Catalysis Today 150 (2010) 179–185

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Effect of EDTA addition on the structure and activity of the active phase of cobalt–molybdenum sulfide hydrotreatment catalysts

M.A. Lélias [1], E. Le Guludec, L. Mariey, J. van Gestel, A. Travert, L. Oliviero *, F. Maugé

Laboratoire de Catalyse et Spectrochimie, ENSICAEN, Université de Caen, CNRS, 6 bd du Maréchal Juin, 14050 Caen, France

ARTICLE INFO

Article history:
Available online 11 September 2009

Keywords:
Chelating agent
IR spectroscopy
CO
Thiophene HDS
Dimethylaniline HDN

ABSTRACT

Two series of (Co)Mo/Al_2O_3 catalysts were compared: one set was prepared with a constant amount of Mo, and various amounts of Co (from 0 to 4.5%), the second one containing the same amount of metals, but with ethylene diamino tetraacetic acid (EDTA) addition (27 wt%). The sulfided catalysts were characterized by IR spectroscopy of adsorbed CO. IR reveals that EDTA leads to a strong increase in the concentration of Co-promoted sites. EDTA has also a significant positive effect on thiophene hydrodesulfurization at atmospheric pressure, and 2,6-dimethylaniline hydrodenitrogenation at high pressure. Combination of spectroscopic and activity data shows that EDTA chiefly increases the amount of promoted sites having lower average intrinsic activities. This decrease in intrinsic activity should be due to a change of the site structure. Two models can be proposed to account for EDTA effect on the site structure such as the formation of type II slabs or that of nitrogeno-sulfide Co-promoted sites, "CoMoSN".

1. Introduction

The presence of sulfur as impurity in fuels poisons catalytic converters and generates polluting emissions. Drastic regulations are thus set up to limit the sulfur content of fuels. Hydrotreatment is the most largely used process to remove sulfur from oil streams. Hydrotreating catalysts are generally described as small MoS_2 crystallites promoted by cobalt (or nickel), dispersed on alumina-based support [1,2]. For CoMo catalysts, Co atoms anchored on the edges of the MoS_2 slabs generate active sites (CoMoS sites), whereas cobalt can also be present as CoS_x phase or as spinel in the support [3]. Several preparation methods have been developed in order to improve the performances of CoMo hydrotreating catalysts. Among them, addition during catalyst synthesis of chelating agents like nitrilo triacetic acid (NTA), ethylene diamino tetraacetic acid (EDTA), and cyclohexane diamine tetraacetic acid (CyDTA) has been studied [4–17]. In these studies, an increase of hydrodesulfurization (HDS) activity of CoMo catalyst was reported upon addition of chelating agent although the extent of increase could strongly differ. The origin of the beneficial effect of chelating agent addition is generally explained by an increase of the promotion of the sulfide phase by Co [9] due to either a decrease of cobalt loss by diffusion in the support or a limitation of CoS_x particle growth [13]. Such modification has been explained by the stability of the promoter–chelating agent complex at high temperature towards the H_2S/H_2 mixture [6]. Similarly, de Jong et al. [5] and Coulier et al. [10,11] have shown that NTA delays the sulfidation of cobalt to temperatures at which MoS_2 is already formed. However, IR analysis of the sulfide phase formed on supported sulfide NTA-catalysts did not confirm this conclusion [16]. Another proposal, alternative to the increase of promotion and made by van Veen et al., is the formation of the type II CoMoS phase [4].

Thus from literature, it appears that chelating agents have a role on the concentration of active sites but could also change their structure and thus their intrinsic activity. In this study, in order to determine more precisely the role of one of these chelating agents, namely EDTA, on the structure and activity of CoMo/Al_2O_3 catalysts, both catalytic tests and spectroscopic analysis were performed.

Two series of catalysts were then compared: one series was prepared with a constant amount of Mo, and various amounts of Co (from 0 to 4.5 wt%), the second one containing the same amount of metals, but in which EDTA was introduced (27 wt%). Taking into account the previous studies [4,16], the chelating agent was added together with the metal precursors during the pore-volume impregnation. After drying, the catalyst was directly sulfided (without calcination step). The effect of EDTA was studied in two catalytic tests: HDS of thiophene, which is commonly used to rapidly evaluate the catalyst performances, and hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA) that enables to

---

* Corresponding author.
E-mail address: laetitia.oliviero@ensicaen.fr (L. Oliviero).

