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New aspects of catalytic functions on sulfide catalysts

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Abstract

The influence of Co on the acidic properties (Lewis and Brønsted) of molybdenum sulfide catalyst were determined by infrared studies of adsorbed pyridine or 2,6-dimethylpyridine. These studies show that the promoter addition increases the strength of the Lewis sites and the number of Brønsted sites. These results are correlated to those obtained for dibenzothiophene conversion. For this reaction, it was observed that the influence of the promoter is very different for the two different routes involved in the reaction scheme. Consequently, the role of the promoter is not only to increase the number of sulfur vacancies but also to modify the acid–base properties of the catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Sulfide catalysts; Lewis and Brønsted sites; Infrared studies

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1. Introduction

Nowadays, the necessity to develop better sulfide catalysts in order to achieve very low concentration of sulfur compounds in gasoil cuts has pushed up research on hydrotreating catalysis [1]. In this respect, the utilization of new and very powerful physico-chemical techniques has led to important progresses in the characterization of these catalysts. For instance, using STM, Helveg et al. [2] have provided new important information concerning the atomic-scale realm of molybdenum disulfide nanoclusters, which are of interest as a model system in hydrodesulfurization catalysis. The first direct images have been presented of the catalytically active sites in the form of S vacancies at the edges of MoS_2 created by in situ treatment of the nanoclusters. However, industrial catalysts are composed of molybdenum sulfide promoted by Co or Ni and various theories based on structural models have been proposed to explain this promoting effect. These theories agree on the fact that the presence of a promoter enhances the liability of sulfur anions, thus leading to more numerous active sites in the reductive atmosphere of the hydrotreatment processes [3–6].

Meanwhile we have been interested to get a better knowledge on the mechanism of hydrotreating reactions, hydrodenitrogenation or hydrodesulfurization. We have shown that for both types of reactions, the reaction schemes are very complicated and involve successive steps of hydrogenation and elimination or nucleophilic substitution [7–9]. For the conversion of a series of pentylamine [9] with different structures, it has been shown that the acid–base properties of the catalyst and the nature of the molecule to be converted are the main parameters involved in the

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reaction mechanism. Therefore, we have decided to examine the acid–base properties of the cobalt molybdenum catalyst and to compare these properties to those of a non-promoted molybdenum sulfide. This was achieved by in situ FTIR study of probe molecule adsorption, pyridine and 2,6-dimethylpyridine (lutidine). Pyridine was used to detect the Lewis acidity, while lutidine was preferred for dosing Brønsted acidity. However, the exact nature of the surface in the real hydrotreating processes (high pressure of hydrogen, hydrogen sulfide and hydrocarbons, temperature range 573–673 K) cannot be determined because solid composition varies with reaction conditions [10]. Thus, the evolution of the acid properties was studied for various reduced states of the catalyst obtained by means of hydrogen pretreatment at various temperatures. The aim of this work was to examine the effect of Co on the acidity and catalytic properties for dibenzothiophene conversion of MoS_2-based catalysts.

2. Experimental

2.1. Infrared spectroscopy

For these studies, a silica carrier (Grace Davison 432) was chosen in order to avoid any contribution of the support to the acidity of the system. The catalysts were prepared by the pore filling method using cobalt nitrate and molybdenum heptamolybdate as precursor salts. The impregnated solids were sulfided at 673 K with a 15%H_2S–85%H_2 mixture. The Mo loading was 6 wt.% and the amount of Co added to the Mo phase was adjusted in order to have $Co/(Co + Mo)$ ratio equal to 0.3.

The catalysts were resulfided in situ at 673 K in the IR cell. Then 200 Torr of hydrogen was introduced in the cell, which was heated up to the desired temperature. Several reduction–evacuation cycles were done in order to remove the H_2S formed upon reduction. The so-treated catalysts were contacted with 2 Torr of pyridine or 2,6-dimethylpyridine (DMP) at room temperature, and then evacuated at room temperature or at 423 K. The IR spectra were recorded using a Nicolet 60SX FTIR spectrometer. Spectra and band area values presented in this work correspond to those obtained for a disk of $5\,mg\,cm^{-2}$.

