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New trends in the concept of catalytic sites over sulfide catalysts

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Abstract

Following the numerous and contradictory results reported in the literature about the origin of the different functionalities of MoS_2 based catalysts, an approach using the 4,6-dimethyldibenzothiophene as a probe molecule is reported. That has been done by the study of the variations of selectivities during poisoning of 4,6-DMDBT HDS (using olefin, aromatics and nitrogen containing compounds), and by a careful study of the variations of selectivities during the transformation of 4,6-DMDBT over fresh and aged catalysts.

The ratio of selectivities between the hydrogenation (HYD) and the direct desulfurization (DDS) routes are found to be the same whatever the inhibiting compound and the aging has the same effect on both routes of reaction. These results will be discussed assuming adsorptions on the same type of sites (uncoordinated molybdenum atom) and a general mechanism will be proposed.

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1. Introduction

Although Mo- and W-based hydrotreating catalysts promoted by cobalt or nickel are widely used in the oil industry for the removal of organo-sulfur and organo-nitrogen contaminants and for hydrogenation of aromatics, there is still a lack of fundamental understanding about the nature of the active sites. Several models have been proposed to account for the catalytic activity of these sulfides. However, even if some recent results could reinforce the remote control model [1], the most recent Co-Mo-S phase model appears now to be well accepted. Initially proposed by Topsoe et al. [2] for the HDS reaction over CoMo catalysts, this model has been extended to NiMo catalysts and to HDN reactions [3].

According to this model, the CoMoS phase is made of MoS_2 slabs with Co atoms decorating the edge plane. That suggests a possible effect of the morphology of MoS_2 on activity and selectivity and could explain the numerous studies dealing with the structure–function relationship of these systems [4,5].

However, the results on the effect of the stacking degree of MoS_2 slabs on the catalyst activity in HDS and hydrogenation (HYD) are contradictory. According to the ‘‘rim-edge’’ model, proposed by Daage and Chianelli [6] for unsupported MoS_2, the basal plane of MoS_2 is inactive and there are two different types of active sites at the edge plane: rims (the top and bottom layers of the slab) and edges (layers in between). They reported that the HDS reaction was catalysed by both the rim and the edge sites, while HYD is predominantly performed by rim sites. Opposite to that, Hensen et al. [7] found that a higher stacking degree improved the intrinsic dibenzothiophene (DBT) HDS and HYD activity to the same extend. They concluded that HDS and HYD of DBT occur via a common planar-oriented adsorption mode. A similar periodic behaviour for HDS of DBT and 4,6-DMDBT (dimethyldibenzothiophene) over several unsupported second transition metal sulfides has led Hermann et al. [8] to propose the existence of similar type of active sites for both HYD and HDS.

In order to clarify such an effect of stacking, Vradman and Landau [9] investigated NiW sulfided catalysts prepared on alumina and silica. For the same metal loading, the two catalysts presented the same activities in HDS of DBT, but the activity of the NiW/SiO_2 sample was six times higher than the NiW/Al_2O_3 one for toluene hydrogenation. That was correlated to a higher WS_2 slab stacking of the silica-supported sample.

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Conclusions about the effect of stacking over the different functionalities are, therefore, clearly divergent and that could be due to the difficulty to distinguish between stacking effects and some possible electronic support effects, since in many case variations of stacking were obtained on changing the support.

Information about the existence of different sites for hydrogenation and hydrogenolysis have also been drawn from the effect of H_2S upon the different functionalities of the catalysts. That has been done firstly by Owens and Amberg [10] who concluded to the existence of different types of sites for hydrogenolysis and subsequent hydrogenation of butenes during thiophene HDS. On the contrary, for $CoMo/Al_2O_3$ catalysts modified by boron and for several Mo/Al_2O_3-TiO_2/Al_2O_3 mixtures, Ramirez et al. [11,12] observed the same maximum for thiophene HDS and hydrogenation of butenes, suggesting that butene hydrogenation takes place on a site similar to HDS one.

However, the challenge for deep desulfurization of diesel fuel had stimulated numerous studies on the transformation of heavy refractory compounds and it is now admitted that 4,6-DMDBT is desulfurized according to two pathways commonly designated, respectively, as ‘‘hydrogenation’’ (HYD) and ‘‘direct desulfurization’’ (DDS) as illustrated in Fig. 1. Therefore, we propose to use this molecule to reinvestigate the different functionalities of a $CoMo/Al_2O_3$ and of $NiMo/Al_2O_3$ industrial catalysts.