[1] Present address: Axens – Usine de Salindres, BP 8, 30340 Salindres, France.

0920-5861/$ – see front matter © 2009 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2009.07.107

evaluate the various catalytic functions of the catalysts [18]. The nature and amount of sulfide phase of both sets of catalysts were characterized by IR spectroscopy of adsorbed CO [19,20]. Then, the effect of EDTA on the active phase structure was discussed.

2. Experimental

2.1. Catalyst preparation

The catalysts (Table 1) were prepared by pore-volume impregnation of a γ-alumina (S_{BET} = 258 $m^2 g^{-1}$, Vp = 0.66 $cm^3 g^{-1}$). The γ-Al_2O_3 support was calcined at 773 K for 3 h before impregnation. The Mo/Al_2O_3 catalyst (8.7 wt% Mo) was prepared by impregnation of the γ-Al_2O_3 support with a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (Aldrich) solution. The sample was dried at 393 K for 5 h and calcined at 773 K for 3 h.

Two series of $CoMo/Al_2O_3$ (1.5–4.5 wt% Co) catalysts with and without chelating agent were prepared. The first series of $CoMo/Al_2O_3$ catalysts (without chelating agent) was prepared by impregnation of the calcined Mo/Al_2O_3 with a cobalt nitrate (Aldrich) solution, drying, and finally calcination at 773 K for 3 h with a heating rate of 3 K min^{-1}. The catalysts of this series are designated as X.XCoMo where X.X corresponds to the Co content (1.5–4.5 wt%).

The second series with chelating agent was prepared by contacting the calcined Mo/Al_2O_3 with a solution containing cobalt nitrate (Aldrich) and EDTA. The amount of EDTA in each catalyst was chosen to be constant, i.e. 27 wt% EDTA, and exceeds the full complexation of Co. Before sulfidation, the catalysts prepared with EDTA were not calcined but only dried at 393 K for 5 h, in order to keep the chelating agent in its initial form [15]. These catalysts are designated as X.XCoMoEDTA, where X.X corresponds to the percentage of Co in the EDTA-free catalyst (1.5–4.5 wt%). The Mo/Al_2O_3 catalyst was also contacted with EDTA in absence of cobalt salt. The obtained catalyst is named $MoEDTA/Al_2O_3$.

Table 1 reports the catalyst composition measured by AAS before sulfidation. Note that the molar ratio between Co and Mo is almost the same in the two series after sulfidation which is expected to totally eliminate EDTA. Upon sulfidation, the loss of catalyst weight due to EDTA elimination, water desorption and precursor decomposition was measured experimentally. In the following, weight of catalyst referred to the weight of catalyst after sulfidation.

2.2. Catalytic tests

The catalysts were tested by means of two reactions: hydrodesulfurization (HDS) of thiophene and hydrodenitrogenation (HDN) of 2,6-dimethylaniline (DMA).

2.2.1. Thiophene hydrodesulfurization

The thiophene HDS activity test was carried out in a flow microreactor working at atmospheric pressure and 623 K. Appropriate amounts of catalyst (about 20 mg) were used in order to keep the conversion lower than 5%. Before the reaction, the catalysts were sulfided *in situ* with 30 mL min^{-1} of H_2S/H_2 (10 vol%) at 623 K (heating rate of 3 K min^{-1}) for 30 min.

Table 1
Composition of the as-prepared $(Co)Mo/Al_2O_3$ catalysts (before sulfidation) measured by AAS.

