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# In Situ EXAFS Study of the Sulfidation of a Hydrotreating Catalyst Doped with a Non Chelating Organic Additive

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**Résumé — Étude par absorption X *in situ* de la sulfuration d'un catalyseur d'hydrotraitement dopé par un composé organique non chélatant** — Un catalyseur industriel de type CoMoP supporté sur alumine a été imprégné à sec par une solution aqueuse de diéthylenglycolbutyléther (DEGbe) puis séché à 393 K pendant 12 h. Après activation sous H<sub>2</sub>/H<sub>2</sub>S, ce catalyseur se révèle plus actif que la référence non modifiée. Afin de comprendre l'effet de cet additif organique sur la cinétique de sulfuration, des analyses *in situ* par EXAFS au seuils K du cobalt et du molybdène ont été réalisées. Ces caractérisations ont été effectuées sur le catalyseur CoMoP + DEGbe séché à 393 K, sulfuré à température ambiante, puis à 373 et 473 K. La sulfuration du cobalt et surtout celle du molybdène sont inhibées par la présence du composé organique jusqu'à environ 473 K. Les résultats EXAFS obtenus dans le cadre de cette étude ont permis de mieux appréhender le rôle des composés organiques ajoutés aux catalyseurs d'hydrotraitement. Ces composés ralentissent la sulfuration du Mo et du Co présents sur le catalyseur.

**Abstract — In Situ EXAFS Study of the Sulfidation of an Hydrotreating Catalyst Doped with a Non Chelating Organic Additive** — An industrial alumina-supported CoMoP catalyst was impregnated (incipient wetness method) with an aqueous solution of diethyleneglycolbutylether (DEGbe) and then dried at 393 K overnight. After sulfidation under H<sub>2</sub>/H<sub>2</sub>S, this catalyst has a higher activity than the non impregnated CoMoP. In order to check if the presence of such an organic additive in contact with the oxidic form of the active phase influences the kinetics of sulfidation of the cobalt and the molybdenum, EXAFS spectroscopy (K-Co or K-Mo edges) experiments were performed *in situ* during the sulfidation of CoMoP + DEGbe catalyst and of the non DEGbe treated one. The results showed that the sulfidation of Co and Mo is inhibited by DEGbe up to 473 K. EXAFS helped to understand the role of the organic compounds added to the oxidic catalysts and to establish the role of the organic compound in the sulfidation of Co and Mo elements.

## INTRODUCTION

In the recent past, numerous papers have been dealing with the improvement of the catalytic activity of hydrodesulfurization (HDS) catalysts in order to allow refiners to respect the new stringent regulations concerning the maximum sulfur contents in gasoline and diesel fuel imposed by federal laws in United-States, Japan or by the EEC [1].

Several patents have been recently published claiming the unusual effect of organic additives on the activity of hydro-treating catalysts [2-4]. Some of the organic compounds are almost infinitely water soluble and can be added during the incipient wetness impregnation of the active metals [2] or impregnated directly on the oxidic form of the catalyst in a second step [3]. In the Sumitomo patents [2, 3], the organic additive is still present on the surface of the catalyst when the sulfidation starts. The organic additive is selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms and the (poly)ethers of these compounds, for example triethyleneglycol or diethyleneglycolbutylether. Some studies in the academic literature explain the positive role played by the organic compound on the hydrodesulfurization activity of hydrotreating catalysts. Van Veen *et al.* [5] were the first to use nitrilotriacetic acid (NTA) or ethylenediaminetetraacetic acid (EDTA) to prepare different catalysts at iso dispersion on different model carriers. They obtained a CoMo + NTA supported on alumina twice as active in thiophene HDS than the same non treated CoMo catalyst [6]. A higher percentage of type II CoMoS phase was proposed to explain this promoting effect. For the CoW system, the organic agent seems to favour the synergistic effect of cobalt with the WS<sub>2</sub> phase, effect that was never observed with the cobalt-tungsten sulfide system. The proposed explanation for the improved activity of the doped catalysts was a delayed sulfidation of the promoter, favouring the sulfidation of molybdenum or tungsten [7, 8]. The promoting effect of the chelating agent is also effective in the conversion of refractory sulphur compounds such as 4,6 dimethyldibenzothiophene [9]. More recently, Hensen *et al.* [10, 11] studied NTA addition to Mo-based catalysts and showed an increasing activity in thiophene HDS when using NTA. In this particular case of an unpromoted catalyst, the positive effect was attributed to a higher stacking of MoS<sub>2</sub> slabs and a lower interaction between the active phase and the carrier. In these studies, NTA-treated catalysts are sulfided without pre calcination of the oxidic form containing the organic agent and are compared to the corresponding calcined oxidic form. This point is of particular importance, since several patents recently pointed out the beneficial effect of omitting the calcination step of the oxidic form of NiMo or CoMo type catalyst doped with phosphorus on the catalytic activity [12].