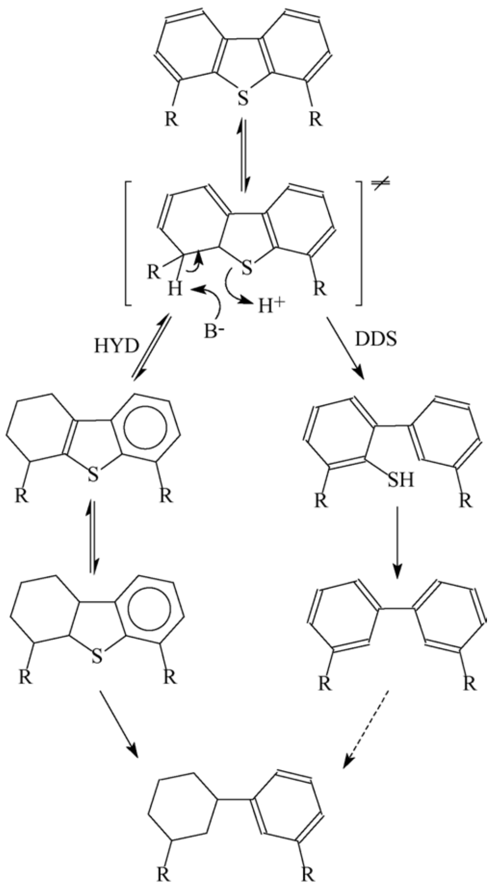


Fig. 1. Reaction scheme for HDS of 4,6-DMDBT.

That will avoid any change in the support or active phase and will be performed following two new approaches:

- the study of the variations of selectivities during the poisoning of 4,6-DMDBT HDS by olefin, aromatics and nitrogen containing compounds;
- the study of the variations of selectivities during HDS of 4,6-DMDBT over fresh and aged catalysts.

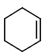
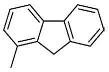
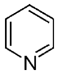
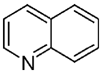
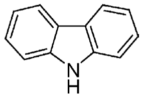
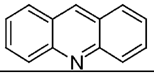
2. Experimental

2.1. Inhibiting effects during the HDS of 4,6-DMDBT

Cyclohexene, 1-methyl-fluorene, pyridine, quinoline, carbazole and acridine were purchased from Sigma–Aldrich and 4,6-dimethyldibenzothiophene (>99% purity) from Acros. A $NiMo/Al_2O_3$ commercial catalyst (HR346 from Procatalyse: Mo: 9 wt.%; Ni: 2.4 wt.%)) was used for the catalytic tests. The catalyst was first crushed, sieved (80–125 μm), sulfided for 4 h at 673 K under atmospheric pressure with a H_2S/H_2 gas mixture (molar ratio 15/85, total flow 4 L/h) and cooled down to room temperature under the same atmosphere.

The reactor used for catalytic tests was a 200 mL stirred slurry tank reactor (STR) operated in the batch mode. In every case, the reactants (1.2 mmole of 4,6-DMDBT, 0–12 mmole of olefin, aromatic or nitrogen compound, as indicated in Table 1) was dissolved in *n*-dodecane (80 mL) and then introduced into the reactor. Fifty milligrams of freshly presulfided catalyst was then placed into the reactor and the system was closed. To avoid any air contamination, N_2 was bubbled through the solution for 10 min. Still under N_2 the reactor was heated up to the reaction temperature of 573 K. The system was stirred during the heating period. N_2 was then replaced by H_2 by pressurizing the reactor to 5 MPa

Table 1
Nature and concentration of the inhibitors

Inhibitor	Amount (mmol)
Cyclohexene 	12
1-Methyl-fluorene 	1
Pyridine 	0.7
Quinoline 	0.6
Carbazole 	0.5
Acridine 	0.5

through a pressure controller which keeps the pressure constant during the course of the experiment. Samples were periodically taken during the reaction course and analyzed by GC-FID equipped with a silicon capillary column (HP-5 crosslinked 5% PhMe Silicone 30 m) at a temperature between 373 and 523 K.

The inhibiting effect was determined by comparison of initial rates of disappearance, allowing therefore avoiding to take the transformation of the inhibitors into account. Selectivities for both routes were determined from conversions into the various products at a total conversion level of 10%.

