molybdenum disulfide catalysts obtained by decomposition of ammonium thiomolybdate crystals are independent of the crystallite size of the precursors.

(b) Deactivation of MoS_2 catalysts during the HDS of thiophene produces both a decrease of surface area and a decrease of sulfur concentration. It is concluded that the deactivation process is mainly related to surface area loss, in agreement with a previous result [7]. Active sites relevant to the HDS reaction are located in the internal surface of MoS_2 particles.

(c) The deactivation process affects preferentially hydrogenation sites more than hydrodesulfurization or isomerization sites. This result suggests that active sites are located on different crystallographic planes, i.e., HDS sites in edge planes and hydrogenation sites in rim positions, as proposed by Daage [30]. In that way, the selectivity change can be explained through a sintering process that increases the lateral size of crystallites.

(d) X-ray diffraction showed a slight increase in the number of stacking layers in MoS_2 crystallites, due to the reaction test, in agreement with previous results by HREM [31] which indicated that the average number of layers in MoS_2 crystallites increased by effect of the HDS reaction [13]. The increase in stacking of crystallites due to the reaction is not related with the observed decrease of the activity.

(e) Microstructure variation in MoS_2 crystallites due to sintering results in selectivity variations which are in agreement with the model of Daage, where active sites are localized in different crystallographic planes.

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