Shimizu *et al.* studied the effect of NTA, EDTA or CyDTA (1,2 cyclohexanediamine N, N, N', N' tetraacetic

acid) on NiMo, CoMo and NiW type catalysts [13-15]. They observed, as did van Veen *et al.*, a beneficial effect of the organic molecule on the CoMo and NiW catalysts, and, to a lesser extent, on the NiMo. No promotional activity was observed with Mo/Al<sub>2</sub>O<sub>3</sub>, Co/Al<sub>2</sub>O<sub>3</sub>, Ni/Al<sub>2</sub>O<sub>3</sub> or W/Al<sub>2</sub>O<sub>3</sub>. They also proposed the hypothesis of a delayed sulfidation of the promoter due to the formation of a complex between the promoter and the organic molecule and a better dispersion of the promoter on the surface. By EXAFS measurements, they observed an increased coordination number of Mo-Mo and Mo-S in the modified catalyst. Prins *et al.* also studied the effect of chelating agents on NiMo supported on silica [16-20] and alumina [21]. On silica, it appears that the formation of a complex between Ni and the chelating agent limits the carrier-promoter interaction and favors the Ni dispersion. No significant effect on Mo is observed unless high concentrations of chelating agent are used. Moreover, delayed sulfiding kinetic of the Ni is observed with chelating molecules other than ethylenediamine. With this molecule, an increase in activity is observed without any effect on the nickel sulfidation. This strongly supports the idea of a decreasing interaction between the carrier and the active phase precursor when organic chelating additives are used. Blanchard *et al.* [22] also thoroughly studied the influence of ethylenediamine (En) on Mo and CoMo supported on alumina. Only the Co promoted catalyst is more active when using En, whereas Mo/alumina is unchanged even at high Mo loading. Ethylenediamine seems to inhibit the formation of cobalt molybdate and Co<sub>3</sub>O<sub>4</sub> and to increase the cobalt dispersion. It appears that the effect of chelating agents is still not completely understood.

The effect of non chelating agents has been studied in a much lesser extent. Recently, Sun *et al.* [23] published results on the effect of glycol based organic compounds (molecules chosen according to references [2, 3]) on the activity of CoMoP type catalysts. When using triethyleneglycol they did not observe, by <sup>31</sup>P NMR and Raman spectroscopy, any chelating effect of this compound with Co<sup>2+</sup> species in solution, and have checked that molybdenum species are present as the P<sub>2</sub>Mo<sub>5</sub>O<sub>23</sub><sup>6-</sup> phosphomolybdate anion. They supposed that glycols may bind to the coordinatively unsaturated Al<sup>3+</sup> located on the surface of  $\gamma$ -alumina. According to these authors [23] these acidic sites play a fundamental role in the anchoring of the metal precursors on the surface. When using glycols, these sites could be blocked and only a weak metal-support interaction could prevail, leading to the highly active type II Co-Mo-S phase. Nicosia and Prins [24, 25] studied catalysts prepared from MoO<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub> and CoCO<sub>3</sub> as reported in ref. [2]. EXAFS experiments showed that in presence of glycols, the sulfidation mechanism is modified and a faster sulfidation is observed but HDS activity is not increased. Nevertheless, this sulfidation step for such catalysts needs to be better

understood since it is a key stage in obtaining high catalytic activities. This is the major aim of this study, which is focused on the effect on the kinetics of sulfidation of an industrial CoMoP catalyst impregnated with a model glycol compound (diethyleneglycol n-butylether or DEGbe).

## 1 EXPERIMENTAL

### 1.1 Catalyst Preparation

An industrial CoMoP catalyst (12 wt% Mo, 3 wt% Co, 2 wt% P, specific surface area—BET method—of 149 m<sup>2</sup>/g) supported on alumina was impregnated with an aqueous solution of DEGbe with a molar ratio Mo/DEGbe = 0,75. After the incipient wetness impregnation, the CoMoP + DEGbe is matured at 293 K overnight then dried at 393 K for 10 h under air.

### 1.2 Catalytic Activity Measurements

#### 1.2.1 Tetralin Hydrogenation in the Presence of H<sub>2</sub>S

Catalytic activity has been checked for DEGbe modified catalysts and compared with the reference industrial CoMoP by using a model molecule test (tetralin hydrogenation in the gas phase under pressure and in the presence of H<sub>2</sub>S).

The hydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) was performed in a fixed-bed gas-flow microreactor at 573 K, at a constant H<sub>2</sub> pressure of 4.6 MPa (45 atm). The total flow rate was 56 mL/min. The partial pressure of tetralin (Fluka, purity >99%) was kept constant at 6.1 kPa by using a gas-phase saturator system (corresponding flow of tetralin, 5.48 10<sup>-8</sup> mol/s). The products of tetralin hydrogenation were analyzed every 30 min by gas chromatography. Cis and trans decalins were always obtained, together with small amounts of naphthalene, while no detectable amounts of isomerization or cracking products were observed. The amount of catalyst (about 500 mg) was chosen in order to obtain a conversion below 15%, ensuring the validity of a differential model for the determination of the specific rates. The deactivation of the catalyst appeared always to be negligible and within the experimental errors. The catalyst is almost fully sulfided before the test by a conventional treatment under a H<sub>2</sub>/H<sub>2</sub>S mixture (15% vol H<sub>2</sub>S) at 400°C (5°C/min) for 2 h at atmospheric pressure.

#### 1.2.2 4,6 Dimethyldibenzothiophene (DBT) Conversion

The reactor used to evaluate the conversion of 4,6-DMBT was a 200 cm<sup>3</sup> stirred slurry tank reactor (STR) operated in the batch mode. The autoclave was equipped with a four blade mechanically driven turbine (900 rpm). A baffle was also placed into the reactor to achieve a perfectly stirred system.

The samples were collected through a 1/16 in. diameter tube and the liquid remaining in the tube was forced back into the reactor by H<sub>2</sub>, so that the dead volume was minimized. Hydrogen was introduced into the reactor through a pressure controller which keeps the pressure constant during the course of the experiment.

In every case the reactants (1.2 mmole of 4,6-DMDBT, 0 to 8.3 mmole of aromatic or nitrogen compound) was dissolved in n-dodecane (80 ml) and then introduced in the reactor. 50 mg of freshly presulfided catalyst was then placed into the reactor and the system was closed. To avoid any air contamination N<sub>2</sub> was bubbled through the solution for 10 minutes. Still under N<sub>2</sub> atmosphere, the reactor was heated up to the reaction temperature of 573 K and stirring was switch on. N<sub>2</sub> was then replaced by H<sub>2</sub> by pressurizing the reactor to 5 MPa. This last step was taken as the starting time of the reaction. Sampling was periodically performed during the reaction. The samples were analyzed using hexadecane (SIGMA Aldrich) as an internal standard. HDS and hydrogenation products of 4,6-DMDBT and aromatics were analyzed qualitatively by GC-MS and quantitatively by GC-FID equipped with a silicone capillary column (HP-5 crosslinked 5% PhMe Silicone 30 m × 0.53 mm × 0.88 mm film thickness) at a temperature between 373 and 573 K. Response factors of reactants and products were measured from solutions of known concentrations.

### 1.3 Catalysts Characterizations

#### 1.3.1 C-S Analysis

Carbon and sulfur contents of the catalysts were determined by combustion at 1623 K and IR analysis of the produced SO<sub>2</sub> and CO<sub>2</sub> in a C,S-mat 5500 (Jüwe Instrument). Data are accurate within +/- 10%. This elemental analysis technique gives consistent S/Co+Mo data as compared to other techniques such as XPS or TEM-EDS [26].

#### 1.3.2 TEM Analysis

High resolution electron microscopy was performed using a JEOL 2010 TEM microscope (point to point resolution 0.19 nm) equipped with a EDS Link-Isis detector. For sample preparation, the catalysts were ultrasonically dispersed in ethanol and the suspension was then collected on a carbon-coated copper grid.

#### 1.3.3 EXAFS Experiments

All the EXAFS experimentations and spectrum recordings were performed on the storage ring of the *Laboratoire d'Utilisation du Rayonnement Electromagnétique (LURE)*. The spectra were recorded in transmission mode at the K-edge of Co (7709 eV) and of Mo (20 keV) using a dedicated cell to perform *in situ* analysis [27]. In some cases, dilution with boron nitride was used to obtain an absorbance

of 1.5. *In situ* sulfiding was performed with a  $H_2/H_2S$  mixture (10%  $H_2S$  volume) at the desired temperature ( $5^\circ C \cdot min^{-1}$ ) for 30 minutes then the sulfided catalyst was cooled down to room temperature under a nitrogen flow.

Standard analysis of the EXAFS spectra (normalization, background removal, Fourier transformation, and curve fitting) were carried out using the SEDEM software [28] with FEFF [29] theoretical phase and amplitude functions. The curve fitting procedure was performed in *R*-space. Fourier transformation of the normalized  $k^3$ -weighted EXAFS signal was performed over the  $2.5$ - $16 \text{ \AA}^{-1}$   $k$ -range with Kaiser window functions. Coordination numbers ( $N$ ), interatomic distances ( $R$ ), Debye-Waller parameters ( $\sigma^2$ ), and energy shifts ( $\Delta E_0$ ) were used as variables in the fitting procedure. Scale factors  $S_0^2$  were fixed at 0.8.

