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Journal of Catalysis 223 (2004) 404–418

JOURNAL OF CATALYSIS

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Activation of alumina-supported hydrotreating catalysts by organosulfides: comparison with H_2S and effect of different solvents

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Received 6 October 2003; revised 26 January 2004; accepted 2 February 2004

Abstract

The sulfidation of nonpromoted and Co(Ni)-promoted MoS_2/Al_2O_3 catalysts with different organosulfide compounds (dimethylsulfide, dimethyldisulfide, and ethanethiol) has been investigated in this study. Comparison with H_2S sulfidation was performed using similar procedures of activation except the origin of sulfur (particularly the H_2S partial pressure generated inside the reactor during the activation procedure). The aim of this study was to better evaluate the different possibilities proposed in the literature to explain the well-known advantage of using organosulfides instead of H_2S during the activation of hydrotreating catalysts. Using organosulfide agents with alkane solvents to perform sulfidation of $NiMo/Al_2O_3$ leads to a very limited gain in activity for the HDS of dibenzothiophene or 4,6-dimethyldibenzothiophene compared to that of H_2S sulfidation. Even if the formation of thiolate species and their interaction with the catalyst surface is demonstrated, their role does not seem of prime importance to reach highly active catalytic systems. Moreover, in our experimental conditions, the catalytic results rule out a better balance between reduction and sulfidation when using organosulfides instead of H_2S. If the sulfiding agents are used under rigorously identical conditions, there is no significant difference in HDS performances of the obtained catalysts at the laboratory scale. Therefore, it is concluded that the actual beneficial effect of organosulfides as activating agents observed in industrial practice is not mainly chemical in nature. A “thermal well” effect of the organosulfides diluting the effect of the exothermicity of the oxide–sulfide transformation should be rather envisaged to explain the better efficiency of organosulfides. Finally, suppressing H_2S added to the reactant feed during the HDS reaction clearly evidences the higher activity of NiMo catalysts compared to CoMo catalysts at low H_2S concentration. Increasing the H_2S partial pressure results in a more severe inhibition of NiMo catalysts than CoMo catalysts, leveling off HDS activity differences between these two catalysts.

Keywords: Activation; Hydrodesulfurization; Sulfidation; Dimethyldisulfide; Sulfide catalysts; NiMo; CoMo

1. Introduction

Hydrotreatment refers to several important hydrogenation processes used in refineries to remove heteroelements (S, N, O), polyaromatics, and metals from petroleum feedstocks. High hydrogen pressures and elevated temperatures (573–673 K) are required to perform C-heteroelement hydrogenolysis reactions [1]. Alumina-supported molybdenum disulfide promoted by cobalt or nickel are typical examples of industrial hydrotreating catalysts. However, commercial catalysts are usually sold in an inactive form and must be activated in a first step by a sulfiding agent either in situ, i.e., directly inside the hydrotreating reactor, or ex situ by pre-impregnation with polysulfides followed by a subsequent reactivation of the catalyst inside the reactor. There is a general agreement that the in situ activation procedure (gas composition, heating rate, temperature of treatment, etc.) strongly influences the final activity and stability of hydrotreating catalysts. Nowadays, gas-phase activation by H_2S is scarcely used and is limited to laboratory-scale applications. H_2S as an activating agent has long been superseded by organosulfide agents (also called “spiking” agents) ($CH_3–S–CH_3$, $CH_3–S–S–CH_3$, polysulfides, etc.) for performing activation of $Co(Ni)Mo/Al_2O_3$ catalysts. In a famous account, Hallie [2] reported that the use of spiking agents, mainly dimethyldisulfide, $CH_3–S–S–CH_3$ (DMDS), increased the hydrodesulfurization (HDS) activity

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0021-9517/$ – see front matter © 2004 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2004.02.011

of VGO (Vacuum Gas Oil) by 60% compared to a gas-phase H_2/H_2S sulfiding procedure particularly for $CoMo/Al_2O_3$ catalysts. Prada Silvy et al. [3] have systematically compared an H_2/H_2S sulfiding mixture to different organosulfide agents (CS_2, dimethyldisulfide, dimethylsulfide, butanethiol, and thiophene) diluted in cyclohexane for the HDS of thiophene on $CoMo/Al_2O_3$. Their results showed a temperature dependency of the nature of the activating agent on the HDS of thiophene. Butanethiol was found the most effective activating compound. DMDS was found to be less efficient than H_2S at a treatment temperature of 573 K while similar results between these two agents were obtained at 623 K. Van Gestel et al. [4] studied different in situ activation procedures by H_2S or DMDS at 4.0 MPa and 623 K for the simultaneous HDS of thiophene and hydrogenation of cyclohexene. They found that the DMDS activation resulted in a 40% increase of the C–S bond-breaking rates in the HDS reaction scheme of thiophene. Moreover, the hydrogenation step from thiophene to thiolane was hardly influenced by the nature of the sulfiding agent. Similar results were reported by Arretz [5]. However, these results were obtained for the gas-phase HDS of thiophene, a model compound easily removed by hydrodesulfurization and no longer representative of sulfur-containing compounds present at the high HDS conversion requested nowadays. Only recently, Yamada et al. [6] and Qian et al. [7] have reported systematic studies respectively on the HDS of dibenzothiophene and of straight-run light gas oil (SRLGO). While the DMDS activation results in a lower final HDS activity for dibenzothiophene than the H_2S activation, the former led to a catalyst which was around 50% more active in the HDS of one of the most refractory compounds, 4,6-dimethyldibenzothiophene. In conclusion, inconsistencies were often observed when comparing the results of all these studies. It should be pointed out that these discrepancies may come from the fact that the sulfiding agents were used in different conditions: H_2S sulfidation at atmospheric pressure versus DMDS activation under high pressure, single-step sulfidation versus multiple-steps sulfidation, and inappropriate procedures (absence of solvent, direct pre-heating to the final temperature of sulfidation without wetting catalysts by the sulfiding feed, etc.) Finally, as stated by Jacquin et al. [8], the beneficial effect of DMDS compared to H_2S could also depend markedly on the nature of the solvent used during the activation procedure.

Understanding the activation by organosulfides ($S + C$) of hydrotreating catalysts is a part of a general effort to better ascertain the role of carbon in hydrotreating applications. This aspect was studied in detail in several reports [9–20]. Two main effects were observed: (1) a geometrical effect by which carbon deposit isolates sulfide particles from each other maintaining a high dispersion [9–12] and/or (2) a structural effect by which surface carbide-like species are formed at the surface of the active phase during the hydrodesulfurization reaction [13–20]. If the use of spiking agents leads to more active HDS catalytic systems, one of the two or both effects might be (partly) responsible for an enhancement of the activity or selectivity. However, other assumptions were made to explain a beneficial role of organosulfides like a thermal well effect reducing the exothermicity produced by the sulfidation of oxide precursors [21,22] or a well-balanced equilibrium between sulfidation and reduction of Mo(VI) oxide species into Mo(IV) sulfide moieties [3,4].

Therefore, to clarify the exact role of organosulfide agents and their influence on the hydrodesulfurization of dibenzothiophene and alkyldibenzothiophenes, herein is reported a study in which spiking agents are compared to H_2S while strictly respecting similar procedures of activation.

2. Experimental

2.1. Activation procedure

Activation was performed to compare precisely the effect of the nature of the sulfiding agent on the HDS activity. For each experiment, except the nature of the activating molecule and/or solvent, other parameters were kept similar: injection temperature of the liquid feed and activating agent (gas or liquid), temperature and duration of sulfidation plateaus if present, heating rate, duration and value of the final temperature of sulfidation, partial pressure of H_2S itself or of H_2S generated by the activating molecule, partial pressure of solvent and/or CH_4, partial pressure of H_2, H_2/HC ratio, and total pressure.

The typical sulfiding procedure was divided into five steps:

1. Heating at 0.05 K/s (3.0 K/min) from room temperature to 423 K under H_2,
2. Injection of the sulfiding feed at 423 K and plateau for 1 h (time needed to obtain a complete wetting of the catalyst),
3. Heating at 0.05 K/s from 423 to 623 K,
4. Plateau at 623 K for 12 h, and
5. decrease of the temperature from 623 K to the temperature of the HDS test (563 K) under the sulfiding atmosphere.

If not explicitly reported, typical sulfidation conditions were as follows.

2.1.1. Sulfidation by CH_3–S–S–CH_3 (DMDS) or by other spiking agents

The sulfiding feed consisted of 7.6 mol% DMDS diluted in one of the following solvents: *n*-heptane, decane, decalin, cyclohexane, cyclohexene, and 1-methylnaphthalene. Sulfiding feed and H_2 flow were respectively 8.0 cm^3/h and 4.7 L/h for a H_2/HC ratio of 587 L/L. The total pressure was 4.0 MPa. The various partial pressures were as follows: $P_{H_2} = 2.96$ MPa, $P_{H_2S} = 0.13$ MPa, $P_{CH_4} = 0.13$ MPa, and $P_{solvent} = 0.78$ MPa.

For other spiking agents, all the experimental conditions were kept equal to the standard procedure for DMDS, particularly regarding the molar percentage of sulfur introduced.

2.1.2. Sulfidation by H_2S

In that case, hydrogen sulfide was directly provided by a 10% (v/v) H_2S/H_2 gas cylinder. The H_2/H_2S rate was adjusted to keep the same H_2S partial pressure as for the DMDS (or other spiking agent) activation. The liquid feed flow, uniquely consisting of solvent, was adjusted to compensate the absence of methane previously formed by the decomposition of DMDS. The total pressure was 4.0 MPa. The various partial pressures were as follows: $P_{H_2} = 2.96$ MPa, $P_{H_2S} = 0.13$ MPa, and $P_{\text{solvent}} = 0.91$ MPa.