2.2. *Selectivities over fresh and aged CoMo/Al$_2$O$_3$ catalysts*

Aged catalysts were obtained from the same precursor, an industrial CoMo/Al$_2$O$_3$ catalyst (Mo: 12.3 wt.%, Co: 3.6 wt.%, Co/[Co + Mo] = 0.31) after use in a pilot plant (samples P1–P3) or in an industrial unit (samples R1 and R2). History of the catalysts could be presented as:

P1: 1 week in a pilot plant for classical HDS of a straight run gas oil;
P2: 2.5 months in a pilot plant for classical HDS of a straight run gas oil;
P3: accelerated aging test in HDS of a straight run during 2 months at higher temperature;
R1: 6 months in an industrial unit;
R2: 13 months in a refinery.

As regard to the transfer of the samples, unload of pilot plant and of the industrial unit was performed under nitrogen atmosphere and catalysts stored in pentane or gas oil. After that, samples are treated in a Soxhlet equipment with heptane and under N$_2$ atmosphere during 10 h, and dried under vacuum.

2.2.1. *Characterizations of the catalysts*

For XPS analysis, the sulfided samples were transferred into a glove box without air exposure. The samples were pressed on an indium foil attached to the sample holder and transported into the preparation chamber of the XPS apparatus. The XPS spectra were recorded on a VG Instrument ESCALAB 200R system. The sample excitation was done by Al Kα X-rays (1486.6 eV). Peak shifts due to charging of the samples were corrected by taking the Al 2p line of Al$_2$O$_3$ at 74.0 eV as a reference.

High resolution electron microscopy (HREM) examinations were performed with a JEOL 2010 (200 kV) instrument equipped with a Link ISIS micro-analysis system. Its resolution is 0.195 nm. Freshly sulfided catalyst sample was ultrasonically dispersed in an ethanol solution at room temperature and the suspensions were collected on a carbon-coated copper grid.

In the sulfided state, alumina-supported Mo catalysts exhibit MoS$_2$ slabs building a layered structure. The average number of layers per stack and the average stack length were calculated from examination of more than 500 particles, according to the first moment of the distribution:

$$\overline{L} = \frac{\sum_{i=1}^{n} n_i l_i}{\sum_{i=1}^{n} n_i} \quad \text{and} \quad \overline{N} = \frac{\sum_{i=1}^{n} n_i N_i}{\sum_{i=1}^{n} n_i}$$

where l_i is the length of slabs of particle i, n_i the number of particles with a l_i length or N_i layers, N_i is the number of layers in the particle i.

2.2.2. *Catalytic activities*

The catalysts were first evaluated in the conversion of a real feed (straight run gas oil: 1.32 wt.% sulphur, total nitrogen content 89 wt. ppm, initial boiling point 502 K, 95% at 656 K) to determine the activity loss. Experiments were carried out in an automated unit which allows consecutive experiments to be performed under variable process conditions [13]. The reactor is a stainless steel tube (120 mm long, 6 mm i.d.) packed with 0.1–2 mL of catalyst placed between two layers of inert alumina. An automated gas–liquid phase separator (4 mL internal volume) and a collector allow periodical sampling of the liquid effluent. Non-impregnated α-alumina of the same particle size was used for the layers of inert packing. First, the catalyst is sulfided by a H$_2$S(5%)/H$_2$ mixture during 11 h at 653 K. The next part of the run consists in is composed of programmed sequences performed under the following conditions: pressure 30.10^5 Pa, temperature 593–653 K, VVH 8 h^{-1} and a H$_2$/liquid reactants ratio equal to 147 L/L. Liquid samples were analyzed by X-ray fluorescence (Horiba, SLFA 1800 H). The aged catalysts were also evaluated in HDS of 4,6-DMDBT under the same conditions as for the inhibiting experiments.

3. Results

3.1. *Inhibiting effects during the HDS of 4,6-DMDBT*

The absence of mass transfer 4,6-DMDBT (at 573 K) limitations as well as the effects of the stirring rate and of the granulometry of the catalysts were controlled in previous studies [14,15]. Moreover, the transformation of 4,6-DMDBT alone indicated that under our experimental conditions the order of reaction relative to this sulfur compound is zero, in agreement with previous observations [15]. As regard to the nature and the concentration of the compounds which could be poisons for hydrodesulfurization, we refer to the work of Koltai et al. [16].