Catalysts	Co (wt%)	Mo (wt%)	EDTA (wt%)	EDTA/(Co + Mo) molar ratio
Mo/Al_2O_3	0.0	9	0	0
1.5CoMo	1.6	8.9	0	0
3.0CoMo	3.3	8.5	0	0
4.5CoMo	4.6	8.2	0	0
$MoEDTA/Al_2O_3$	0.0	6.6	27	0.82
1.5CoMoEDTA	1.3	6.6	27	0.69
3.0CoMoEDTA	2.6	6.2	27	0.62
4.5CoMoEDTA	3.5	5.9	27	0.58

Thiophene was introduced into the reactor by flowing hydrogen (70 mL min^{-1}) through a thiophene saturator maintained at 291 K and mixed to 20 mL min^{-1} of H_2S/H_2 (10 vol%). Products were analyzed on-line by using a Varian gas chromatograph equipped with a flame ionization detector (FID) and CPSIL-5CB capillary column. The specific reaction rate was calculated as $r_{HDS} = (F/w)X$, where F/w is the molar flow rate of reactant per mass of catalyst (after sulfidation) and X is the thiophene conversion.

2.2.2. 2,6-Dimethylaniline hydrodenitrogenation

The 2,6-dimethylaniline HDN activity test was carried out in a stainless steel flow reactor (Sotelem) at 4 MPa and 573 K. Around 0.35–0.40 g of catalyst was first sulfided *in situ* under 60 mL min^{-1} of H_2S/H_2 (10 vol%) at 4 MPa up to 623 K with a temperature ramp of 3 K min^{-1} and maintained 2 h at 623 K. Thereafter, the catalyst was cooled under H_2S/H_2 to the reaction temperature and the H_2S content adjusted at 1.4% in hydrogen. The liquid feed (10 vol% 2,6-dimethylaniline, reactant; 80% heptane, solvent; and 10% decane, internal standard) was introduced by an HPLC pump and vaporized in the H_2S/H_2 stream. The reaction products were condensed at the reactor exit and the liquid was analyzed with a Varian gas chromatograph equipped with a CPSIL-5CB capillary column and a FID detector.

The partial pressure of 2,6-dimethylaniline was kept constant at 13 kPa for all experiments. Reaction conditions at steady state were varied by changing the contact time (55–250 h g mol^{-1}) at 56 or 0 kPa of H_2S. We determined the reaction orders in 2,6-dimethylaniline for the hydrogenation (HYD), xylene (XYL) and disproportionation (DIS) reaction pathways as zero, zero and 0.4 respectively [18]. In this work, we report the activities for HYD and XYL expressed by the rate constant (mol h^{-1} kg^{-1}) where the mass of catalyst was corrected for the weight loss due to sulfidation.

2.3. IR spectroscopy of adsorbed CO

2.3.1. IR experiments

The samples were ground and pressed to obtain a wafer (area 2 cm^2, mass about 10 mg, but precisely weighted) before introduction in the IR cell. The spectra were recorded on a Fourier Transform IR spectrometer from Thermo Optek with a MCT detector. Spectra were recorded with 256 scans using a resolution of 4 cm^{-1}. All the spectra presented in this paper are normalized to a disc of 5 mg cm^{-2} of sulfided catalyst.

2.3.2. Standard sulfidation procedure

A standard sulfidation was carried out *in situ* in the IR cell, according to the following procedure. The disc was sulfided under a flow of H_2S/H_2 (10/90) at 30 mL min^{-1}, with a heating rate of 10 K min^{-1} up to 543 K, and then maintained at this temperature for 30 min. The temperature was then raised to 623 K and maintained during 1.5 h. At this temperature, the H_2S/H_2 flow was stopped and replaced by a flow of N_2 at 30 mL min^{-1} for 30 min. Then, the sample was cooled down to room temperature under N_2. Afterward, an evacuation was performed from RT to 573 K (with a rate of 10 K min^{-1}) and maintained at 573 K until reaching a pressure of 10^{-3} Pa. Finally, the sample was cooled down to liquid nitrogen temperature before CO introduction.

2.3.3. H_2 post-treatment procedure

In some cases after standard sulfidation, the sample was submitted to a H_2 post-treatment in order to mimic the working conditions for HDN of DMA without H_2S. Thus, after the evacuation at 573 K (described in the previous section), a first pressure of

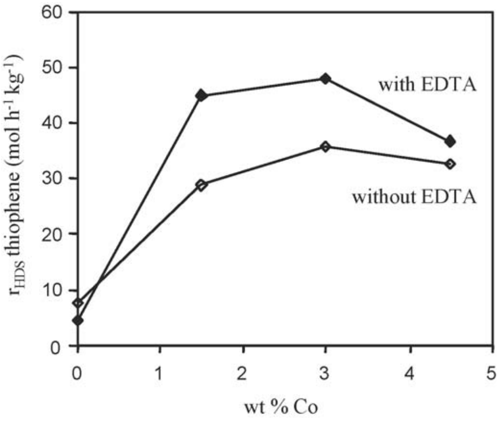

Fig. 1. Influence of Co amount and EDTA addition on the thiophene HDS activity of (Co)Mo/Al_2O_3 catalysts.