2.2. Dibenzothiophene and 4,6-dimethyldibenzothiophene HDS test

The aim of this study was to determine a possible effect of the nature of the sulfiding agent on the activation of alumina-supported hydrotreating catalysts. Therefore, dimethyldisulfide, generally used to keep a nearly high constant H_2S partial pressure during the HDS test, was not added to the feed. The HDS test with dibenzothiophene (DBT) was performed at 563 K, 4.0 MPa. The reactant mixture consisted of dibenzothiophene (1.11 mol%) diluted in decalin. The various partial pressures were as follows: $P_{H_2} = 3.06$ MPa, $P_{\text{reactant}} = 0.01$ MPa, and $P_{\text{decalin}} = 0.93$ MPa. In typical HDS conditions, the reactant feed rate and the H_2 flow were 42.7 cm^3/h and 20.0 L/h for 100 mg of catalyst. The H_2/HC ratio was then 470 L/L. For the HDS test with 4,6-dimethyldibenzothiophene (4,6-DMDBT), the low solubility of 4,6-DMDBT in decalin resulted in a less concentrated reactant solution (0.28 mol% instead of 1.11 mol%). The partial pressure of 4,6-DMDBT was then 0.0025 MPa. Other conditions were kept equal.

Catalyst activity was determined according to the following equation considering a pseudo-first order for the individual HDS rate constant:

$$k = \frac{F}{m} \ln\left(\frac{1}{1-\tau}\right).$$

The hydrodesulfurization of dibenzothiophene proceeds through two different pathways: (1) the direct desulfurization pathway (DDS) leading to biphenyl (BP) and (2) the hydrogenating pathway (HYD) resulting in the formation of a hydrogenated intermediate, tetrahydrodibenzothiophene (THDBT) subsequently converted into cyclohexylbenzene (CHB) by C–S bond rupture. Therefore, when differing greatly from the "total" activity values, "HDS" activity data are reported. "HDS" activity refers to the conversion to desulfurized products only (for instance, for the HDS of DBT, the hydrogenated intermediate of the desulfurization of DBT into cyclohexylbenzene, tetrahydrodibenzothiophene (THDBT) is excluded).

2.3. Catalysts

The commercial $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ hydrotreating catalysts contained 3.0 wt% CoO or NiO and 14.0 wt% MoO_3. The Mo/Al_2O_3 catalyst, containing 16.6 wt% MoO_3, was prepared by incipient wetness impregnation of γ-Al_2O_3 (BET surface area $= 260\ \text{m}^2/\text{g}$; pore volume $= 0.56\ \text{cm}^3\,\text{g}^{-1}$) with an aqueous solution of ammonium heptamolybdate (1.6 M), $(NH_4)_6Mo_7O_{24} \cdot 6H_2O$. To obtain a good impregnation of the γ-Al_2O_3 support by the precursor solution, a slight excess ($0.7\ \text{cm}^3\,\text{g}_{\text{cat}}^{-1}$) of solution was used. The catalyst was dried at 393 K and calcined under air flow at 773 K.

2.4. Chemicals

Dimethyldisulfide (98%), dimethylsulfide (97%), *n*-heptane (99%), cyclohexene (99%), 1-methylnaphthalene (98%), and decalin (98%) were purchased from Fluka, ethanethiol (97%) from Aldrich, cyclohexane (99.5%) from Riedel–de Haën, dibenzothiophene (98%) from Lancaster, 4,6-dimethyldibenzothiophene from Eburon, and H_2S/H_2 from Air Liquide.

The activation procedure was followed on-line by gas chromatography with a Varian 3400 equipped with a 50-m DB17 capillary column (J&W Scientific) with the following temperature programming: 320 K (5 min), from 320 to 362 K at 0.116 K/s (7 K/min), and from 362 to 523 K at 0.3 K/s (18 K/min).

For the HDS test, owing to the high boiling point of the reactants, on-line analysis of the reaction products was not convenient. Consequently, the reactor effluents were condensed and liquid samples were periodically collected to be analyzed by gas chromatography. The analyses were carried out with a temperature programming from 323 to 423 K at 0.166 K/s (10 K/min), 10 min at 423 K, from 423 to 523 K at 0.333 K/s (20 K/min) and 20 min at 523 K.

2.5. Elemental analysis

C and S contents were determined using a total combustion analyzer CE Instruments NA2100. Prior to elemental analysis, catalyst samples were first washed with CH_2Cl_2 (Prolabo) at reflux in a Soxhlet apparatus and dried for 24 h at 323 K to remove lixiviable carbon.

3. Results

3.1. Hydrodesulfurization of dibenzothiophene on $NiMo/Al_2O_3$ activated by dimethyldisulfide

The aim of this study was to determine a possible effect of the nature of different sulfiding agents used during the activation process on the final activity for the hydrodesulfurization of dibenzothiophene. For this purpose, experimental

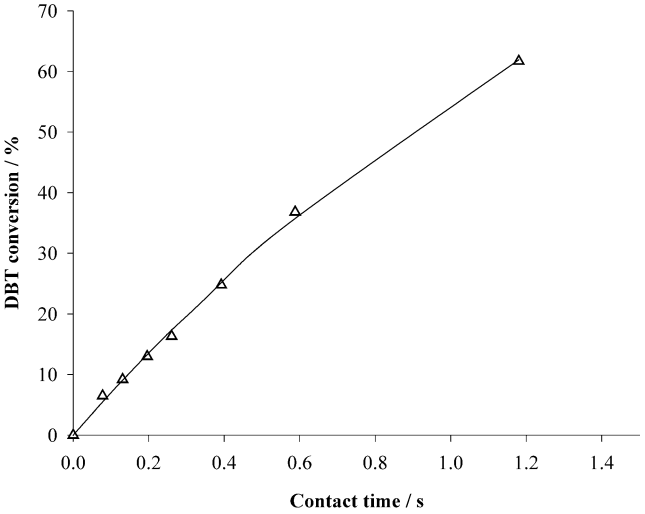


Fig. 1. Evolution of the DBT conversion versus contact time on NiMo/Al_2O_3 (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa). Sulfidation was performed using DMDS (7.6 mol%) in n-heptane at 4.0 MPa, 623 K.

activation conditions were maintained strictly equal for the different sulfur compounds. In previous studies, DMDS was often added to the reactant feed under standard conditions for the HDS of dibenzothiophene. This DMDS addition was used to maintain good stability of the active phase during the HDS test and/or for kinetic analyses, to limit the variations of the H_2S concentration due to different levels of DBT conversion. In our case, since our objective was to compare precisely spiking agents (mainly DMDS) activation to H_2S sulfidation, DMDS was not added to the HDS reactant feed to avoid any subsequent interaction with the active phase after the activation procedure. Therefore, the first part of our study was to verify that the absence of DMDS in the reactant feed did not have consequences for the stability of the hydrotreating catalysts. Fig. 1 shows the evolution of the DBT conversion versus contact time for NiMo/Al_2O_3 at 563 K and 4.0 MPa after a standard activation procedure using DMDS as sulfiding agent. Results showed a quasi-linear variation of the DBT conversion with contact time up to ca. 35% of conversion. A possible slight inhibiting effect by H_2S generated by the HDS reaction could not be excluded at high HDS conversions. Therefore, in the following experiments, DBT conversion will be maintained at conversion levels which fall in the range where the linear relationship is obtained.

Two parallel pathways are generally observed during the hydrodesulfurization of dibenzothiophene. The so-called direct desulfurization pathway (DDS) leads to biphenyl (BP) through an apparently direct C–S bond-breaking reaction. Leading to the formation of cyclohexylbenzene (CHB), the so-called hydrogenating pathway (HYD) needs in a first step the hydrogenation of at least one of the two aromatic rings, leading to tetrahydrodibenzothiophene (THDBT) before the C–S bond rupture can occur. Changes in the HDS selectivity depending on the compound used during activation could

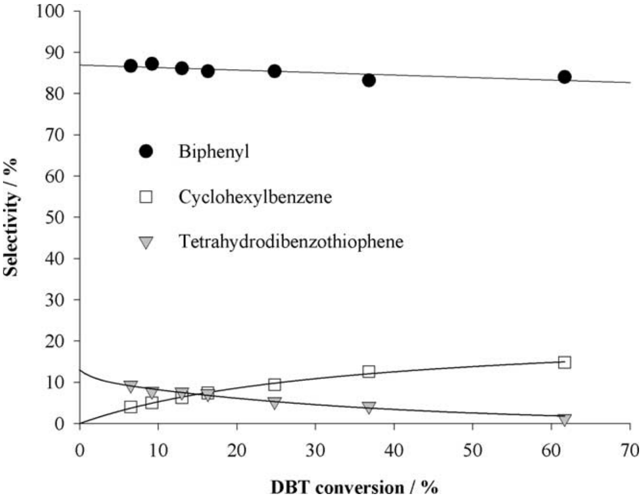


Fig. 2. Evolution of the selectivity versus DBT conversion during the HDS of DBT on NiMo/Al_2O_3 (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa). Sulfidation was performed using DMDS (7.6 mol%) in n-heptane at 4.0 MPa, 623 K.