The reaction products of the HDS of the 4,6-DMDBT indicate a reaction scheme according to two parallel routes, as schematized in Fig. 1. The first one, called the direct desulfurization pathway (DDS), gives 3,3-dimethylbiphenyl (3,3-DMBP), which is then slowly hydrogenated into substituted cyclohexylbenzene. The second pathway, called the hydrogenation route (HYD), consists in a preliminary hydrogenation of one aromatic ring, giving substituted tetrahydro- and hexahydrodimethyldibenzothiophenes which can be then desulfurized. It was previously observed that under the experimental conditions of this study the 3,3-DMBP is not hydrogenated [14]. Ratios of selectivities HYD/DDS could be therefore calculated as following:

$$\frac{\mathrm{DMBP}}{[\mathrm{UHDMDBT} + \mathrm{MCHT} + \mathrm{DMDCH}]}$$

in which DMBP is dimethylbiphenyl, UHDMDBT are the undesulfurized hydrogenated DMDBT, MCHT and DMDCH resulting from the desulfurization and successive hydrogenation.

As can be seen in Fig. 2a, with the choose concentrations, cyclohexene, 1-methyl-fluorene, pyridine, quinoline, carbazole and acridine all have an inhibiting effect on the HDS of 4,6-DMDBT, and inhibition appears on both transformation routes (Fig. 2b and c). Whatever the inhibitor, the HYD/DDS ratio is the same within the limits of experimental errors.

3.2. Selectivities over fresh and aged CoMo/Al$_2$O$_3$ catalysts

3.2.1. Characterizations

Chemical analysis of the samples deduced from XPS analysis are reported in Table 2. It can be seen that the carbon content of the catalyst is relatively high as soon as the catalyst worked for a week in a pilot plant (Sample P1) and only increases slightly during aging tests or use in the industrial unit (excepted for sample R1). For this later catalyst, high amount of coke (not explained but probably coming from some specific conditions during the process), does not modify more the selectivities during DMDBT transformation and reinforces our finding on the concept of catalytic sites. Moreover, XPS shows that during these processes the dispersions of molybdenum and cobalt do not change.

Table 2
Chemical analysis of the various aged catalysts deduced from XPS

Catalyst	Carbon (at.%)	Mo/Al	Co/(Co + Mo)	S/(Co + Mo)
P1	11.5	0.09	0.29	1.87
P2	18.8	0.09	0.31	1.91
P3	19.2	0.09	0.31	1.99
R1	26.2	0.09	0.32	1.53
R2	12.2	0.09	0.30	2.12

Fig. 3 shows representative HREM views of the five samples. It reveals the presence of typical structures of the MoS$_2$ phase, which are homogeneously dispersed on the support. The average length and number of layers of the MoS$_2$ crystallites are given in Figs. 4 and 5. The average particle length is equal to 1.9–2 nm for the three catalysts coming from the pilot plant whereas this value appears to be closed to 2.4 nm for samples R1 and R2 aged in the industrial unit. Such values are in agreement with those generally reported in the literature for CoMo catalysts. As regard to the stacking, mean values between 1.58 and 1.64 indicate that the stacking does not varies with the aging of the catalyst.

3.2.2. Catalytic activities and selectivities

Aged catalysts were first compared in the HDS of a gas oil. The apparent rate constant was calculated using the classical equation for a piston flow reactor:

$$\frac{1}{(n-1)} \times \left(\left(\frac{1}{\mathrm{S_p}}\right)^{(n-1)} - \left(\frac{1}{\mathrm{S_e}}\right)^{(n-1)}\right) = k_{\mathrm{app}} \times \frac{1}{\mathrm{VVH}}$$

in which n is the reaction order relative to the sulfur compounds ($n = 2.2$ for this feed), S$_e$ the sulphur concentration in the entrance feed and S$_p$ the sulfur concentration in the final products.