## 2 RESULTS AND DISCUSSION

Catalytic activity measurements in tetralin conversion are summarized in Table 1. A promoting effect is observed when the catalyst is treated with an organic compound. If a calcination step is performed before sulfidation, the activity enhancement is suppressed.

One can estimate simply the impact of the organic compound on the sulfidation procedure by analyzing carbon and sulphur content after step-wise treatments under  $H_2/H_2S$ . Figure 1 shows the evolution of the S/Co+Mo ratio and C content (weight %) determined after the activation

treatment at various temperatures. The presence of DEGbe slows down the sulfidation below  $100^\circ C$ , *i.e.* in the temperature range where the organic compound is still mainly present at the surface of the catalyst as suggested by C analysis. These data illustrate the complex behaviour of this kind of organic compound since Nicosia *et al.* observed no promotion and a faster sulfidation in the case of TEG [25]. In order to discriminate if this slowing down process concerns Co or Mo or both elements, XAS studies were performed at both K-edges after *in situ* sulfidation at various temperatures.

TABLE 1  
Activity rate in tetralin hydrogenation  
of non treated and DEGbe treated CoMoP catalyst

Catalyst	$r_{HYD}(300^\circ C)$ $10^{-7} mol \cdot g^{-1} \cdot s^{-1}$	Activity increase (%)
CoMoP	0,9	/
CoMoP + DEGbe	1,2	30

### 2.1 Effect of DEGbe on Sulfidation at the Co K-Edge

During sulfidation, the white line intensity of the XANES spectra (see Fig. 2) diminishes, indicating, as observed previously [30], the partial sulfidation of Co. This can also be seen on the evolution of the Fourier transform on sulfidation, the maximum of the first peak of the Fourier transform being shifted to higher distances, corresponding to the evolution of

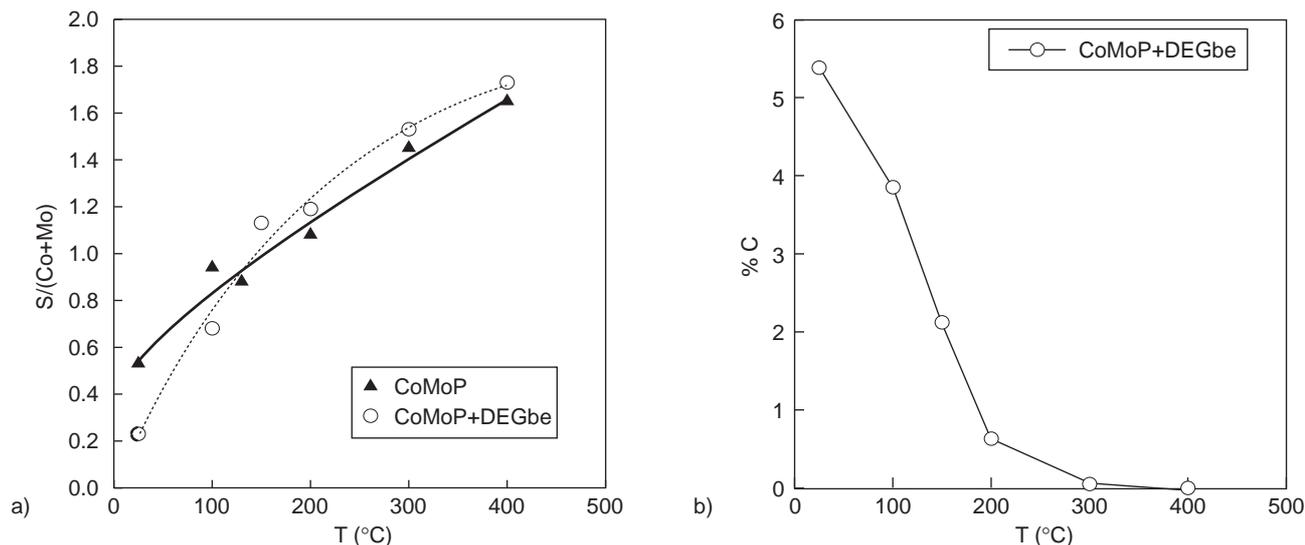


Figure 1

Evolution of S content and carbon content on sulfidation of CoMoP prepared with DEGBE (A and B) or diA-EDTA (B and C) and comparison with the CoMoP reference catalyst.