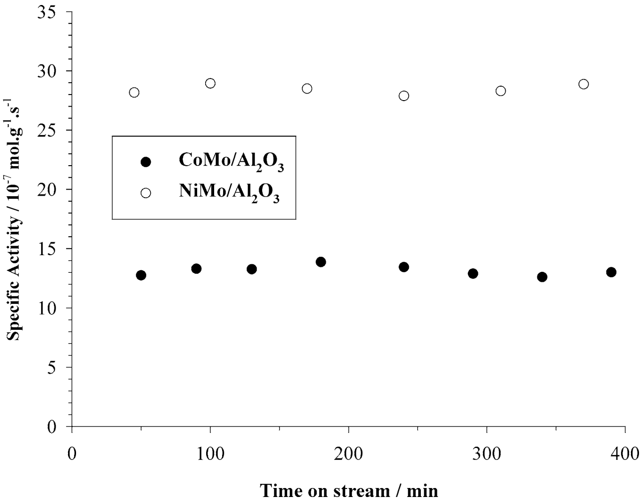


Fig. 3. Evolution of the activity versus time on stream during the HDS of DBT on CoMo/Al_2O_3 and NiMo/Al_2O_3 (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa, contact time = 0.39 s). Sulfidation was performed using DMDS (7.6 mol%) in n-heptane at 4.0 MPa, 623 K.

provide useful information on the nature of the resulting active phase. Particularly, a high increase of the selectivity along the DDS pathway is often a good indication of the formation of a cobalt (or nickel)-promoted phase [23]. However, the HYD/DDS selectivity has a meaning only if the two pathways are parallel, i.e., if biphenyl is not converted into cyclohexylbenzene under our experimental conditions. Fig. 2 shows the selectivity distribution for the three products of the transformation of DBT versus its conversion. As expected, biphenyl and tetrahydrodibenzothiophene were primary products since extrapolation of the curves representing their concentration to a “zero” DBT conversion gives values of 87% and 13%, respectively. Evolution of the selectivity in THDBT and CHB along the hydrogenating pathway clearly reveals that successive reactions of hydrogenation of DBT

Table 1
Activity and selectivity results for the HDS of DBT (without DMDS added) with MoS_2/Al_2O_3, $CoMo/Al_2O_3$, and $NiMo/Al_2O_3$; sulfidation was performed with DMDS (7.6 mol%) in n-heptane

Catalyst	Activity (10^{-7} mol g^{-1} s^{-1})	Selectivity (%) HYD	Selectivity (%) DDS
MoS_2/Al_2O_3	1.6	42	58
$CoMo/Al_2O_3$	13.0	5	95
$NiMo/Al_2O_3$	28.5	16	84

into THDBT and transformation of THDBT into CHB occurred. Indeed, the CHB selectivity increases at the expense of the THDBT selectivity with increasing values of DBT conversion. The selectivity along the DDS pathway (BP only) hardly changes with the DBT conversion. Only a very small decrease of the BP selectivity is observed from 87% to 84% when DBT conversion increases from 6% to 62%. Consequently, the hydrogenation of BP into CHB can be considered negligible and constant values for the HYD/DDS ratio can be expected for moderate DBT conversion ranges. Moreover, typical activity versus time on stream curves did not reveal any deactivation phenomenon when the catalysts were sulfided using standard conditions with DMDS (see Fig. 3).

3.2. Hydrodesulfurization of dibenzothiophene: comparison between MoS_2/Al_2O_3, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ activated by DMDS

The HDS activity and selectivity results were obtained for two commercial alumina-supported CoMo and NiMo catalysts after the standard activation by DMDS to determine the best candidate for further activation studies (Table 1 and Fig. 3). Results with MoS_2/Al_2O_3 were also reported to better ascertain the role of the Ni (or Co) promoters on the activity and selectivity in the present conditions. The non-promoted MoS_2/Al_2O_3 catalyst presented poor HDS activity since it was 10–20 times lower than that for promoted catalysts. More interestingly, a large difference in activity was observed between NiMo and CoMo catalysts under our HDS experimental conditions. Indeed, $NiMo/Al_2O_3$ was twice as active as $CoMo/Al_2O_3$. These results should be compared to preceding studies by Bataille et al. [24]. They observed only a 10% difference in activity between the two commercial catalysts. A lower temperature of reaction (563 vs 623 K) and the absence of a high H_2S partial pressure added to the reactant feed could explain these differences. Concerning selectivity, results reported in Table 1 confirm that promoters strongly favor the selectivity along the DDS pathway, particularly for cobalt. Indeed, $CoMo/Al_2O_3$ exhibited a 95% selectivity along the DDS pathway while a 58% value was found for MoS_2/Al_2O_3. The Ni promoter enhanced also the DDS pathway but its effect was less significant. This result is in agreement with previous studies reporting the more hydrogenating character of NiMo catalysts compared to CoMo catalysts [1,25]. $NiMo/Al_2O_3$ was chosen to study the influence of different activating compounds since this catalyst was both the most active under our experimental conditions and the catalytic system with which potential selectivity variations will be the most easily detectable.

Table 2
Effect of the H_2S partial pressure added during the HDS of DBT on activity and selectivity results of $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts; sulfidation was performed with DMDS/n-heptane

	P_{H_2S} added (MPa)	Activity (10^{-7} mol $g^{-1}s^{-1}$)	Selectivity DDS	Selectivity HYD
$NiMo/Al_2O_3$	0	28.5	84	16
	0.01	7.0	76	24
	0.05	3.0	71	29
	0[a]	25.8	84	16
$CoMo/Al_2O_3$	0	13.0	95	5
	0.01	4.3	86	14
	0.05	2.3	77	23
	0[a]	13.1	92	8

[a] After successive increasing values of H_2S partial pressure, H_2S was finally suppressed from the feed to check if reversible effects are observed.

3.3. Effect of the H_2S partial pressure on the dibenzothiophene HDS activity and selectivity of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts

In the absence of DMDS added to the reactant feed, $NiMo/Al_2O_3$ appears much more active than $CoMo/Al_2O_3$ while similar results were observed when 0.05 MPa of added H_2S was present in the reactant feed [24]. Therefore, experiments with H_2S added to the reactant feed were carried out with samples presulfided by using the standard DMDS procedure to check if under our experimental conditions $NiMo/Al_2O_3$ was more sensitive than $CoMo/Al_2O_3$ to the H_2S partial pressure or not. In these experiments, H_2S was provided from a H_2/H_2S gas cylinder and did not result from the decomposition of an organosulfide agent. These experiments made it possible to verify if the standard DMDS sulfidation led to a final stable active catalyst or not. Therefore, our main objective was not to study the effect of H_2S on the HDS of DBT since well-developed kinetic studies are available already elsewhere [26]. Table 2 reports the effect of the H_2S partial pressure added during the HDS of DBT on the activity and selectivity of $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts. For both catalysts, adding H_2S to the reactant feed strongly reduced the HDS catalytic activity. More interestingly, increasing the H_2S partial pressure leveled off the differences in activity between $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$. Indeed, $NiMo/Al_2O_3$ appeared more sensitive to the H_2S partial pressure present in the HDS reactant feed than $CoMo/Al_2O_3$. While $NiMo/Al_2O_3$ was 120% more active than $CoMo/Al_2O_3$ without H_2S added to the feed, its activity was only 30% higher with 0.05 MPa of H_2S. The results also clearly indicate a strong influence of the H_2S partial pressure on the HDS selectivity. The DDS selectivity decreased with increasing H_2S partial pressure, in agreement with previous results [27–29]. Without H_2S added to the

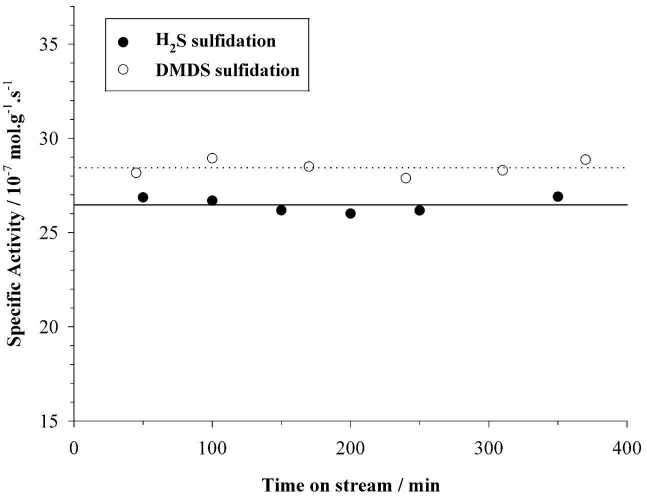


Fig. 4. Evolution of the activity versus time on stream during the HDS of DBT on $NiMo/Al_2O_3$ (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa, contact time = 0.39 s). Sulfidation was performed using either H_2S or DMDS at 4.0 MPa, 623 K. Flows of DMDS or H_2S were adjusted to generate the same partial pressure of H_2S ($P_{H_2S} = 0.13$ MPa) during the activation.

feed, the DDS selectivity reached an 84% value but dropped to 71% when 0.05 MPa of H_2S was present. Similar results were observed for $CoMo/Al_2O_3$. Suppressing H_2S from the feed resulted in a complete recovery of both activity and selectivity for $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts. This reversible poisoning effect of H_2S supports the fact that a stable HDS active phase was reached as a result of the standard DMDS activation.