2.2. Catalytic activities measurements

The reactions were carried out in a flow reactor at 613 K under a 4 MPa total pressure [7,8]. Decalin was used as a solvent, to which dimethyldisulfide was added to generate H_2S (0.05 MPa). The various steps involved in the hydrodesulfurization of dibenzothiophene (DBT) are schematized in Scheme 1. Two parallel reactions occur: (i) direct desulfurization (DDS) leading to biphenyl, and (ii) desulfurization with hydrogenation (HYD) giving cyclohexylbenzene [11–13]. In agreement with several studies, it is assumed that the two pathways have dihydroDBT as intermediates [14,15]. It was verified that, under our experimental conditions, biphenyl did not transform into cyclohexene and consequently the total activity is the sum of the activity for the DDS and for the HYD reactions. The activity measurements were made in the 10–20% dibenzothiophene conversion range [7].

The Mo catalyst (9.3 wt.%) was prepared [7] by incipient wetness impregnation of γ-alumina with an aqueous solution of ammonium heptamolybdate. The catalyst was dried at 693 K and calcined under air flow at 773 K. The CoMo/alumina catalysts were prepared [7] by impregnating the Mo catalyst with aqueous solutions of cobalt nitrate. The amount of promoter corresponds to a molar ratio $Co/(Co + Mo)$ equal to 0.3. The catalysts were sulfided in situ at 623 K by a mixture of 5 vol.% dimethyldisulfide in *n*-heptane (equivalent H_2S partial pressure: 0.125 MPa).

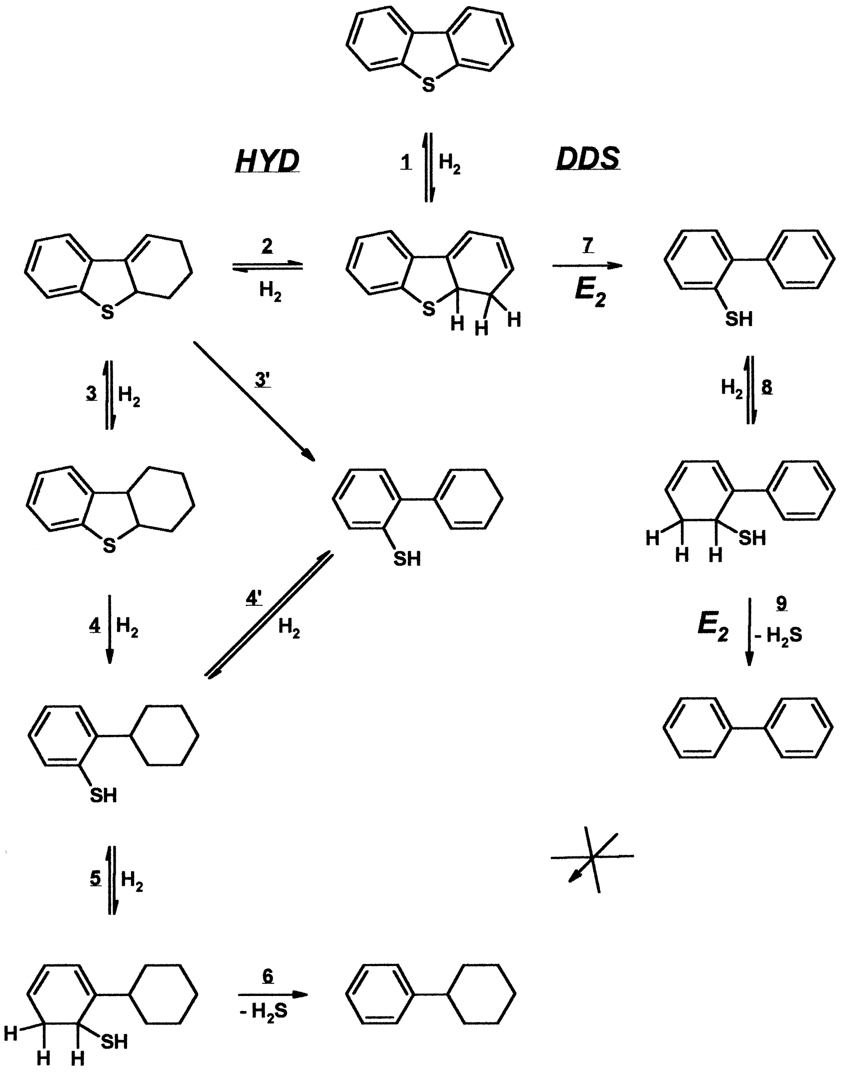
For this reaction, the activities of the molybdenum catalysts, promoted or non-promoted, supported by alumina or silica are almost similar.