The activities reported in Fig. 6 for the different catalysts indicate variations of activities in good agreement with the variations observed in the pilot plant and industrial units (the loss of activity as compared to the fresh catalyst is expressed by ΔT the equivalent decrease in temperature that will lead to such a variation). It also confirms that using a microreactor leads to representative results if the experiments are performed under the same conditions and with the same feed. The evaluation of apparent activation energies in the range 593–663 K gave the same value (130 kJ mol^{-1}) for all the catalysts, suggesting that the electronic properties of the

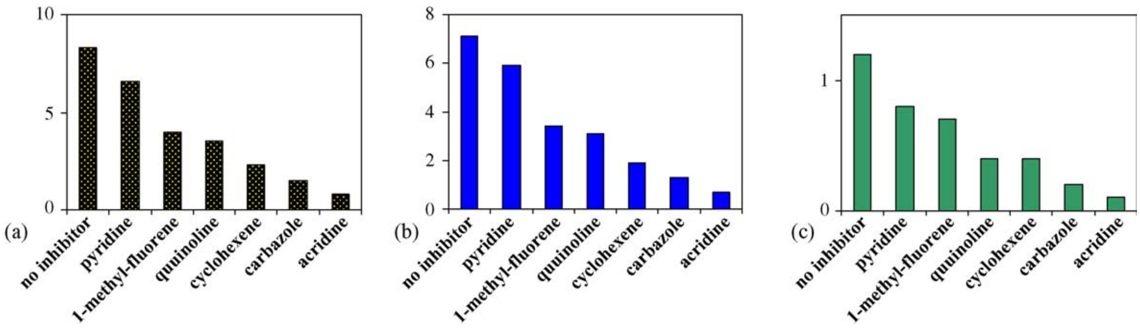
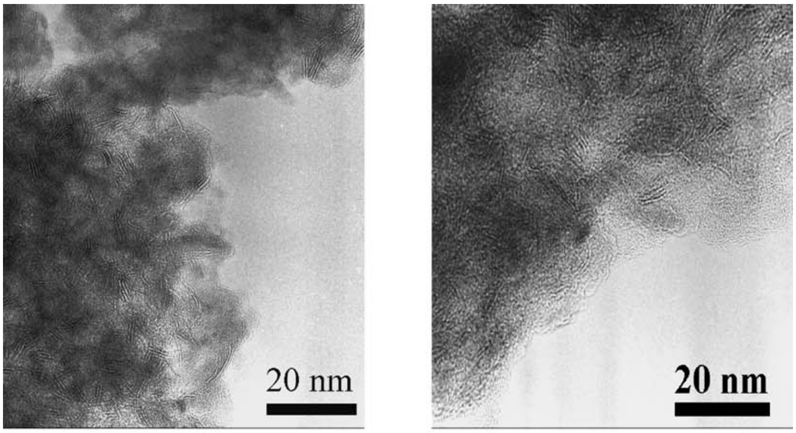
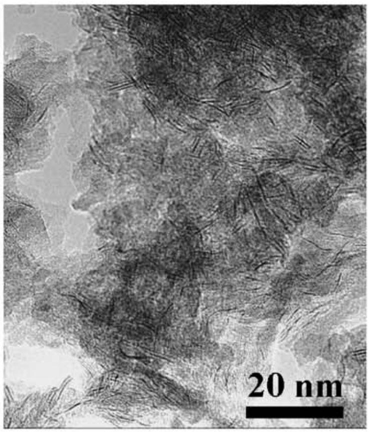


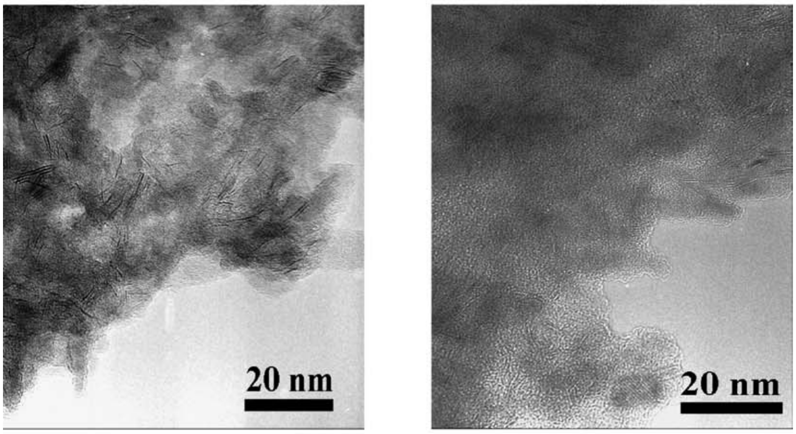
Fig. 2. Rates of 4,6-DMDBT HDS (a: total rate, b: rate along the hydrogenation route, c: rate along the DDS route. Rates are expressed in 10^{-7} mol s^{-1} g^{-1}).