13.3 kPa of H_2 was introduced in the IR cell. After 30 min of H_2 at 573 K, the cell was evacuated under secondary vacuum, and the catalyst was contacted with a second pressure of 13.3 kPa of H_2 during 30 min. The cell was evacuated under secondary vacuum at 573 K, and cooled down to liquid nitrogen temperature.

2.3.4. Procedure for CO adsorption

Before CO introduction, a reference spectrum of the activated catalyst was recorded at liquid nitrogen temperature. Then, small calibrated doses of CO were introduced in the IR cell. Finally an equilibrium pressure of 133 Pa was established. A spectrum was taken after each CO introduction. All the CO spectra presented correspond to difference spectra, i.e. spectrum after CO adsorption minus reference spectrum.

3. Results

3.1. Catalytic activity

3.1.1. Hydrodesulfurization of thiophene

The thiophene HDS activities of both series of catalysts as a function of the Co content are reported in Fig. 1.

For the reference catalysts (without EDTA), the HDS activity increases with Co amount reaching a maximum for 3 wt% Co and slightly decreases at higher loading. This result is in agreement with literature [21].

EDTA addition decreases the HDS activity of the unpromoted Mo/Al_2O_3 catalyst (−41%), whereas the activity of CoMo catalysts is strongly increased. The beneficial effect of EDTA is maximum for the lowest Co loading and decreases for higher Co loading (1.5CoMoEDTA +56%; 3.0CoMoEDTA +34%; 4.5CoMoEDTA +13%). However, the highest HDS activity is still observed for the 3.0CoMoEDTA catalyst. The positive effect of EDTA on the activity of CoMo catalysts as well as its order of magnitude is in agreement with previous studies [7]. However, the negative effect of EDTA on the Mo/Al_2O_3 catalyst activity is surprising since a positive effect was previously reported [12].

3.1.2. Decomposition of 2,6-dimethylaniline

3.1.2.1. Influence of Co amount and EDTA presence on HYD route. The HYD activity versus Co amount, with or without EDTA, measured in presence (A) and in absence of H_2S (B), is presented in Fig. 2. On the two catalyst series (with and without EDTA), an increase of the HYD activity with the Co content is observed both in presence and in absence of H_2S. In all cases, the increase is the most important for the first Co addition (from 0 to 1.5 wt%). EDTA addition has a beneficial effect on HYD activity whatever the Co amount. The activity increase is close to 30% for all the (Co)Mo catalysts. In particular, EDTA has also a positive effect on the HYD activity of the Mo/Al_2O_3 catalyst conversely to what was observed on the thiophene test.

3.1.2.2. Influence of Co amount and EDTA presence on XYL route. Fig. 3A shows that the activities for the XYL formation measured in presence of H_2S strongly increase with the amount of Co. Moreover, the presence of EDTA has a beneficial effect on the XYL activities. Fig. 3B shows a general decrease of the XYL activities with the amount of Co in absence of H_2S. As in presence of H_2S, the presence of EDTA has a beneficial effect whatever the catalysts although this effect is maximum for the Mo/Al_2O_3 catalyst. Whatever the catalysts, the XYL activities measured in presence of H_2S are always smaller than the activities measured in absence of H_2S.

3.1.2.3. Comparison between activity for HYD and XYL routes. The rate constants for the xylene formation route (XYL) obtained in presence or in absence of H_2S are plotted as a function of hydrogenation rate constants (HYD) measured under the same conditions for the two sets of catalysts (Fig. 4A and B).