3. Results

3.1. Pyridine adsorption

The interaction of pyridine (Py) with either the support or the sulfided catalysts gives rise to the appearance of several bands at ~1600, 1485, and at ~1444 cm^{-1} characterizing the presence of weak Lewis acidic sites. However, all these bands vanish upon evacuation at 423 K on the silica support.

After Py evacuation at RT (Fig. 1A), the unpromoted Mo catalyst exhibits mainly an intense band



Scheme 1.

located at 1596 cm^{-1}. The intensity of this band drastically decreases upon evacuation at 423 K (Fig. 1B) and a very weak signal is detected at 1600 cm^{-1} indicating the presence of a small number of weak Lewis acidic sites on the Mo phase. On the Co-promoted catalyst, two bands are observed at 1609 and 1598 cm^{-1} after evacuation at RT, which are still present upon desorption at 423 K. This suggests that the addition of Co to Mo increases the Lewis sites strength. However, it is known that on such a silica support, Co and Mo sulfides may coexist with the CoMoS phase. Consequently, the resulting acidity modification could indicate the presence of a cobalt sulfide phase. On Co/SiO_2, pyridine adsorption gives rise to a band at 1601 cm^{-1} (RT evacuation), whose maximum shifts upwards to 1606 cm^{-1} upon evacuation at 423 K. Thus, the band observed at 1609 cm^{-1} on the CoMo catalyst can be ascribed to a CoMoS phase which possesses a stronger acidic character than the Mo or Co supported sulfides.

If pyridine adsorption shows the modifications of Lewis acidity upon promotion of the sulfided phase,