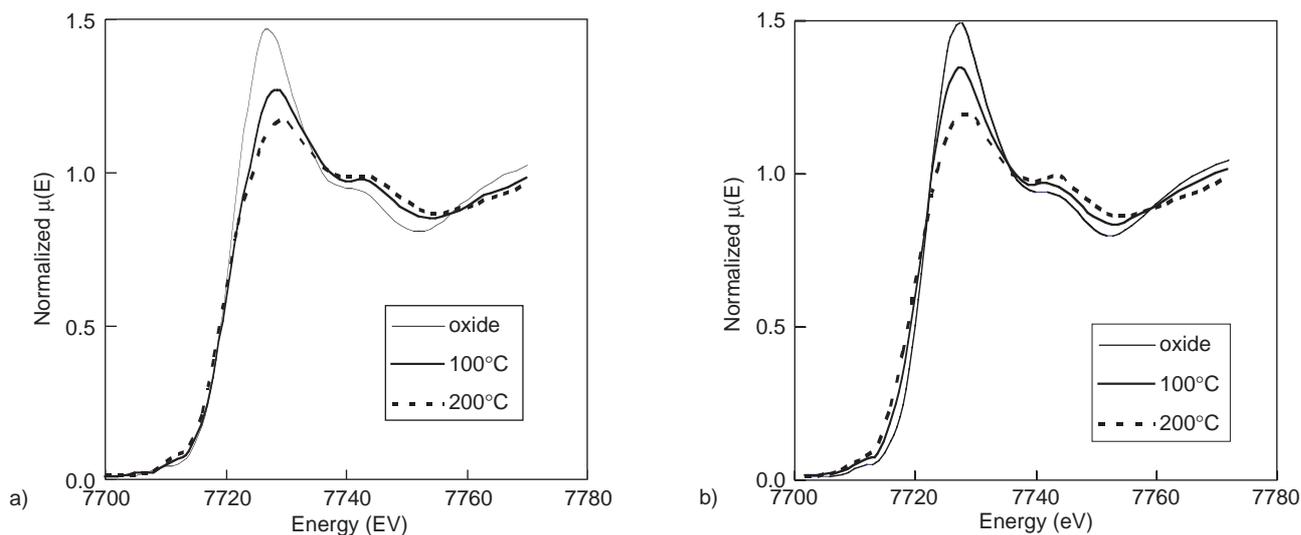


Figure 2

XANES spectra in the oxidic state and after sulfidation at 100 and 200°C at the Co K-edge of CoMo on alumina (a) and CoMo on alumina treated with DEGBE.

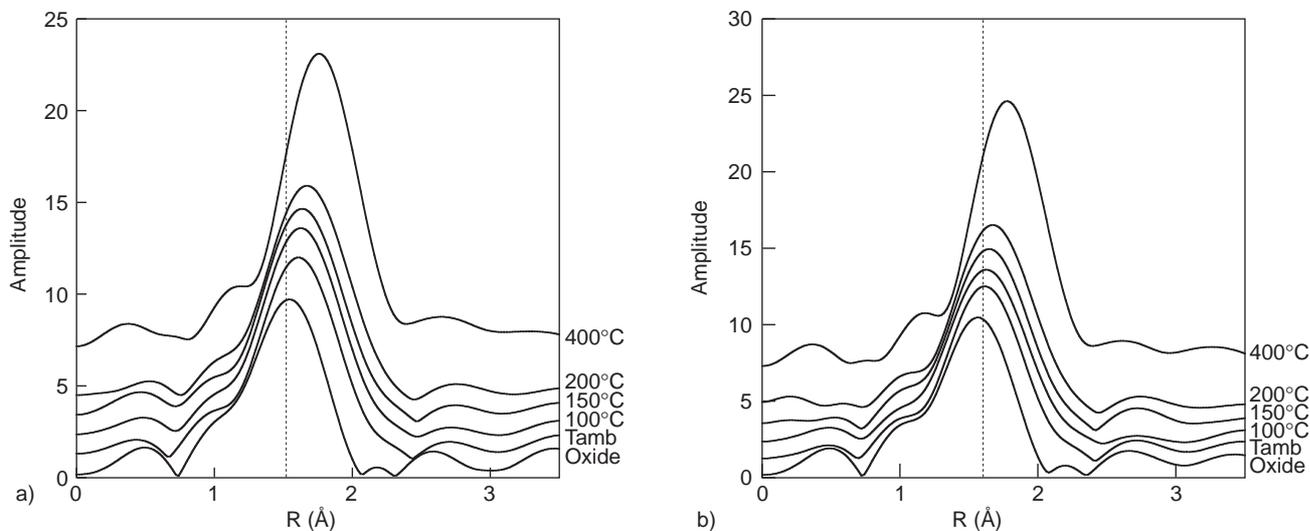


Figure 3

Magnitude of the Fourier transformed  $k^3$ -weighted data at the Co K-edge of the CoMoP reference and DEGBE treated samples at various sulfidation temperatures.

a short Co-O bond to a longer Co-S bond (see Fig. 3). Both XANES and EXAFS spectra show that in the presence of DEGBE, this transformation is slower than for the reference catalyst. In order to estimate locally the extent of sulfidation at each temperature, structural parameters were fitted and the results are presented in Tables 2 and 3. At 100°C, the presence of DEGBE on the catalyst surface inhibits the sulfidation of Co, sulfur coordination being half that of the

reference compound at the same sulfidation temperature. However, at 150°C, both catalysts present almost the same coordination sphere for Co with a remaining contribution of O. At 573 K, only sulfur atoms surround Co atoms.