3.4. *Effect of the nature of the activating agent on the hydrodesulfurization of dibenzothiophene*

Fig. 4 shows activity versus time on stream for the HDS of DBT over $NiMo/Al_2O_3$ after activation by H_2S or DMDS (with n-heptane as the solvent) using the same procedures of activation (the source of sulfur excepted). Neither initial increase in activity nor deactivation phenomena was observed and activity values were remarkably stable after both procedures of activation. The DMDS activation led to a slightly higher activity than the H_2S activation. Selectivity results after activation by these two activating molecules are reported in Table 3. Similar DDS selectivity values were obtained after activation by H_2S and by DMDS (86 and 84%, respectively). These selectivity results support the assumption that similar active phases were obtained in both cases. Since activities (and then conversions) were comparable for the H_2S and DMDS activation procedures (contact times were equal), the conversions into CHB or THDBT within the hydrogenating pathway could be compared. Indeed, since the hydrogenation of DBT into THDBT and the conversion of THDBT into CHB are successive reactions, selectivity comparisons regarding these products are only possible if similar conversion values are obtained. Contrary to the values observed for the HYD/DDS selectivity, the CHB selectivity within the hydrogenating pathway was significantly higher (78%) after the H_2S activation than after the DMDS procedure (65%). The HDS results after the dimethylsulfide and ethanethiol activation procedures were also reported in Table 3. The results are quite similar to those obtained with DMDS. The DDS selectivity results are about the same (84–86%) as well as the selectivity values in CHB within the hydrogenating pathway (66–68%). Activation by organosulfides led to similar HDS results, with slightly better activity than that after H_2S activation. For comparison, the results obtained after an in situ activation by DBT itself was also reported in Table 3. The experimental conditions of activation were the same as those with other organosulfide agents. DBT activation resulted in a 3 times less active catalyst than after the use of other activating molecules. However, the selectivity results were different. The DDS selectivity was very high (97%) and CHB was not formed. Elemental analysis revealed a low degree of sulfidation (50% lower than for other sulfiding agents). This result confirms the poor efficiency of DBT as a sulfiding agent.

Table 3
Effect of the nature of the activating compound used during the sulfidation process on the final HDS of DBT activity of $NiMo/Al_2O_3$; sulfidation was performed using heptane as the solvent even for the H_2S sulfidation

Activating compound	Relative activity	Selectivity		
		DDS	HYD	CHB/(THDBT + CHB)
H_2S	100	86	14	78
DMDS ($CH_3–S–S–CH_3$)	108	84	16	65
DMS ($CH_3–S–CH_3$)	105	86	14	66
$CH_3–CH_2–SH$	107	84	16	68
None[a]	32	97	3	0

[a] The activation procedure was made under an inert gas (N_2) and corresponds to an in situ activation by DBT during the HDS test.

Activation procedures by H_2S and DMDS were also performed with MoS_2/Al_2O_3 and $CoMo/Al_2O_3$ (Table 4). The DMDS activation of MoS_2/Al_2O_3 led to higher activity than the H_2S activation. Selectivity results were also slightly different with a higher DDS selectivity after the H_2S activation (65% vs 58%). With $CoMo/Al_2O_3$, the results were close to those obtained with $NiMo/Al_2O_3$ with a moderate improvement in the activity by the DMDS sulfidation compared to H_2S. However, contrary to MoS_2/Al_2O_3, activation by H_2S resulted in a less favored DDS pathway compared to DMDS.

3.5. *Effect of the nature of the activating agent on the hydrodesulfurization of 4,6-dimethyldibenzothiophene*

New environmental regulations will lower the sulfur content in diesel fuels to a maximum of 50 ppm or less in 2005. Refractory organosulfur compounds have to be converted to reach this level of sulfur concentration. These molecules are mainly alkyldibenzothiophenes and 4,6-dimethyldibenzothiophene (4,6-DMDBT) is now well-recognized as one of the most difficult sulfur impurities to decompose

Table 4
Effect of the activation by H_2S or DMDS on the final HDS of DBT activity of MoS_2/Al_2O_3 and $CoMo/Al_2O_3$ catalysts

Catalyst	Activating compound	Relative activity	Selectivity		
			DDS	HYD	CHB/(THDBT + CHB)
MoS_2/Al_2O_3	H_2S	100	65	35	46
MoS_2/Al_2O_3	DMDS (CH_3–S–S–CH_3)	123	58	42	46
$CoMo/Al_2O_3$	H_2S	100	90	10	60
$CoMo/Al_2O_3$	DMDS (CH_3–S–S–CH_3)	107	95	5	63

Table 5
Effect of the nature of the activating agent used during the sulfidation process in n-heptane on the final HDS of 4,6-dimethyldibenzothiophene (4,6-DMDBT) on $NiMo/Al_2O_3$

Activating compound in n-C7	Total activity (10^{-7} mol g^{-1} s^{-1})	Relative "HDS" activity	Selectivity		
			DDS	HYD	MCHT/(DMTHDBT + MCHT)
H_2S	2.7	100	12	88	72
DMDS	2.8	110	14	86	78

Total activity refers to the activity determined using complete 4,6-DMDBT conversion. "HDS" activity refers to the activity determined using only the desulfurized products [only methylcyclohexyltoluene (MCHT) and dimethylbiphenyl (DMBPh)].

[30,31]. It was therefore interesting to determine the possible effect of different sulfiding compounds on the activity of the catalysts for the HDS of 4,6-DMDBT. To our knowledge, up to now, only one recent paper by Qian et al. [7] has reported an indirect study of the activation by organosulfides for the particular case of 4,6-DMDBT. While studying the HDS of a straight-run light gas oil (SRLGO) with 1.5 wt% S on $CoMo/Al_2O_3$, they observed a higher desulfurization of the SRLGO cut after DMDS activation at 593 K, 3.0 MPa compared to H_2S activation at 673 K, 0.1 MPa. According to these authors [7], this higher desulfurization activity could be ascribed to higher HDS activity for alkyl-substituted dibenzothiophenes after the DMDS activation. However, once again, the quite different procedures of activation by H_2S or DMDS led to uncertainties about the conclusions reached in this study. In our case, the HDS of 4,6-DMDBT was performed following similar procedures of activation by H_2S and DMDS both in the presence of n-heptane as the solvent. Activity and selectivity results are reported in Table 5. Total and "HDS" activities based on the total conversion of 4,6-DMDBT did not evidence any real difference between H_2S and DMDS. Even if similar after H_2S or DMDS activation procedures, selectivity results were strikingly different from the preceding results obtained in the HDS of DBT. While for the HDS of DBT the DDS pathway was largely predominant, for the HDS of 4,6-DMDBT, the main route for hydrodesulfurization was the hydrogenating pathway leading first to dimethyltetrahydrodibenzothiophene (DMTHDBT) and second to methylcyclohexyltoluene (MCHT); the DDS pathway to dimethylbiphenyl (DMBP) represented only 12–14%. This result is in agreement with preceding studies [23] revealing a quite restrained DDS pathway for alkyl-substituted dibenzothiophenes.

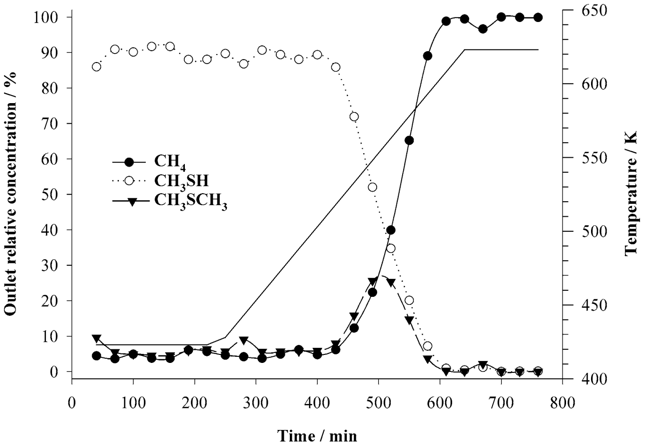


Fig. 5. On-line GC evolution of the outlet relative concentrations of the different products coming from the DMDS decomposition during the procedure of activation (DMDS = 7.6 mol% in n-heptane, H_2/HC ratio of 587 L/L, $P_{tot} = 4.0$ MPa, heating rate = 0.5 K/min).

3.6. On-line analysis of the decomposition products formed from dimethyldisulfide (DMDS), dimethylsulfide (DMS), and ethanethiol during the activation process

The activation process by organosulfide agents of hydrotreating catalysts can only be understood if the nature of the products formed from the decomposition of the spiking agents is known. For this purpose, on-line analysis by gas chromatography was carried out for different spiking agents. Figs. 5 and 6 present the outlet concentrations of the main products obtained by decomposition on $NiMo/Al_2O_3$ of dimethyldisulfide (DMDS) and of dimethylsulfide (DMS), respectively. Only carbon-containing compounds could be detected here since a FID detector was used. The heating rate was reduced from 3 to 0.5 K/min to increase the number of experimental points between 423 and 623 K. HDS tests were

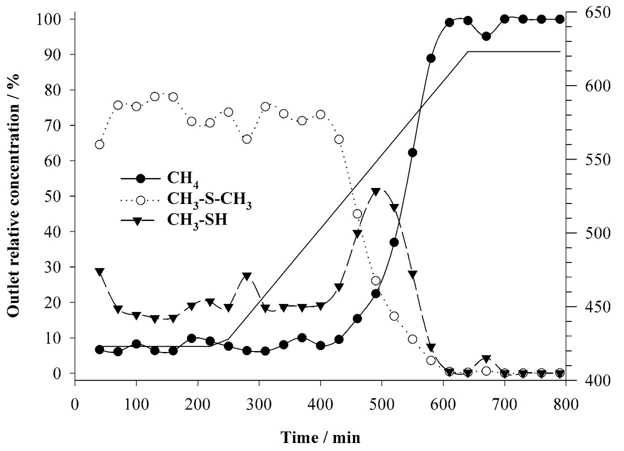


Fig. 6. On-line GC evolution of the outlet relative concentrations of the different products coming from the DMS decomposition during the procedure of activation (DMS = 15.2 mol% in *n*-heptane, H_2/HC ratio of 587 L/L, $P_{tot} = 4.0$ MPa, heating rate = 0.5 K/min).

performed to check that this change in heating rate did not modify the activity and selectivity of the catalyst. Apart from the main products presented in Figs. 5 and 6, heavier products, such as CH_3–S–S–S–CH_3 and CH_3–S–CH_2–S–CH_3 in the case of DMDS, were found in very small amounts.