In presence of H_2S (Fig. 4A), a linear relationship can be drawn between the two rate constants for the different catalysts that contain or not EDTA. This is in agreement with the DMA reaction scheme which shows a common dearomatized intermediate for the HYD and XYL routes. In agreement with previous work of van Gestel et al. [18], the straight line intercepts the ordinate at a positive value, which is attributed to an extra, but constant, xylene formation route (DDN route), independent of dearomatization. The presence of chelating agent increases in the same extent the HYD and XYL activities for all the catalysts including the unpromoted one. Thus, an increase of the activity due to an increase of the number of active sites could be envisaged in this case. However,

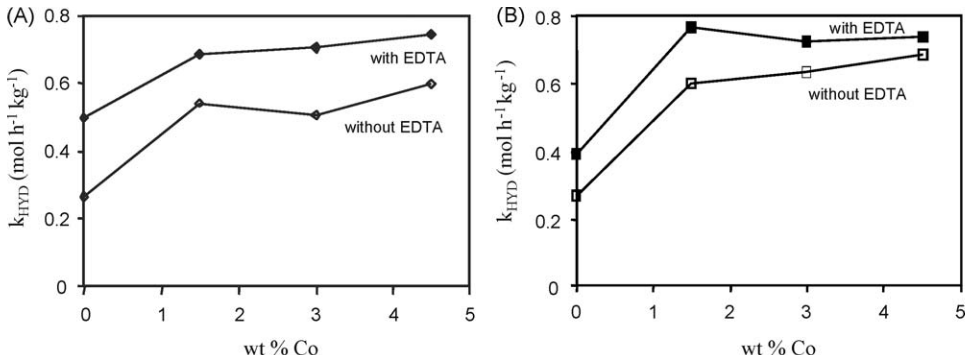

Fig. 2. HDN of DMA: HYD activity of the (Co)Mo/Al_2O_3 catalysts with and without EDTA. [A] Activity measured in presence of H_2S (56 kPa); [B] activity measured in absence of H_2S.

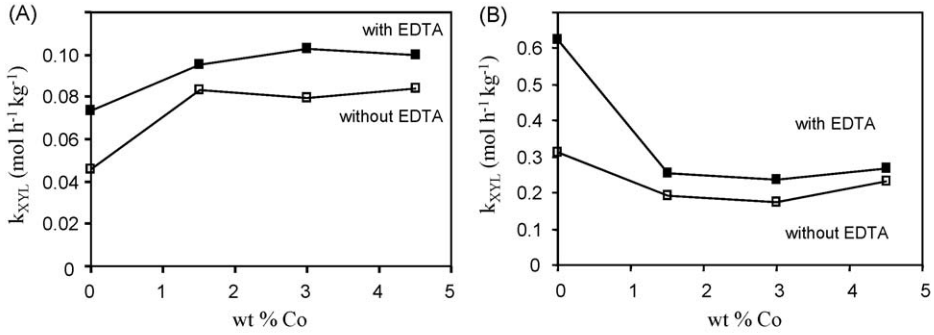

Fig. 3. HDN of DMA: XYL activity of (Co)Mo/Al_2O_3 catalysts with and without EDTA. [A] Activity measured in presence of H_2S (56 kPa); [B] activity measured in absence of H_2S.

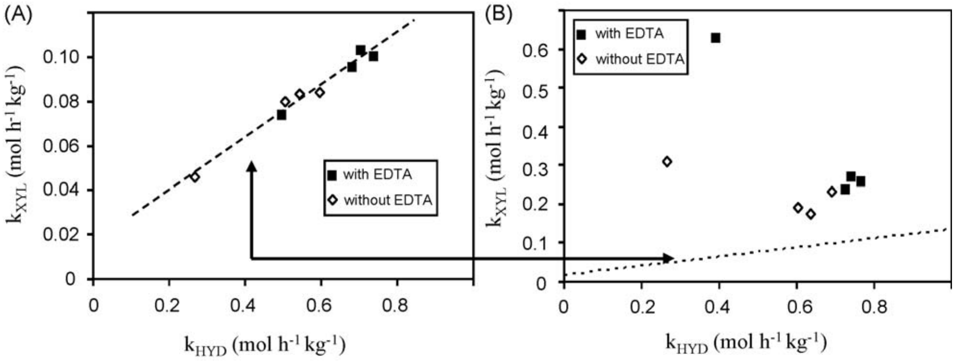

Fig. 4. HDN of DMA: XYL versus HYD activity of the (Co)Mo/Al_2O_3 catalysts with and without EDTA [A] activity measured in presence of H_2S (56 kPa); [B] activity measured in absence of H_2S (the dotted line corresponds to XYL versus HYD in presence of H_2S).