Catalyst P1 (7 days pilot plant) Catalyst P2 (pilot plant, -12 K)



Catalyst P3 (pilot plant, -20 K)



Catalyst R1 (6 months refinery, -15 K) Catalyst R2 (13 months refinery, -30 K)

Fig. 3. TEM images of the CoMo/Al_2O_3 catalysts at different levels of aging.

catalytic sites (and therefore the quality of the site) are not modified. These results suggest that deactivation is probably due more to a decrease in the number of catalytic sites than to a decrease in the quality of the sites.

The same comparison was also performed for HDS of thiophene under atmospheric pressure, but the variations of activities (not given here) between the different samples could not be correlated with those observed on the real feed.

More interesting are the results obtained from the HDS of 4,6-DMDBT. As it could be observed in Fig. 7, the variations of activities between the different samples are close to those determined with the real feed and in good agreement with the ΔT given by our industrial partner. Hydrodesulfurization of 4,6-DMDBT in the liquid phase is therefore more representative of a real feed that the thiophene gas phase reaction.

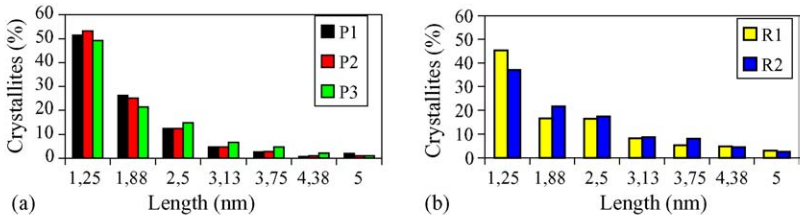


Fig. 4. Crystal length distribution of the MoS_2 slabs in aged catalysts (a: aging in pilot plant, b: aging in industrial unit).

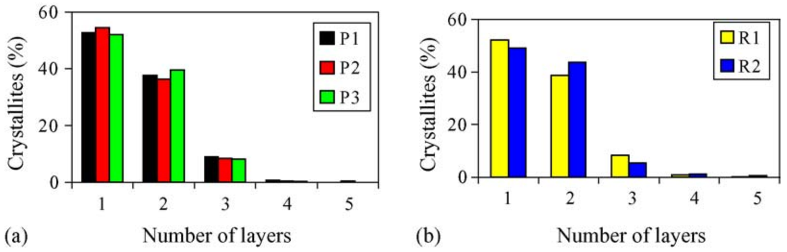


Fig. 5. Stacking distribution of the MoS_2 slabs in aged catalysts (a: aging in pilot plant, b: aging in industrial unit).

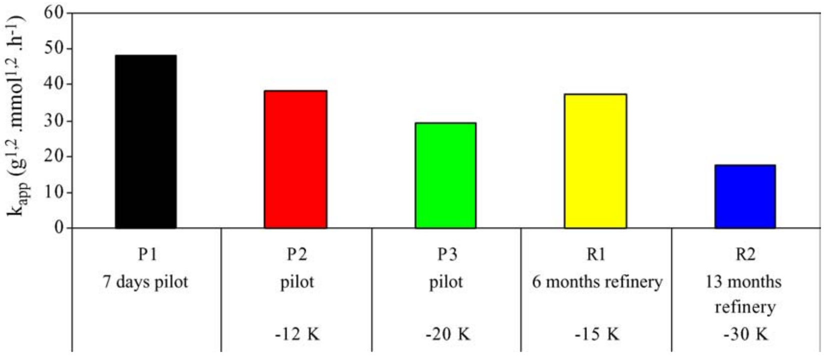


Fig. 6. Evaluation of aged catalysts in the laboratory micro-pilot plant over the real feed (rate constants calculated at 613 K).