Three different steps could be distinguished during the DMDS decomposition between 423 and 623 K (Fig. 5). First, below 503 K, DMDS was completely transformed into methanethiol, CH_3SH (90%) on the one hand and DMS and CH_4 (5% each) on the other hand. Between 503 and 603 K, the amount of CH_3SH decreased sharply while symmetrically the CH_4 concentration increased. The dimethylsulfide concentration also increased in a first step, reached an optimum value for a temperature of around 560 K (30%) before decreasing for higher temperatures of activation. Above 603 K, CH_4 was the only carbon-containing product to be detected.

It can therefore be concluded that dimethyldisulfide is very reactive and was completely decomposed into methanethiol at a temperature as low as 423 K:

$$CH_3\text{–S–S–}CH_3 + H_2 \rightarrow 2CH_3SH. \quad (1)$$

In a second step, for higher temperatures of activation ($T° > 503$ K), hydrogenolysis into CH_4 and H_2S became increasingly important and was the only reaction above 603 K:

$$CH_3\text{–S–S–}CH_3 + 3H_2 \rightarrow 2CH_4 + 2H_2S. \quad (2)$$

The condensation reaction of CH_3SH into dimethylsulfide was also observed between 503 and 603 K:

$$2CH_3SH \rightarrow CH_3\text{–S–}CH_3 + H_2S. \quad (3)$$

For dimethylsulfide, three steps of decomposition were identified as for DMDS (Fig. 6). However, contrary to DMDS, below 503 K, DMS was only partly converted into CH_3SH (18%) and CH_4 (7%). Seventy-five percent of DMS did not decompose up to 503 K. This is in accordance with the decomposition of DMDS where the as-formed DMS started to disappear at temperatures higher than about 560 K. Between 503 and 603 K, the DMS outlet concentration strongly decreased while CH_4 was formed in increasing quantities. Moreover, the CH_3SH concentration passed through an optimum (50%) for a temperature of activation of 545 K.

Dimethyldisulfide appears much more reactive than dimethylsulfide, revealing the easy cleavage by H_2 of the weak S–S bond of alkyldisulfides [32,33]. Dimethylsulfide did not undergo hydrogenolysis into CH_4 and H_2S below 503 K but this was the only reaction at $T° > 603$ K:

$$CH_3\text{–S–}CH_3 + 2H_2 \rightarrow 2CH_4 + H_2S. \quad (4)$$

The conversion of dimethylsulfide into CH_3SH was mainly observed for medium activation temperatures (503 K < $T°$ < 603 K):

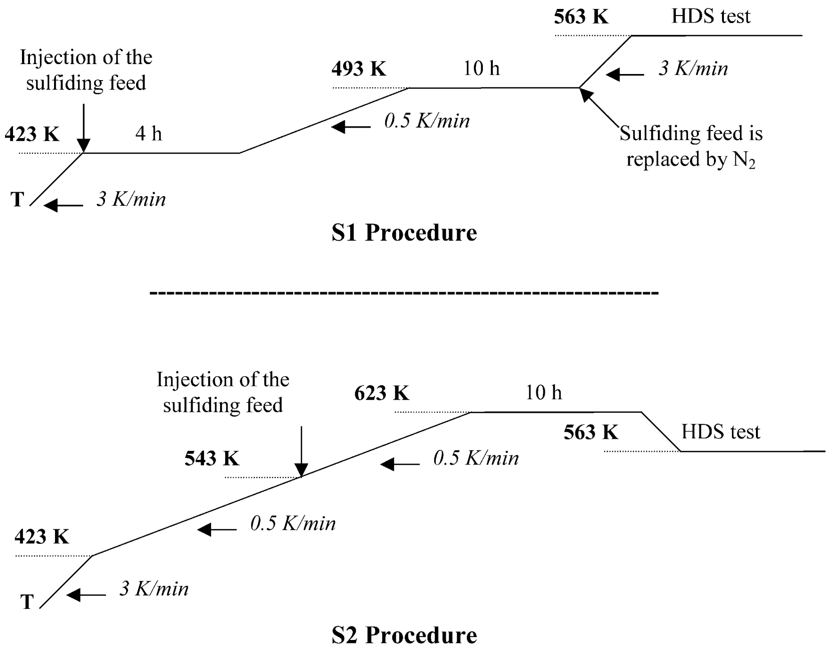
$$CH_3\text{–S–}CH_3 + H_2S \rightarrow 2CH_3SH. \quad (5)$$

On-line analysis was also performed with ethanethiol (not shown here). Ethanethiol only decomposed into C_2 (ethane and ethylene) products. The decomposition yield stayed low (20%) up to 503 K and then reached 100% above 603 K. Ethane and ethylene were not completely separated with our on-line chromatographic analysis. However, ethylene appeared as the main product at the beginning of the activation procedure before decreasing to the benefit of ethane at higher temperatures.

3.7. Modification of the procedures of activation: determination of key steps during the activation process

The on-line analysis of the products formed by the decomposition of DMDS during the activation process revealed three different zones: (i) between 503 and 603 K, DMDS was transformed mainly into CH_3SH; (ii) between 503 and 603 K, the CH_3SH concentration decreased symmetrically with an increase in the CH_4 concentration while CH_3–S–CH_3 was formed by condensation of CH_3SH; (iii) finally, above 603 K, CH_4 and H_2S were the only products of the DMDS decomposition. Therefore, based on these results, two new procedures of activation at low temperatures ($T° < 493$ K) called S1 and at high temperatures ($T° > 543$ K) called S2 were tested to compare organosulfides versus H_2S efficiency as sulfiding agents for the low and high activation temperature regions.

Scheme 1 reports respectively the S1 and S2 procedures of activation with the injection of the sulfiding agent at low or high temperatures of activation. Partial pressures and flow rates of H_2, H_2S, and hydrocarbon compounds were kept equal to those used for the standard procedure of activation. For the S1 activation, the sulfiding feed was still injected at 423 K. After a plateau at this temperature for 4 h, the temperature was increased up to 493 K at 0.5 K/min where a second plateau was maintained for 10 h. The sulfiding feed was then replaced by N_2 only (4.7 L/h) and the temperature was then increased at 3 K/min up to 563 K. The HDS reactant feed was then injected. Therefore, according to the



Scheme 1. Temperature program for the S1 and S2 procedures of activation.

preceding results of the on-line analysis of the DMDS decomposition (Fig. 5), sulfidation was essentially performed by H_2S or by CH_3SH formed by hydrogenolysis of DMDS.

For the S2 activation, the first part of the standard procedure of activation was suppressed. Therefore, the initial plateau at 423 K was removed and the temperature was increased from 423 K to 543 K at 0.5 K/min under N_2 only. At 543 K, the sulfiding feed was injected and a subsequent increase in temperature up to 623 K was carried out at 0.5 K/min. A plateau was then maintained for 10 h at 623 K before being decreased to 563 K, the temperature used for the HDS of DBT. According to the on-line analysis for DMDS, sulfidation was then performed essentially by H_2S. This S2 procedure of activation was then applied to check the importance of the sulfidation by H_2S formed from DMDS at high temperatures of activation.

The low-temperature S1 procedure of activation led to very different results if performed with H_2S or DMDS (Table 6). First of all, as expected, activity results were significantly lower than the results obtained using the standard procedure of activation up to 623 K. The H_2S-S1 activation resulted in a $NiMo/Al_2O_3$ catalyst presenting activity 20% lower than that for the standard procedure. Interestingly, using the S1 procedure, the H_2S activation led to a catalyst twice as active as with CH_3SH produced by the decomposition of DMDS. Selectivity results also showed higher DDS values (89–94%) than those reported using the standard procedure (85%). In our experimental conditions, sulfidation by a thiol compound like CH_3SH appeared much less efficient at low temperatures of activation than sulfidation by H_2S. Conversely, the high-temperature S2 procedure of activation led to very similar activities whatever the sulfiding agent, H_2S or DMDS. Activity and selectivity results were also quite close to those obtained using the standard activation. Bypassing the initial stages of sulfidation at low temperatures of activation below 543 K is not critical in achieving an active catalyst. The final sulfidation step above 550 K by H_2S, produced in any case from the decomposition of organosulfides, is therefore quite important for obtaining a highly HDS active catalytic system.

3.8. Effect of the nature of the solvent used during the activation procedure

The role of the solvent has to be examined to better understand the activation of hydrotreating catalysts. Actually, the nature of the solvent may not be without consequences on the catalyst activation. The solvent used during activation by alkyldisulfides (DMDS) or thiols is generally an alkane [5]. The use of aromatics is seldom considered but seems beneficial when combined with alkanes in minor proportions [8]. Olefinic compounds should be avoided in the activation by alkyldisulfides but seem profitable in the presence of elemental sulfur [34]. Indeed, combination reactions probably occur in this case and lead to the formation of polysulfides [34,35]. Table 7 shows the influence of the nature of the solvent used during the activation procedure on the HDS of DBT on $NiMo/Al_2O_3$. DMDS activation of $NiMo/Al_2O_3$ in the presence of alkane or cycloalkane compounds did not result in marked differences in activity for the HDS of DBT. Nevertheless, the catalysts seem to be slightly less active when DMDS is used in the presence of cyclic alkanes. The highest activity was still obtained in the case of activation by DMDS in the presence of *n*-heptane. Selectivity results were once again very similar.