Fig. 4B points out that, in absence of H_2S, there is no linear relationship between the two rate constants anymore: the XYL rate constant decreases when HYD rate increases. The chelating agent enhances this effect.

3.1.2.4. Influence of Co amount and EDTA presence on DDN route. A previous work [18] has shown that, in presence of H_2S, xylene (XYL) is mainly formed by NH_3 elimination from dearomatized DMA (HYG). This elimination could occur after substitution of the amino group to form a thiol as proposed by Zhao and Prins [22]. By contrast, in absence of H_2S, xylene formation is strongly increased. In this case, xylene is formed by both NH_3 elimination from dearomatized DMA (HYG) and by direct carbon–nitrogen bond cleavage (DDN) (i.e., XYL = HYG + DDN). Comparison of the xylene formation in presence and in absence of H_2S allows one to calculate the DDN activity.

Fig. 5 presents the DDN activity plotted as a function of the amount of Co present on the catalysts prepared with and without EDTA. On the two series, DDN activity decreases with the addition of Co. This result is in agreement with the above mentioned study which related the DDN activity to the presence of highly unsaturated unpromoted MoS_2 sites. However, it should be mentioned that the presence of EDTA increases the activity for DDN both on Mo and Co-promoted catalysts.

3.2. Nature and concentration of the sulfide phase sites—IR spectroscopy of CO

3.2.1. Unpromoted catalysts

IR spectroscopy experiments of CO adsorbed at low temperature are performed on *in situ* sulfided catalysts. Fig. 6A represents the IR spectra of CO adsorbed on the sulfided Mo/Al_2O_3 and MoEDTA/Al_2O_3 catalysts (133 Pa at equilibrium). They are typical of Mo/Al_2O_3 catalysts [20] and can be decomposed in four main bands: two of them (2188 and 2156 cm^{-1}) are attributed to the alumina sites (alumina Lewis and Brønsted sites respectively), the band near 2110 cm^{-1} is attributed to the adsorption of CO on the molybdenum edge of MoS_2 sites and the last one, a broad band at ≈2068 cm^{-1} is attributed to CO adsorbed on the sulfur edge of MoS_2 slab [23]. A decrease of the amount of CO adsorbed on the alumina sites is observed when the catalyst is prepared in presence of EDTA. This can be accounted by the presence of carboxylate species observed by IR spectroscopy (see Fig. 6B) on the MoEDTA/Al_2O_3 catalyst just after the sulfidation. Thus, although most of the chelating agent has decomposed during the sulfidation step, carboxylate species are still present on the support after the sulfidation. Concerning the adsorption of CO on the sulfide phase itself, a downward shift of the maximum of absorbance of about 5 cm^{-1} is observed for MoEDTA/Al_2O_3 as compared to Mo/Al_2O_3. The third spectrum in Fig. 6A represents the difference between

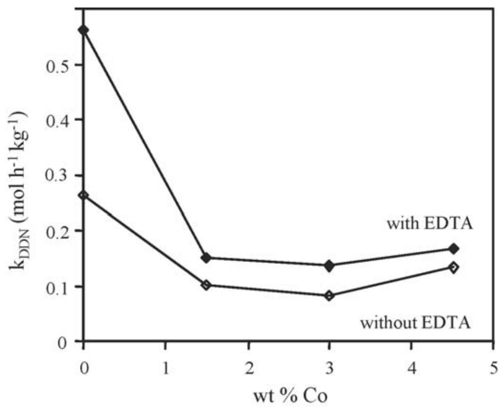

Fig. 5. HDN of DMA: activity for the DDN route of the (Co)Mo/Al_2O_3 catalysts with and without EDTA.