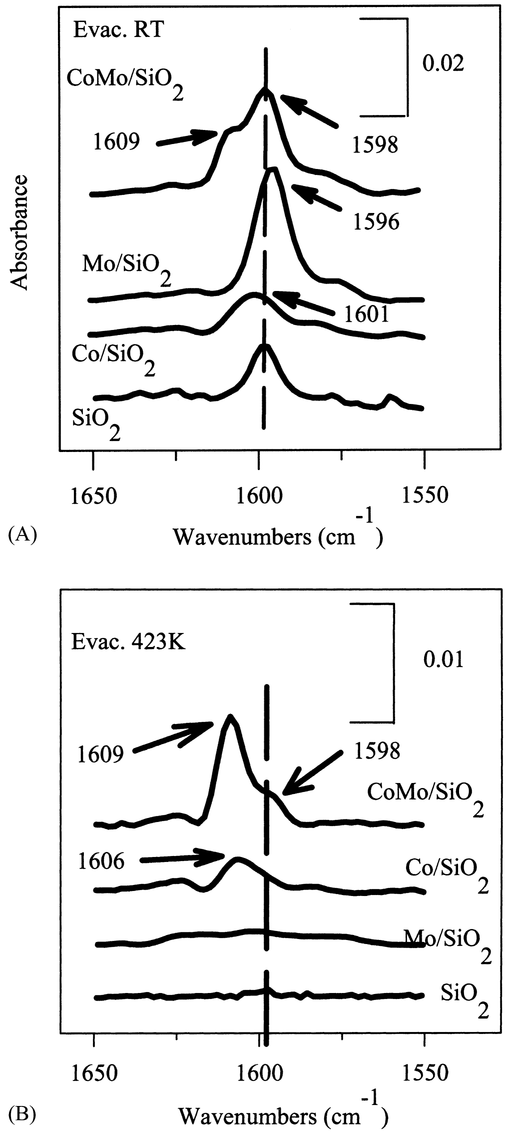


Fig. 1. (A) IR spectra of species resulting from pyridine evacuation at RT on the various silica-supported sulfide (non-reduced Co/SiO$_2$, Mo and CoMo/SiO$_2$ reduced at 573 K). (B) IR spectra of species resulting from pyridine evacuation at 423 K on the various silica-supported sulfide (non-reduced Co/SiO$_2$, Mo and CoMo/SiO$_2$ reduced at 573 K).

its sensitivity is not high enough to accurately characterize Brønsted acidity. Indeed, lutidine adsorption experiments were undertaken because this probe is more sensitive to weak Brønsted acidity [16].

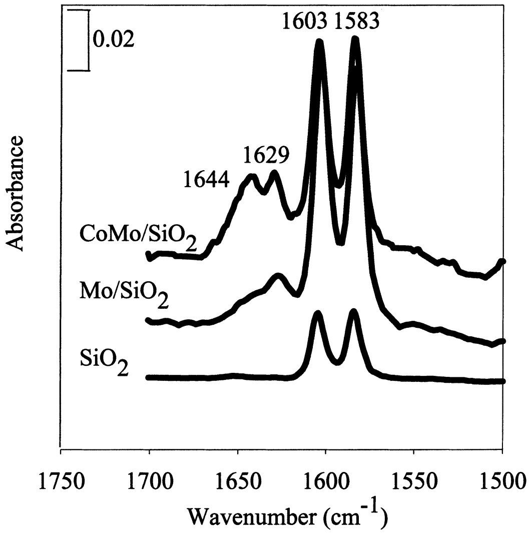


Fig. 2. IR spectra of adsorbed 2,6-dimethylpyridine (lutidine) after evacuation at RT. Solids reduced at 423 K.

3.2. Lutidine (2,6-dimethylpyridine) adsorption

Fig. 2 gives an example of the spectra recorded after lutidine adsorption and evacuation at RT for the Mo, CoMo and silica support sulfided and reduced at 573 K. In the 1550–1750 cm^{-1} range, lutidine adsorption gives rise to four main bands. The two intense signals located at 1583 and 1603 cm^{-1} observed also on the support correspond both to lutidine adsorbed on Lewis acid sites and to hydrogen bonded species. The positions of the two other bands at 1629 and 1644 cm^{-1} agree fairly well with those reported in the literature for protonated species and they are ascribed to ν8b and ν8a vibration modes of the lutidinium species, respectively [17–19]. Interestingly, these bands are not present on the silica support treated in the same conditions.

3.3. Evolution of the acidic properties as a function of the reducing state

The modification of the relative number of Lewis sites induced by a reductive treatment has been determined by integrating the PyL band at 1444 cm^{-1} for the unpromoted and Co-promoted catalysts. As reported in Fig. 3, the number of Lewis acidic sites is

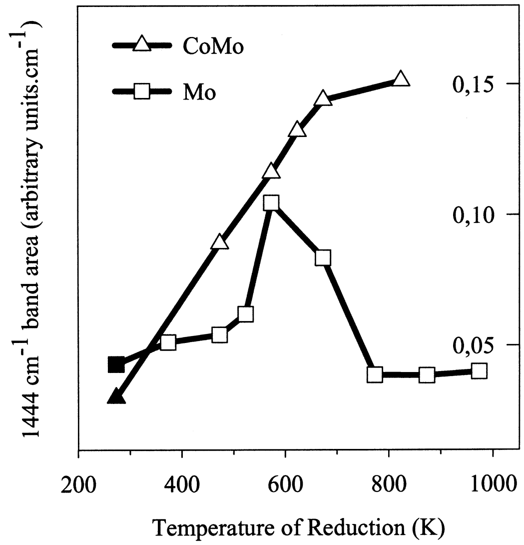


Fig. 3. Evolution of the relative number of Lewis sites ν19b band area after pyridine evacuation at 423 K as a function of the reduction temperature.