Table 6
Effect of the nature of the sulfiding agent (H_2S or DMDS) on the HDS of DBT of $NiMo/Al_2O_3$ catalysts activated using the low-temperature S1 or high-temperature S2 procedure of activation

Activating compound in n-C7	Procedure of activation	Activity (10^{-7} mol g^{-1} s^{-1})	Selectivity DDS	HYD	CHB/(THDBT + CHB)
H_2S	S1	21.7	89	11	55
DMDS	S1	9.6	94	6	50
H_2S	S2	27.7	86	14	66
DMDS	S2	28.0	84	16	62

Table 7
Effect of the nature of the solvent used during the activation procedure by H_2S or DMDS on the final activity and selectivity of $NiMo/Al_2O_3$ for the HDS of DBT

Activating compound	Solvent	Activity (10^{-7} mol g^{-1} s^{-1})	Selectivity DDS	HYD	CHB/(THDBT + CHB)
H_2S	Heptane	26.4	86	14	78
DMDS	Heptane	28.5	84	16	65
DMDS	Decane	25.7	85	15	68
DMDS	Cyclohexane	23.5	83	17	67
DMDS	Decalin	22.7	84	16	62
H_2S	Cyclohexene	18.1	92	8	58
DMDS	Cyclohexene	18.4	89	11	52
H_2S	1-Methylnaphthalene	21.9	88	12	63
DMDS[a]	1-Methylnaphthalene	16.0	90	10	46
DMDS[b]	1-Methylnaphthalene	17.1	93	7	65

[a] Sulfidation by DMDS/1-methylnaphthalene, leading to a 6.5 wt% C deposit.
[b] Sulfidation by DMDS/1-methylnaphthalene, leading to a 10 wt% C deposit.
Sulfidation by DMDS in the presence of 1-methylnaphthalene led to high carbon contents and therefore to less reproducible experiments. Two experiments are then reported, leading to differences in selectivity and carbon contents: the highest DDS selectivity corresponds to a higher carbon content (see Table 8).

Activation by H_2S or DMDS in the presence of an olefin or of an aromatic compound like 1-methylnaphthalene led to even lower HDS activities than in the presence of an alkane or a cycloalkane compound. Activation in the presence of cyclohexene resulted in less active catalysts than with an alkane as solvent. However, in that case, the H_2S and DMDS activation procedures led to very similar activities. The DDS selectivity is somewhat higher with the H_2S activation than with DMDS. Contrary to the DMDS activation in the presence of n-heptane, activation in the presence of 1-methylnaphthalene could lead to significant variations in the levels of HDS activity with respect to H_2S activation. Interestingly, selectivity along the DDS pathway was favored when the catalyst was sulfided with DMDS in the presence of 1-methylnaphthalene. If activities for the DDS or the HYD pathway are considered ("DDS" or "HYD" activity), the inhibiting effect of 1-methylnaphthalene is much stronger on the "HYD" activity when compared to n-heptane than for the "DDS" activity (cf. Fig. 7). Therefore, the higher DDS selectivity reported in Table 7 was in fact related to a very depleted activity along the HYD pathway. As shown in Fig. 8, the "DDS" activity strongly increased at the beginning of the HDS test before reaching a steady-state value after 300 min whereas the "HYD" activity stayed constant all along the HDS experiment.

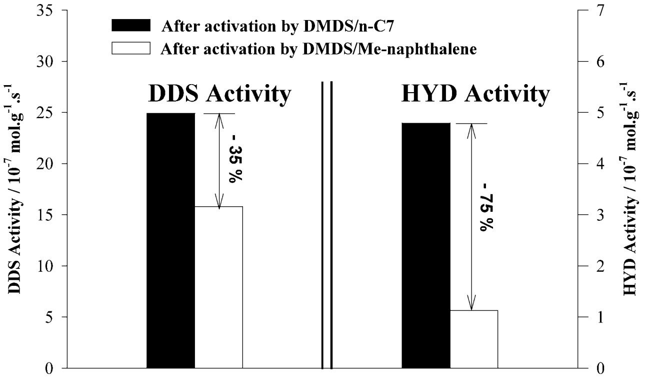


Fig. 7. Comparison of the "DDS" and "HYD" activities during the HDS of DBT on $NiMo/Al_2O_3$ (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa, contact time = 0.39 s) after sulfidation using DMDS diluted either in n-heptane or in 1-methylnaphthalene.

Table 8 gives the results of C and S elemental analyses of the samples after the various activation procedures. Except for the activation with 1-methylnaphtalene which gave lower sulfur percentages, these procedures led to percentages of sulfur higher than those expected for the complete sulfidation into Co_9S_8 (or Ni_3S_2) and MoS_2. Carbon contents were quite low when activation was performed with an alkane solvent but increased significantly in the presence of cyclohexene and reached the highest value in the presence

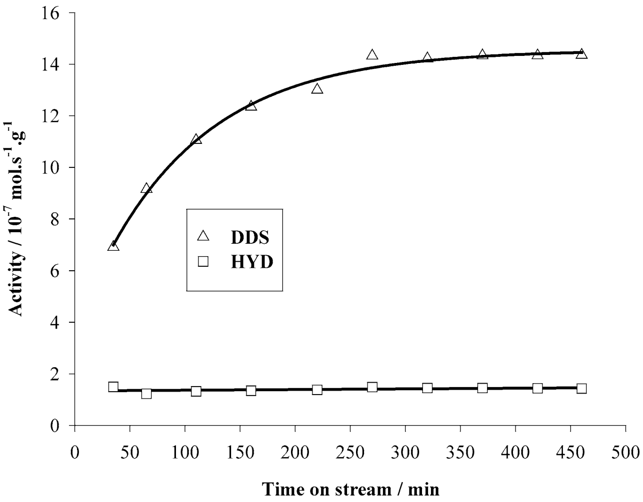


Fig. 8. Evolution of the “DDS” and “HYD” activities versus time on stream during the HDS of DBT on $NiMo/Al_2O_3$ (decalin, $T° = 563$ K, $P_{DBT} = 0.01$ MPa, $P_{tot} = 4.0$ MPa, contact time = 0.39 s). Sulfidation was performed using DMDS diluted in 1-methylnaphthalene.

Table 8

C and S elemental analysis for $NiMo/Al_2O_3$ catalysts after the activation by H_2S or DMDS with different solvents

Activating agent	Solvent	% C	% S
H_2S	Heptane	0.2	7.4
DMDS	Heptane	0.8	7.0
H_2S	Cyclohexene	2.6	7.6
DMDS	Cyclohexene	4.2	6.9
H_2S	1-Methylnaphthalene	2.0	6.8
DMDS[a]	1-Methylnaphthalene	6.5	6.6
DMDS[b]	1-Methylnaphthalene	10.0	5.2

[a] Sulfidation by DMDS/1-methylnaphthalene leading to a HYD/DDS = 10/90 selectivity.

[b] Sulfidation by DMDS/1-methylnaphthalene leading to a HYD/DDS = 7/93 selectivity.

of 1-methylnaphthalene. For a given solvent, DMDS activation led systematically to higher concentrations of carbon. This is particularly true in the case of 1-methylnaphthalene where DMDS seems to promote the formation of carbon deposit (up to 10 wt%).

4. Discussion

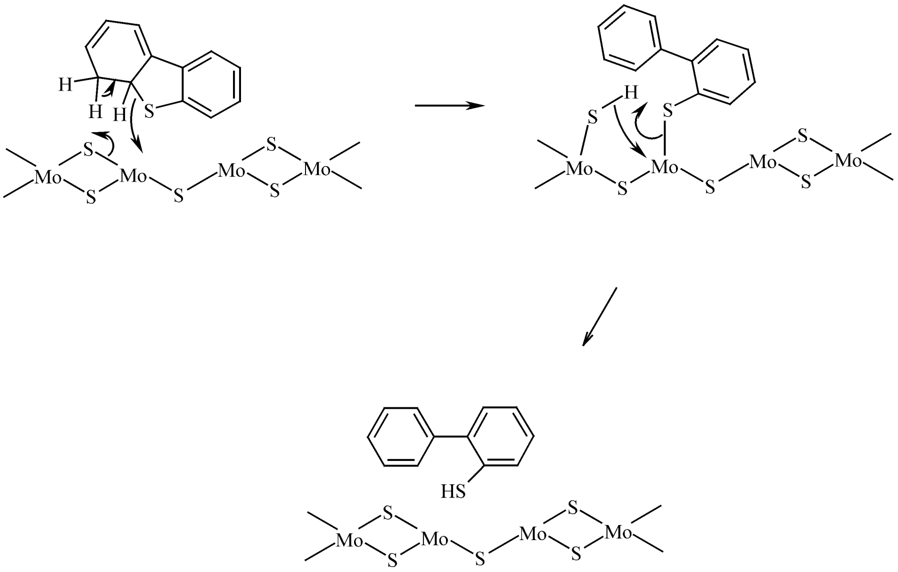
The effect of different activating agents used during sulfidation of hydrotreating catalysts has been studied by several authors [2,4,5,7,8]. These studies generally led to the conclusion that the use of organosulfide agents is more beneficial to the final activity of HDS catalysts than sulfidation by H_2S. However, comparison between activating agents was often carried out using different experimental procedures (P_{H_2S}, temperature of sulfidation, pressure, presence or absence of solvent, etc.) and might lead to inconclusive results. Moreover, certain studies [3,6] have surprisingly concluded deleterious effects regarding the well-known beneficial effect of spiking agents. For instance, Prada Silvy et al. [3] compared sulfidation by H_2S/H_2 at 3.0 MPa to activation by DMDS diluted in cyclohexane using catalysts initially preheated under Ar at different temperatures of activation. Similarly, Yamada et al. [6] compared H_2/H_2S sulfidation at 0.1 MPa with several plateaus of sulfidation at 373, 473, 573, and 673 K to DMDS activation performed at 593 K and 3.0 MPa without any plateau during the heating ramp. Various causes for the positive effect of organosulfides were also reported and vary from (i) an increase of the dispersion of the active phase [6,7,10], (ii) a structural effect [14–17,36–38], (iii) a better balance between reduction and sulfidation during the transformation of Mo(VI) oxides into Mo(IV) sulfides [3,4], and finally (iv) a “thermal well” effect that reduces the negative effect of exothermicity inherently occurring during the oxide–sulfide transformation [22].