Moreover, this model compound allows a more detailed analysis of the different functionalities of the catalysts by a quantitative evaluation of its transformation along to the two HYD and DDS routes. It was observed that most of the transformation of the 4,6-DMDBT is mainly performed by the hydrogenation route, as generally reported for refractory polyaromatic sulfur compounds [5,17]. Moreover, the evolution of the products with the total conversion is the same for all the catalysts. Initial selectivities toward 3,3-dimethylbiphenyl (DMBP, coming from the DDS route) and hydrogenation route (DMHN) are reported in Fig. 8. Excepted for sample R2, and within the limits of the

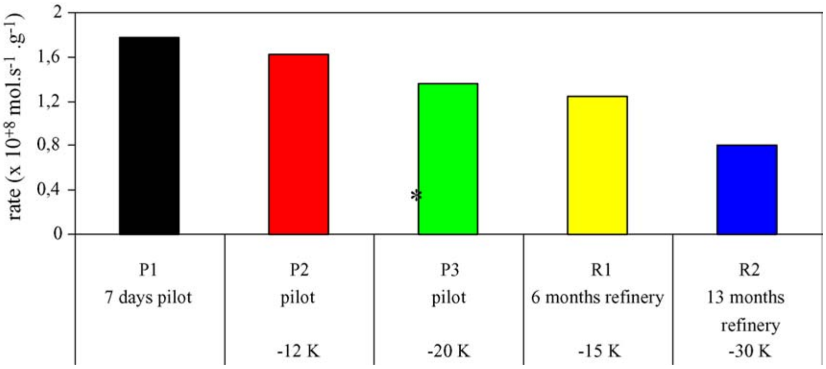


Fig. 7. Evaluation of aged catalysts in the HDS of 4,6-DMDBT (at 573 K).

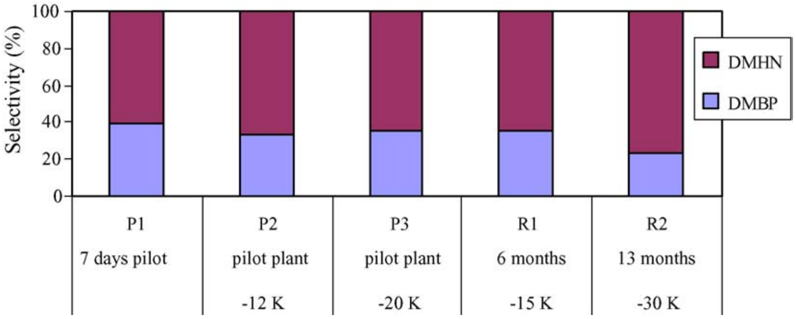


Fig. 8. Selectivities toward hydrogenation route and direct desulfurization during HDS of 4,6-DMDBT (at 573 K).

chromatographic analysis, selectivities are exactly the same for all the catalysts studied, even when a loss of activity of 20 K was observed (sample P3). For the catalyst R2, used for more than one year in an industrial unit, the slight increase in selectivity toward the hydrogenation route could be explained by the high amount of vanadium (0.65 wt.%), since it is well known that vanadium sulfide exhibits good hydrogenating properties [18].

4. Discussion

The results of Fig. 2a show that the HDS of 4,6-DMDBT could be poisoned to a large extend by organo-nitrogen molecules, polyaromatics or even olefins, if these contaminants are introduced in a high enough amount. For nitrogen containing molecules, such an inhibition is noticed for basic and non-basic molecules, suggesting that partially hydrogenated N-compounds may have a more important effect than the parent structure, as proposed previously by some of us [16]. For fluorene and 4,6-DMDBT, the geometrical and orbital similarities have led us to conclude to adsorption on the same catalytic sites [16]. Such a proposal could be re-examined considering the new results of this paper, seeing that the selectivity does not vary with the poisoning. Since it may be difficult to imagine 1-methyl fluorine having different types of adsorption sites, these results support the concept of a common intermediate adsorbed on the catalyst surface. Results with others inhibitors, also reported in Fig. 2b and c, lead us to generalize this mechanism in which the molecule is adsorbed on the same site for hydrogenation or direct desulfurization. Depending on the nature of the alkyl groups adjacent to the sulfur atom, or on the acid base properties of the solid, the reaction will proceed following one route or the other, as detailed in Fig. 9. In this mechanism, first proposed by Kazstelan and Guillaume [19] for hydrogenation and later extended to HDS [20], the adsorption site leading to HYD and HDS of 4,6-DMDBT would be an uncoordinated molybdenum atom, on which H_2 and H_2S could also be dissociated.