nearly similar on the two non-reduced solids (black symbols). However, reductive treatments lead to a strong modification of the number of acid sites with different evolution. Indeed, the amount of Lewis acidic sites continuously increases upon sulfur removal for the CoMo system, while a maximum was found around 600 K for the non-promoted catalyst.

After lutidine adsorption and evacuation at RT, Brønsted acidity is already detected on the non-reduced Mo catalyst (Fig. 4A). The relative concentration of these sites increases with reduction temperature and reaches a maximum for $T_r = 500\,K$ and then diminishes progressively for higher temperatures of reduction. Evacuation at 423 K leads to a significant decrease of the adsorbed lutidine amount, particularly for the non-reduced solid. This indicates that the initial Brønsted acidity observed before solid reduction is strikingly weak. Moreover, the effect of the evacuation temperature is less dramatic for the reduced Mo states.

For the Co-promoted system, similar observations can be drawn from Fig. 4B. However it should be underlined that the presence of the promoter strongly increases Brønsted site density. Indeed, the lutidinium

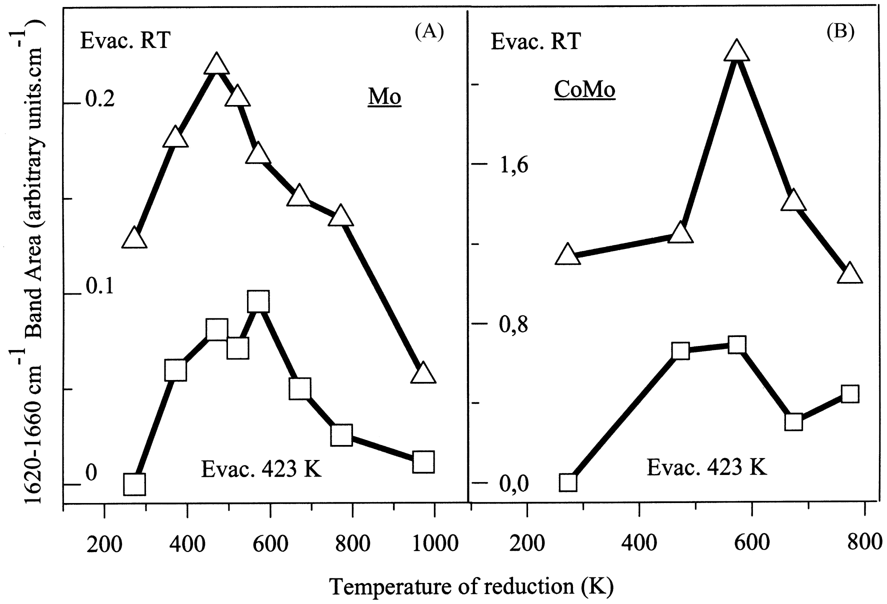


Fig. 4. Evolution of the relative number of Brønsted acid sites (1620–1600 cm^{-1} band area) after lutidine evacuation at RT (△) or at 423 K (☐) as a function of the reduction temperature: (A) Mo/SiO_2; (B) CoMo/SiO_2.

Table 1
Activities and selectivities of the Mo, and CoMo on alumina catalysts for the transformation of DBT[a]

Catalyst	Mo	CoMo
A_T	0.4	7.2
A_{DDS}	0.1	6.3
A_{HYD}	0.3	0.9
S_{DDS}	25	87
S_{HYD}	75	13
THDBT/CHB	4.3	0.5

[a] A_T: total activity; A_{DDS}: activity for the DDS pathway; A_{HYD}: activity for the HYD pathway. Activities in mol h^{-1} kg^{-1}. S_{DDS} and S_{HYD}: selectivities for the DDS and HYD pathways, respectively. THDBT/CHB: tetrahydroDBT/cyclohexylbenzene at a 10% HYD conversion.

band area intensity is 10 times higher than on the Mo system, whatever be the temperature of reduction.