From this study, we can conclude that the presence of DEGBE slows down the sulfidation of Co atoms below 423 K but to a much lesser extent as compared to chelating agents.

TABLE 2

Structural parameters obtained from fitting the EXAFS of the CoMoP sample (Co K-edge) in the oxidic form and treated by H<sub>2</sub>/H<sub>2</sub>S at various sulfidation temperatures

	Oxide	Room Temp	100°C	150°C	200°C
R <sub>Co-O</sub> (Å)	2.018	2.046	1.99	1.98	
N(O)	5.7	6.1	2.7	2.2	
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	1	0.8	0.8	0.7	
Δ E0 (eV)	-1.1	6	-5.7	-6.9	
R <sub>Co-S</sub> (Å)			2.22	2.21	2.18
N(S)			3.3	3.8	4.3
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )			1.2	1.1	1.0
Δ E0 (eV)			-3.6	-4.3	-9

TABLE 3

Structural parameters obtained from fitting the EXAFS of the CoMoP sample treated with DEGbe (Co K-edge) in the oxidic form and treated by H<sub>2</sub>/H<sub>2</sub>S at various sulfidation temperatures

	Oxide	T <sub>room</sub>	100°C	150°C	200°C
R <sub>Co-O</sub> (Å)	2.03	2.05	2.00	2.02	
N(O)	6.1	6	3.1	1.98	
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	0.9	0.76	0.62	0.74	
Δ E0 (eV)	-1.28	3.83	-2.48	-7	
R <sub>Co-S</sub> (Å)			2.25	2.210	2.19
N(S)			1.75	4.02	4.33
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )			0.69	1.17	0.92
Δ E0 (eV)			-5.27	-6	-9.8

## 2.2 Effect of DEGbe on Sulfidation at the Mo K-edge

The near edge spectra of the reference and DEGbe impregnated samples are shown in Figure 4. Oxidic samples present a characteristic pre-edge peak attributed to a 1s-4d bound state transition corresponding to a dissymmetric octahedral surrounding of the Mo atoms. During sulfidation, this pre-edge contribution shifts to lower energies and disappears due to the reduction reaction. In the presence of DEGbe, this shift is less pronounced and the shape of the edge is closer to that of the oxidic sample, indicating that the sulfidation is slowed down. This is also visible in the Fourier transforms in Figure 5. The first contribution due to oxidic environment is shifted to a new contribution at a longer distance. At 423 K, the comparison of the Fourier transforms

of the two samples shows that sulfidation is strongly inhibited at Mo edge. For the reference compound, the sulfur contribution is clearly seen, whereas such a contribution is not visible on the DEGbe treated sample. Even at 473 K, it seems that oxidic contribution is higher on the DEGbe treated sample than on the reference. This is confirmed by the analysis of the structural parameters obtained from the fitting of the EXAFS signal as reported in Tables 4 and 5. The oxidic form is composed of several O contributions, illustrating the complex signature of a variety of Mo-O bond lengths in these distorted systems [31]. Upon sulfidation, samples with both oxidic and sulfidic neighbours are highly disordered. For the reference compound, the contribution of one sulfur neighbour appears at 373 K whereas it was not possible to introduce such a contribution with the DEGbe