4.1. *Effect of H_2S on the catalytic properties of $CoMo/Al_2O_3$ and $NiMo/Al_2O_3$ catalysts during the HDS of DBT*

In an effort to better ascertain the causes of the beneficial role of spiking agents on the activation of hydrotreating catalysts, the present study was carried out by comparing precisely different activating agents under identical experimental conditions. To avoid any subsequent interaction of DMDS during the HDS test, DMDS addition to generate a high and constant H_2S partial pressure in the reactant feed was not used. Preliminary results (cf. Table 1) demonstrated that, in the absence of H_2S other than the H_2S generated by the HDS reaction (ca. 0.003 MPa), $NiMo/Al_2O_3$ was twice as active as $CoMo/Al_2O_3$. At higher H_2S pressures, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ present similar HDS activities. The effect of H_2S added to the feed confirmed the higher sensitivity of $NiMo/Al_2O_3$ to an increase in the H_2S concentration [25,39]. H_2S also decreased preferentially the DDS pathway during the HDS of DBT.

4.1.1. *H_2S inhibition of the DDS pathway*

The higher H_2S inhibition of the DDS pathway seems contradictory to the well-known inhibition of aromatic hydrogenation reactions by H_2S [40,41]. However, recent mechanistic studies on the HDS of DBT and 4,6-DMDBT may help in proposing a sensible explanation [23,24]. A possible way to cleave a C–S bond in DBT would be first to hydrogenate one of the double bonds in the vicinity of the sulfur atom of the DBT molecule to obtain a dihydrogenated intermediate product and then to break the C–S bond thanks to an E_2 elimination process. The first step of the elimination process would be the nucleophilic attack by a basic sulfur of a H atom in the β position with respect to the sulfur atom of DBT, allowing a rearomatization process and the simultaneous cleavage of the C–S bond (Scheme 2). In this respect, the main effect of the promoter is to improve the C–S bond cleavage activity of MoS_2 and then the DDS pathway [24, 42–45]. As demonstrated by Berhault et al. using FTIR spec-



Scheme 2. E_2 mechanism of the C–S bond cleavage in the DDS pathway of the hydrodesulfurization of dibenzothiophene on MoS_2-based catalysts [23].

troscopy [46], this improvement was related to an increase of the basicity of sites (ex: sulfur anions) shared between Mo and promoter atoms. This result is also in agreement with an electronic origin for the promotion. Indeed, as revealed by Harris and Chianelli [47], Co and Ni present the unique ability to interact electronically with Mo. Co or Ni can donate electrons to Mo, resulting in a formal reduction of Mo and formal oxidation of Co (or Ni). This electron donation weakens the metal–sulfur bond strength in NiMo or CoMo sulfides compared to MoS_2, leading to less strongly bound sulfur atoms, i.e., more basic species. The increased basicity would then favor the attack of acidic H atoms in the β position of the DBT molecule. In that case, H_2S would act through its acidic properties, inhibiting strongly the DDS pathway by converting the basic S^{2-} anionic sites (or equivalent anionic sites) into protonic sulfhydryl species inactive for the C–S bond cleavage. This result supports the fact that the main requirement for the elimination step for C–S bond cleavage is the basicity of the S^{2-} entities.

4.1.2. Sensitivity to H_2S of NiMo/Al_2O_3 and CoMo/Al_2O_3 catalysts

While mechanistic considerations could provide an explanation for the preferred inhibition of the DDS pathway by H_2S, mechanistic studies cannot account for the differences of sensitivity to H_2S between NiMo and CoMo. Even if the higher sensitive character to H_2S of NiMo/Al_2O_3 catalysts is already known [25,39], the real cause of this difference of comportment after Ni or Co promotion is not yet understood. Nevertheless, recent progress of theoretical calculations of promoted NiMoS and CoMoS phases could help to distinguish NiMo from CoMo catalytic properties. First of all, density functional theory (DFT) calculations have recently renewed the idea of a Sabatier principle interpretation of HDS activity results [48,49]. In this respect, it has been clearly demonstrated that the synergy effect of Co or Ni reducing the metal–sulfur bond strength to optimum values for HDS activity is electronic in nature. Substitution of Co or Ni for Mo at the edges of MoS_2 slabs results in a reduction of the acceptor character of Mo due to the filling of antibonding states lying below the Fermi level [50,51]. This reduction effect of the acceptor character was found to be stronger after Ni substitution than after Co substitution of Mo edge atoms. Surface metal–sulfur bond strength would then decrease in the following order: $MoS_2 >$ CoMoS $>$ NiMoS. A more reduced metal–sulfur bond strength after Ni substitution than after Co substitution would imply that basic sulfur anions (or similar active sites) shared between Mo and Ni atoms are more basic sites than similar sulfur atoms shared between Mo and Co atoms. The interaction of H_2S with these basic sites would be stronger for the NiMoS phase than for the CoMoS phase. This would induce a higher H_2S inhibiting effect of the NiMoS phase.

4.2. Interaction of organosulfides with the catalyst surface during the activation process

In a first step, the decomposition products of DMDS and DMS were identified to analyze how organosulfide agents could interact with the catalyst surface during the genesis of the active phase. Dimethyldisulfide was found to be very reactive even at 423 K. Indeed, it was completely converted at the beginning of the activation procedure into CH_3SH with a very high selectivity (90%). This result should be compared to a previous study by Cadot et al. [52] on the catalytic synthesis of CH_3SH by reduction of DMDS. Indeed, the hydrogenolysis reaction of DMDS into CH_3SH is not intrinsically selective since the formation of CH_3SH is counterbalanced by the subsequent condensation of the CH_3SH product into CH_3–S–CH_3 and H_2S. Consequently, the CH_3SH selectivity could reach only typical values of 50% whatever the nature of the sulfide catalysts used (NiMo, CoMo,

MoS_2). Interestingly, the addition of water strongly inhibited the consecutive transformation of CH_3SH into CH_3–S–CH_3. In that case, in the presence of water, Cadot et al. [52] could obtain a CH_3SH selectivity of 95% at 100% DMDS conversion. The very high selectivity observed in the present case is in complete agreement with this preceding study since H_2O, very probably formed at the initial stage of the sulfidation process, would limit the DMDS transformation to CH_3SH up to ca. 500 K. At higher temperatures of activation, the consecutive transformation of CH_3SH into CH_3–S–CH_3 is not blocked anymore and DMS concentration increases up to ca. 550 K; C–S bond cleavages and production of CH_4 are predominant only at higher temperatures of reactions. The intermediate condensation reaction of CH_3SH into CH_3–S–CH_3 is quite interesting since the condensation of thiol into thioether is considered as a typical acid–base reaction which occurs at the catalyst surface thanks to a Lewis acid site and a basic site. The interaction of CH_3SH with different sulfide catalysts has been studied by Berhault et al. [46]. The formation of thiolate species linked to coordinatively unsaturated sites (CUS) on the catalyst surface was evidenced by FTIR spectroscopy [53].

Alkylsulfides (DMS) were found to be strikingly less reactive than alkyldisulfides, demonstrating the high reactivity of S–S bonds [32,33,52]. Indeed, contrary to DMDS, DMS did not decompose up to 500 K. However, above this temperature, the transformation of CH_3–S–CH_3 into CH_3SH supports the initial presence of thiolate species at the catalyst surface which could recombine with protonic species to form CH_3SH. The onset for production of CH_4 is similar to the DMDS decomposition case, suggesting C–S bond rupture of similar types of groups “spiked” or linked to the catalyst surface. This on-line analysis demonstrates that alkyldisulfides and alkylsulfides as well as their products of decomposition (mainly thiols) interact with the catalytic sites (sulfide or oxysulfide phase?) during the activation process.

4.3. Analysis of the procedures of activation with different sulfiding agents

The use of similar experimental conditions of activation between H_2S and DMDS (or other spiking agents) shows only a limited gain in HDS activity when organosulfide agents are used instead of H_2S. The present result does not confirm the study by Yamada et al. [6] who observed better activation by H_2S than by DMDS for the HDS of DBT. Our result emphasized clearly the necessity of comparing H_2S and DMDS using similar procedures of activation, which was not the case for the study by Yamada et al. The present study does not confirm an increase in HDS activity for alkyl-substituted DBTs after DMDS activation compared to H_2S. Even if the DMDS activation involves a certain gain in HDS activity for 4,6-DMDBT, this increase is similar to the one observed for the HDS of DBT.