3.4. Transformation of DBT

Table 1 shows that the overall activity of the promoted catalysts for DBT transformation is 20 times higher than the activity of the non-promoted catalyst, which is in accordance with the literature [7]. This promoting effect is essentially due to the enhancement of the DDS route (promoting effect greater than 60), while a factor of only 3–4 is observed for the HYD pathway. Table 1 also shows that at the same HYD conversion, the molar ratio tetrahydroDBT/cyclohexylbenzene is much lower on the promoted catalyst than on the unpromoted one.

These results indicate that the promoter (i) increases the rate of the DDS reaction, and (ii) increases the rate of transformation of the tetrahydrogenated species into cyclohexylbenzene. Then, it can be concluded that the promoter increases the rate of the C–S bond cleavage reactions.

4. Discussion

From a structural point of view, it is well admitted that the promoter atom is located at the edges of the hexagonal MoS_2 platelets [20]. In such a location, the Co ion is surrounded by five sulfur anions, four of which belong to the trigonal prismatic Mo environment [21]. Since the creation of sulfur vacancies is believed to be the first step for many hydrotreating reactions, it has often been proposed that the main influence of the promoter is to decrease the metal–sulfur bond strength. Experimentally, the liability of the sulfur can be evaluated by temperature programmed reduction (TPR) experiments and the number and strength of the Lewis sites created by these reducing treatments can be measured by infrared spectroscopy.

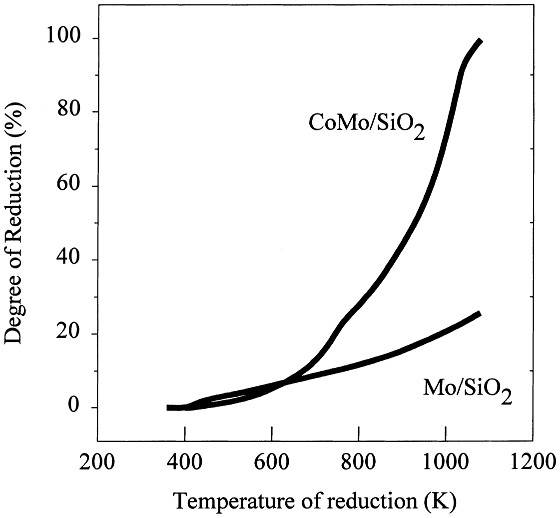


Fig. 5. Variation of the degree of reduction versus the reduction temperature for Mo and $CoMo/SiO_2$ catalysts.

Fig. 5 shows that the degrees of reduction of both the CoMo and Mo systems up to 650 K, which corresponds to the domain of temperatures commonly used in hydrotreating catalysis, are almost similar. However, above this temperature, a marked increase of the reducibility is observed for the CoMo catalyst. As reported in Fig. 3, below a temperature of reduction of 600 K, there is no detectable difference between the number of Lewis sites observed for the Mo and CoMo catalyst. Above this temperature, the variation of the number of Lewis sites is totally different for both catalysts. For the Mo catalyst, a maximum is observed, whereas there is a continuous increase of the number of Lewis sites for the CoMo catalyst. It has been reported previously [16] that these treatments lead to an increase of the size for the Mo catalyst (2.4 nm for the initial catalyst and 3.9 nm after a reduction treatment at 673 K). The decrease of the number of coordinatively unsaturated sites (Lewis sites) created at the edges of the molybdenum crystallites is therefore ascribed to the sintering of the MoS_2 slabs. Oppositely, on the Co-promoted catalyst, no sintering is observed, explaining probably why no decrease of the Lewis acidity is noted. The TPR data presented above as well as the infrared spectroscopy results support the hypothesis of an increase of the number of sulfur vacancies brought about by the promoter even if this effect is rather weak in the temperature range of the catalytic experiments (523–623 K). Moreover, IR data points out that Lewis acid sites are stronger on promoted phase than on the unpromoted one.