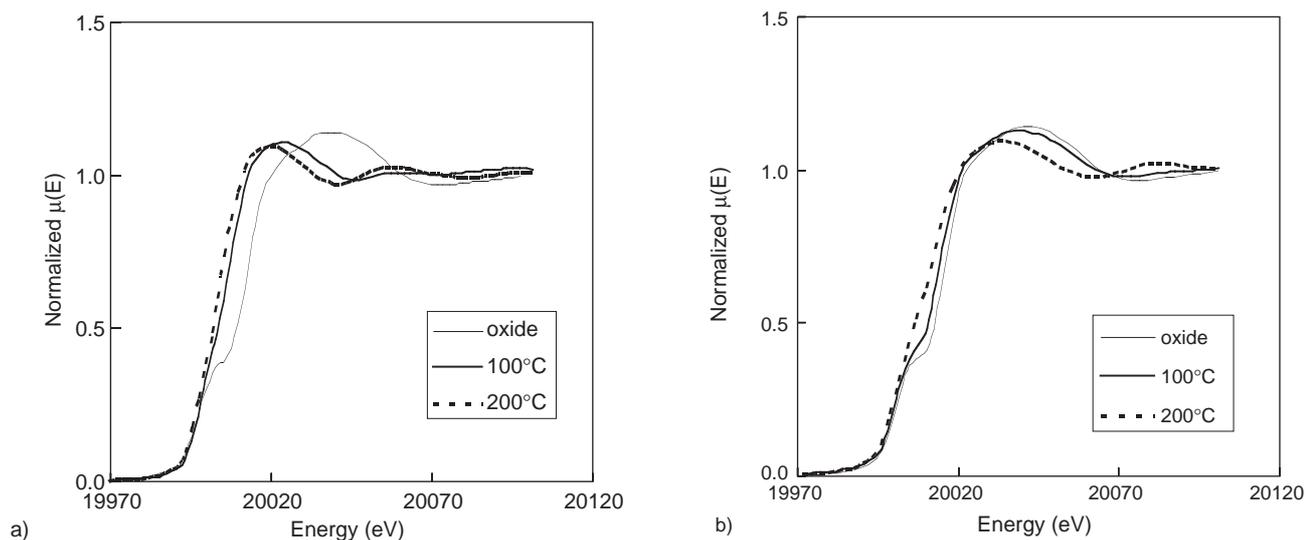


Figure 4

XANES spectra in the oxidic state and after sulfidation at 100 and 200°C at the Mo K-edge of CoMo on alumina (a) and CoMo on alumina treated with DEGbe.

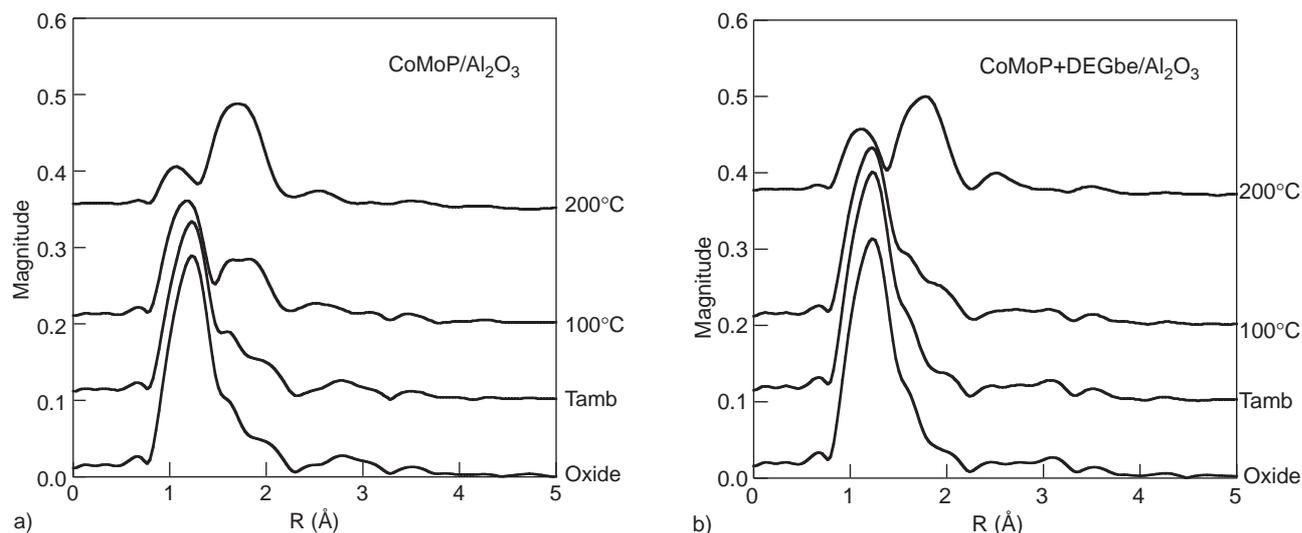


Figure 5

Magnitude of the Fourier transformed  $k^3$ - weighted data at the Mo K-edge of CoMoP on alumina reference catalyst and DeGBe modified catalyst in the oxidic state and after sulfidation at room temperature, at 100°C and at 200°C.

sample. At 473 K this slowing down effect is still observed, the ratio between oxidic and sulfidic neighbours being respectively 0.2 and 0.46 for the reference and the DEGbe treated sample. This study at Mo Kedge shows the drastic effect of DEGbe on the sulfidation of Mo atoms. Mo-S sulphur bonds determined by EXAFS on the non treated sample corresponds to those of MoS<sub>2</sub>, no longer distances attributed to MoS<sub>3</sub> such as those reported by Nicoisa *et al.* [25] were observed.