Some of the different causes which were proposed to explain why better HDS active phases would be obtained in industrial conditions after the use of spiking agents can be rejected. First of all, DMDS appears largely more reactive at low temperatures of activation than DMS since it is already completely transformed into CH_3SH at 423 K whereas DMS is not decomposed below 500 K. This result definitely rules out the assumption about a link between the reactivity of spiking agents at low temperatures of activation and the final HDS activities [2]. It also rules out the explanation based on better HDS activity as a result of the decomposition of spiking agents into H_2S at low temperatures which would enhance the sulfidation at the initial stage of the activation. H_2S is never formed in large amounts below 500 K during the DMDS decomposition while H_2S is of course already present at 423 K for H_2S activation. Another explanation for better HDS activity resulting from the interaction of spiking agents was to consider that sulfiding agents and particularly thiols formed from the DMDS decomposition at low temperatures would be a better activating agent than H_2S [4]. Indeed, Prada Silvy et al. [3] have proposed that if a thiol dissociates into RS^- and H^+ species and H_2S into HS^- and H^+ species, RS^- would be more effective in sulfidation than HS^-. A better balance between sulfidation and reduction would then be accomplished if thiols are used instead of H_2S. The limited gain in HDS activity after DMDS activation compared to H_2S does not support this assumption. This fact was confirmed by using H_2S or DMDS in the modified S1 activation procedure at low temperature (up to 493 K). At these low temperatures of activation, DMDS was essentially decomposed into CH_3SH and the S1 procedure practically corresponds to sulfidation by methanethiol. The S1-activated $NiMo/Al_2O_3$ catalyst was much less active for the HDS of DBT than the catalyst sulfided by H_2S. Moreover, selectivity results suggest that the active phase achieved after the S1 activation was similar to the one obtained after the in situ mode of activation by the DBT molecule during the HDS test (see Table 3). In contrast, selectivity after H_2S activation at low temperatures is closer to those obtained using the standard procedure of activation, suggesting a better sulfided phase.

Similar activity and selectivity results were systematically obtained with organosulfide agents or H_2S using the standard procedure of activation with $NiMo/Al_2O_3$ (Table 3). A leveling effect due to the hydrogen sulfide produced in all cases by the decomposition of the organosulfide agents at temperatures higher than 550 K could be envisaged. The S2 activation at high temperatures confirmed the assumption of a leveling effect with similar activity and selectivity results when the catalysts were activated at high temperatures by H_2S or DMDS. Activity results using the modified S2 activation procedure at high temperatures only ($543\ K < T° < 623\ K$) are quite close to those observed using the standard procedure of activation ($423\ K < T° < 623\ K$). Therefore, the initial stages of sulfidation at low temperatures and particularly the formation of thiolate species at the catalyst surface is not of prime importance to reach better HDS active catalysts in the present experimental conditions. However, these results should be considered cautiously. Particularly, it should be underlined that selectivity results should not be interpreted too extensively. Indeed, results by Chianelli et al. [54] have shown that the active phase in steady-state conditions for the HDS of DBT can incorporate surface carbide-like entities. The present results only suggest a direct relationship between the way of activating hydrotreating catalysts and the final state of the HDS phase but does not help to know the real nature of the HDS active phase.

As reported in Table 4, the gain in activity after the DMDS activation is more significant for the nonpromoted MoS_2/Al_2O_3 than for its promoted counterparts. Since promotion increases the sulfidability of the MoS_2 phase [55,56], it seems that the reported gain in HDS activity due to the use of organosulfides is more easily detectable on catalytic systems, which are more difficult to activate. This fact combined with the use of much lower liquid hour space velocities in industrial conditions (LHSV $= 1.0$–$2.0\ h^{-1}$) than in the present study (LHSV $= 68\ h^{-1}$) might suggest a possible “size” effect to explain our results compared to practical conditions used in industry.

Finally, some authors have proposed that the use of organosulfide agents reduces the whole exothermicity effect of the oxide–sulfide transformation by diluting it inside an organic matrix playing the role of a “thermal well” [21,22,36]. Once again, the low amount of catalysts used in our experimental conditions does not allow us to study the possible thermal or thermodynamic effects likely to be encountered in industrial practice. Anyhow, from the present experiments, it can be concluded that the higher activities obtained in practice after sulfidation by spiking agents [2] are not due to pure chemical phenomena.

4.4. Interaction of different solvents during the activation process

The effect of the nature of the solvent used during the activation procedure clearly demonstrates that the solvent used has consequences on the final HDS catalytic properties. Our study supports preceding results obtained by Jacquin et al. [8] on the minor effect of alkanes used during the activation procedure. Among the different alkane solvents used (cf. Table 7), slight differences were observed and might only result from variations of liquid evaporation of the different alkanes used as observed by Ishihara et al. [57].

Sulfidation in the presence of cyclohexene resulted in less active catalysts than with heptane. Elemental analysis (Table 8) shows a higher amount of C particularly with DMDS, suggesting that a coking process occurred. However, H_2S or DMDS activation led to similar activities.

The most interesting case is 1-methylnaphthalene. Elemental analysis results (cf. Table 8) revealed high amounts of C after activation of $NiMo/Al_2O_3$ by DMDS in the presence of this aromatic compound. Comparison to H_2S activation in the same conditions of activation even suggests a “promoting” effect of DMDS on the final carbon content since its amount is 3–5 times more important if activation occurs in the presence of DMDS instead of H_2S. The carbon amount was also higher if sulfidation was carried out using DMDS with 1-methylnaphthalene as solvent instead of cyclohexene. This result might be related to a previous study by Lebreton et al. [58] who observed that DMDS promotes the formation of “coke” under specific conditions. Indeed, they suggested that DMDS could form $CH_3S^\bullet$ radicals, initiating polycondensation reactions with anthracene. A similar effect could be envisaged with 1-methylnaphthalene. However, the experimental conditions were quite different from ours (9.0 MPa, 713 K) and any conclusion on this subject should be used cautiously. Compared to the activation by DMDS in the presence of an alkane solvent, activation by DMDS with 1-methylnaphthalene clearly favors the DDS pathway as shown in Table 7, or, more precisely, depleted more strongly the HYD pathway (cf. Fig. 7). This suggests very different behavior of the C–S bond cleavage versus hydrogenation functionalities and then the existence of two different types of active sites. This result could be explained by considering the different modes of adsorption of DBT, prerequisites for hydrogenation, or C–S bond cleavages, as developed in the Rim–Edge model [59]. According to this model, hydrogenation steps need an initial parallel η^6 mode of adsorption through the aromatic ring while the C–S bond hydrogenolysis would result from a perpendicular mode of adsorption through the sulfur atom of the DBT molecule. A similar η^6 mode of adsorption would occur for the adsorption of non-heteroatom-containing aromatics like naphthalene-type compounds. Therefore, an initial interaction of the aromatic solvent during the activation process on hydrogenation sites could be considered. The gradual gain in DDS activity during the HDS test (cf. Fig. 8) whereas the HYD activity remains constant supports the assumption of an irreversible poisoning of the HYD sites probably by coke during the activation by DMDS in the presence of 1-methylnaphthalene. Moreover, as reported in Tables 7 and 8, an increase in carbon content is generally accompanied by an increase in the DDS selectivity. Therefore, activation by DMDS in the presence of 1-methylnaphthalene corresponds to a selective coking effect, limiting the hydrogenating properties of the final catalyst.

5. Conclusion

Activation by some organosulfide agents has been compared to H_2S sulfidation on Ni(Co)-promoted and nonpromoted MoS_2/Al_2O_3 catalysts using similar experimental procedures. In our conditions (no dimethyldisulfide was added to the HDS reactant feed to generate a high H_2S partial pressure), $NiMo/Al_2O_3$ was twice as active as $CoMo/Al_2O_3$ for the HDS of DBT. However, NiMo catalysts are more sensitive to H_2S poisoning, and at higher H_2S partial pressures (0.05 MPa) in the HDS reactant feed, $NiMo/Al_2O_3$ and $CoMo/Al_2O_3$ catalysts present similar HDS activities. Using organosulfides (mainly dimethyldisulfide, DMDS) diluted in an alkane solvent for the activation of NiMo/Al_2O_3 leads to a limited gain in HDS activity compared to H_2S sulfidation at the laboratory scale either for the HDS of DBT or for the HDS of 4,6-DMDBT. Varying the procedures of activation clearly demonstrates that a better balance between reduction and sulfidation as the main explanation for the well-known beneficial effect of organosulfides as activating agents in industrial practice should be rejected. A chemical origin for this effect does not seem to be the main cause of the better efficiency of carbon-containing sulfiding compounds. A possible "size" kinetic effect is then proposed to explain our results: at high LHSV values, H_2S produced at high temperatures (> 550 K) during the decomposition of the organosulfides leveled off activity differences among the different sulfiding agents studied. Further studies will clarify this assumption. A "thermal well" effect of the organosulfides diluting the effect of the exothermicity of the oxide–sulfide transformation could also be envisaged. Finally, DMDS can interact strongly with 1-methylnaphthalene when present in high concentration during the activation process, poisoning selectively the sites involved in the hydrogenation (HYD) pathway.

Acknowledgments

This work was carried out with financial support from IFP. S. Texier thanks "Association Nationale de la Recherche Technique" for a grant.

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