Such a mechanism is often discussed since the dihydro-intermediate has never been really identified nor has been the thiol intermediate. That was the reason to try a new approach with the comparison in DMDBT HDS of a series of $CoMo/Al_2O_3$ catalysts of the same origin but aged in a pilot plant and refinery units, resulting in a loss of activity reaching until 60%.

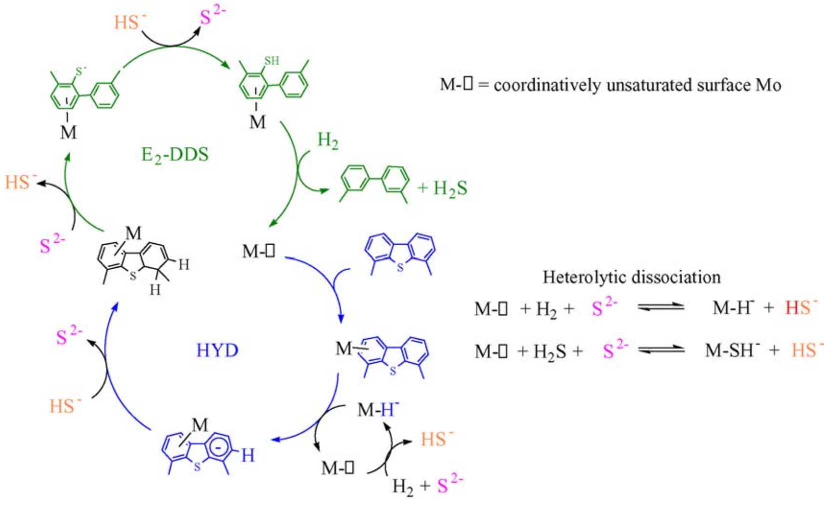


Fig. 9. Mechanism of hydrogenation and hydrodesulfurization.

These catalysts were first tested in the HDS of a straight run gas oil and the variations of activities were in good agreements with those observed during the pilot plant experiments or with the evolution in industrial unit. These samples were therefore characterized by HTEM and XPS to search some possible change in the structure of the active phase. Indeed, aging led to only few variations in the mean length of the crystallites. However, even if considering the geometrical model as proposed by Kazstelan et al. [21] such an increase in the length of the crystallites would induce a decrease of activity; the textural changes are here too slight to explain the large catalytic activity variations observed. Attention was therefore given to the possible effect of aging over the stacking. The results given in Fig. 5a and b show the same stacking repartition for all the catalysts, with a mean value of 1.6. XPS data confirm this observation since the Mo/Al ratio does not vary with aging. Deactivation has been correlated with the blocking of the active sites by carbon accumulation [22].

Moreover, the results given in Fig. 8 demonstrate a constant selectivity toward both transformation routes whatever the origin of the deactivation (long runs or accelerated aging tests). If different types of adsorption sites were to be taken into account for HYD and DDS, it would be difficult to imagine this constant HYD/DDS ratio with such large variations in activities. Therefore, we believe that these new experiments really reinforce the concept of the same type of active site involved in both hydrogenation and HDS, as we proposed some years ago [14] for dimethyldibenzothiophenes, confirmed later for several alkyl-dibenzothiophenes [17] and which was recently reconsidered by Hermann [8]. If such a new idea is clear for HYD and HDS, in the case of hydrodenitrogenation the situation appears somewhat more complex, according to the numerous papers of Qu and Prins ([23] and references therein). However, recent use of NiMo/hydroxyapatite in HDS of DBT, HYD of methylnaphthalene and hydrogenolysis of quinoline and dimethyldisulfide have also led Ezzamarty et al. [24] to conclude to the same type of site for all the chemical reactions studied.

5. Conclusions

In order to get more information on the nature of the catalytic sites for C–S bond breaking and for hydrogenation, a new approach has been attempted. That was done by poisoning 4,6-DMDBT HDS with different compounds (olefin, aromatics, nitrogen containing compound) and by using this model refractory sulfur molecule for a detail analysis of the selectivities of a series of aged CoMo/Al_2O_3 catalysts.

The results show that, whatever the origin of the decrease in activity (addition of inhibitor or deactivation due to aging), the selectivity toward the two routes of transformation of the 4,6-DMDBT does not change. These observations support the proposal of a catalyst with the same type of sites for HDS and hydrogenation, and a mechanism in which the probability of the reaction toward one route or the other one depends on steric effects and on the acid–base properties of the sulfide.

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