The promoter influence is also significant for the Brønsted acidity created by reduction under hydrogen. Indeed, the promoted system presents an 8-fold increase of the lutidinium signal intensity independent of the severity of the hydrogen pretreatment, whereas the strength of these sites appears unchanged. As this type of site probably arises from the interaction of hydrogen with surface sulfur anions leading to SH groups, two hypotheses might be proposed to explain the very large number of acidic SH groups of the CoMo catalyst by comparison to the unpromoted Mo system. Firstly, it can be assumed that the amount of hydrogen dissociated heterolytically on the catalyst is higher for the CoMo. However, in that case, a large increase of the amount of hydrogen adsorbed on the promoted catalyst would be observed which has never been reported. Indeed, in a recent study on the NiMo system [22], we found no difference in the amount of hydrogen adsorbed on the promoted catalyst and on MoS_2. Similarly, Topsøe and co-workers [23] even reported a decrease of the amount of hydrogen adsorbed with Co promotion. Secondly, it can be also proposed that the SH groups do not present the same acidic character depending on the location of the sulfur atoms at the surface of the sulfide as it is recognized for oxide catalysts. Therefore, not all the SH groups present at the surface of the Mo catalyst would be considered as Brønsted sites. These assumptions agree with a recent work devoted to the understanding of the HDN properties of model transition metal sulfides [9,24], in which it was shown that the SH of RuS_2 may act as a nucleophilic moiety, while on NbS_3 they behave like acidic centre. The MoS_2 comportment was found to be intermediate. In this respect, the presence of Co induces some modification on the properties of sulfur anions by comparison to molybdenum sulfide, for instance by increasing their electron density, which would explain our experimental observation of an enhancement in the number of acidic SH groups.

Thus, it can be concluded from the above results that the promoter is double-acting. It increases the number and strength of the Lewis acid sites and enhances the Brønsted sites density. The presence of the promoter has also a complex influence on the catalytic properties of the molybdenum sulfide catalysts since it does not modify similarly the two pathways of the DBT conversion. It is shown above that its main effect is to enhance the rate of the DDS pathway. As represented in Scheme 1, the first step of this DDS pathway is the hydrogenation of the double bond in the vicinity of the sulfur atom to obtain a dihydrogenated product and then the second step is the opening of the C–S bond by an elimination process. Such a mechanism involves the attack of a hydrogen atom (in β position relative to the sulfur atom in the organic molecule) by a sulfur anion acting as basic sites. Then it appears that the acid–base properties of the catalyst play an important role in this elimination step as the one observed for the HDN elimination route mechanism, where we noticed an increase in the C–N bond cleavage reaction when Brønsted sites are present [9]. Two hypotheses can be proposed to explain the enhancement of the elimination step: (i) strengthening of the interaction of the organic substrate with the electron-withdrawing Lewis and Brønsted sites, and (ii) enhancement of the basicity of particular S^{2-} centers.

5. Conclusion

These data clearly evidence that the influence of the promoter is not only to increase the number of active sites, sulfur vacancies, since it does not influence similarly both pathways of the DBT conversion. Co drastically promotes the DDS pathway of DBT as well as the C–S bond cleavage of the hydrogenated intermediates. From IR spectroscopy results, it appears that the promoter also enhances the density of the Brønsted sites generated by hydrogen treatment and the Lewis acid strength. On the one hand, the interaction of the organic substrate with these electron-withdrawing sites is presumably strengthened. Thus, C–S bond cleavage would be favored. On the other hand, one can suppose that an increase in the basicity of certain sulfur atoms in the vicinity of the promoter could help H abstraction in the β position with respect to the sulfur, hence the elimination process.

This work clearly shows that important progress in the understanding of the real role of the promoter in the catalytic reaction might be obtained by in situ spectroscopic techniques. More studies are needed in this field.

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