TABLE 4

Structural parameters obtained from fitting the EXAFS of the CoMoP sample (Mo K-edge) in the oxidic form and treated by H<sub>2</sub>/H<sub>2</sub>S at various sulfidation temperatures

	Oxide	100°C	200°C
R <sub>Mo-O1</sub> (Å)	1.674	1.74	1.699
N(O1)	0.97	0.63	0.46
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	1.8	0.12	0.09
Δ E0 (eV)	4.6	3.18	-2.68
R <sub>Mo-O2</sub> (Å)	1.758	-	-
N(O2)	1.8	-	-
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	0.8	-	-
Δ E0 (eV)	4.61	-	-
R <sub>Mo-O3</sub> (Å)	1.969	-	-
N(O3)	1.4	-	-
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	1.2	-	-
Δ E0 (eV)	4.6	-	-
R <sub>Mo-S</sub> (Å)	-	2.413	2.417
N(S)	-	0.84	2.41
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	-	-9	-2.18
Δ E0 (eV)	-	0.82	1.1

TABLE 5

Structural parameters obtained from fitting the EXAFS of the CoMoP sample treated with DEGbe (Mo K-edge) in the oxidic form and treated by H<sub>2</sub>/H<sub>2</sub>S at various sulfidation temperatures

	Oxide	100°C	200°C
R <sub>Mo-O1</sub> (Å)	1.775	1.76	1.76
N(O1)	2.3	1.2	0.55
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	0.37	0.2	0.25
Δ E0 (eV)	7.28	10.3	13
R <sub>Mo-O2</sub> (Å)	1.92	1.93	-
N(O2)	0.94	1.56	-
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	0.37	1.24	-
Δ E0 (eV)	7.28	5.55	-
R <sub>Mo-S</sub> (Å)	-	-	2.43
N(S)	-	-	1.2
σ <sup>2</sup> .10 <sup>2</sup> (Å <sup>2</sup> )	-	-	0.64
Δ E0 (eV)	-	-	-0.65

The comparison between the K edges demonstrates that DEGbe affects mainly Mo atoms, even if the sulfidation of Co is also slightly slowed down, but not to the extent observed with chelating agents. In this later case, the positive effect of the organic compound is attributed to the fact that, by slowing down Co sulfidation, more CoMoS active structures are formed and consequently enhanced catalytic activities are obtained. Our EXAFS study demonstrates that the effect of the organic compounds is mostly related to the sulfidation of Mo. Statistical analysis of TEM pictures were performed on the samples after sulfidation at 673 K. More than 500 crystallites were analyzed in terms of length and stacking associated with the MoS<sub>2</sub> sheet-like structure, and the results are reported in Table 6. We cannot attribute the

positive effect observed in tetralin hydrogenation to a strong morphological modification, since no visible drastic evolution of the catalyst impregnated with DEGbe is observed. Thus, we attempted to check if, as in the case of chelating agents, more CoMoS-like phases were formed. To test this possibility, we investigated the catalytic performances in the conversion of 4,6-dimethyldibenzothiophene.

TABLE 6

Average length and stacking of CoMoS nanocrystallites determined by TEM

Catalyst	Average length (nm)	Average stacking
CoMo	2.5	1.8
CoMo + EGbe	2.7	2

### 2.3 Catalytic Conversion of 4,6-dimethyldibenzothiophene

4,6-DMDBT is well recognized as one of the major refractory compounds for HDS of gas oils. There is a general agreement on the HDS mechanism: the transformation of DBT follows two different pathways *i.e.* a direct desulfurization one (DDS) and a hydrogenation route (HYD) [32, 33]. It has been demonstrated by Bataille *et al.* [34] that the main effect of the promoter (Co or Ni) is to enhance the rate of the DDS pathway. Thus, we can consider that the analysis of the selectivity in DDS and HYD products is an indicator of the amount of promoted sites on our CoMo catalysts. Catalytic activities and selectivities obtained on CoMo and CoMo DEGbe doped catalysts are summarized in Table 7. The use of the organic compound clearly enhances the catalytic activity but also favors the DDS route as compared to the reference catalyst. We can therefore suggest that the slowing down effect during sulfidation, affecting mainly Mo element, favors also the formation of promoted “CoMoS” phases, but in a different way than that proposed for chelating agents.

TABLE 7

Influence on the catalytic activity and selectivities in 4,6-DMDBT conversion of the impregnation of DEGbe on a CoMo/alumina catalyst

Sample	$r_{\text{HDS tot}}$ ( $10^{-8} \text{ mol.g}^{-1}.\text{s}^{-1}$ )	% HYD	% DDS
CoMo	2,1	84	16
CoMo + DEGbe	3,1	78	22

### CONCLUSION

Simple impregnation of an industrial catalyst with DEGbe allows the enhancement of hydrodesulfurization and hydrogenation catalytic activities. This promotion can be attributed

to the formation of more promoted “CoMoS” type active sites during the activation treatment. The presence of the alcohol slows down the sulfidation process in the range 293-473 K. This is clearly demonstrated by the help of XAS studies at Co K-edge and Mo K-edge. This effect is more pronounced for Mo species and differs from that of chelating agents for which a similar slowing down process was observed but mainly affecting Co elements.

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