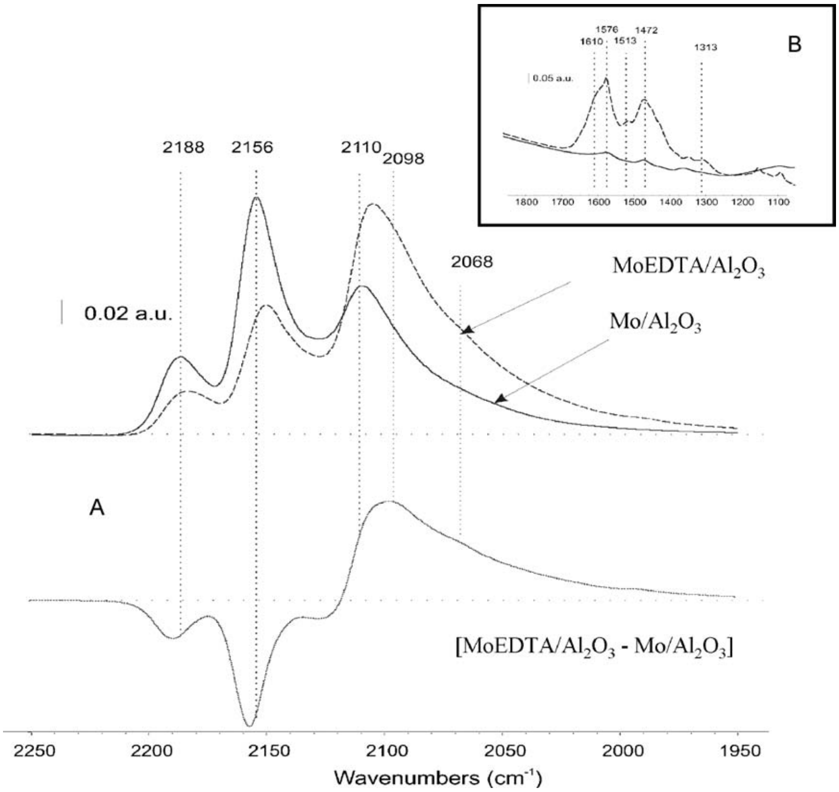

Fig. 6. IR spectra of [A] CO adsorbed on sulfided Mo/Al$_2$O$_3$ and MoEDTA/Al$_2$O$_3$ catalysts; [B] sulfided Mo/Al$_2$O$_3$ and MoEDTA/Al$_2$O$_3$ catalysts.

spectra of the two Mo catalysts: [MoEDTA/Al$_2$O$_3$]–[Mo/Al$_2$O$_3$]. This subtraction allows us to highlight the evolution of sulfide phase sites due to the use of EDTA. Two positive bands are observable, at 2068 cm^{-1} and at 2098 cm^{-1}. This latest band was already observed after a H$_2$ treatment by Dujardin et al. [21] and was attributed to unsaturated MoS$_2$ sites which were proposed to be responsible of the extra DDN activity in the DMA HDN test in absence of H$_2$S.

3.2.2. *Co-promoted catalysts*

The IR spectra of CO adsorbed at low temperature on the two sets of sulfided catalysts are presented in Fig. 7.

They are composed of five main bands. The two bands at 2188 and 2156 cm^{-1} are attributed to CO in interaction with alumina sites. The band around 2110 cm^{-1} is due to CO in interaction with MoS$_2$ sites and the two low wavenumber bands to CO adsorbed on CoMoS sites. More precisely, the bands at 2070 and 2060 cm^{-1} are respectively attributed to fourfold coordinated Co sites and fivefold coordinated Mo sites in the vicinity of Co [23]. In both series, increasing Co content does not lead to any band shift but only to an increase of band intensity due to CO/CoMoS at the expense of bands due to CO/Mo. Addition of EDTA leads to a downward shift of the CO/Mo band (-5 cm^{-1}), as observed on the pure Mo catalyst, whereas no shift of the CO/CoMoS band is noted. Regarding the catalysts sulfided and H$_2$ post-treated, similar band positions are observed while the intensities of the CO/sulfide bands are markedly increased.

The quantification of the different sites was performed using CO/MoS$_2$ and CO/CoMoS molar absorption coefficient previously reported [20]. The evolutions of the total concentration of sites, MoS$_2$ sites and CoMoS sites versus the amount of Co on the H$_2$ post-

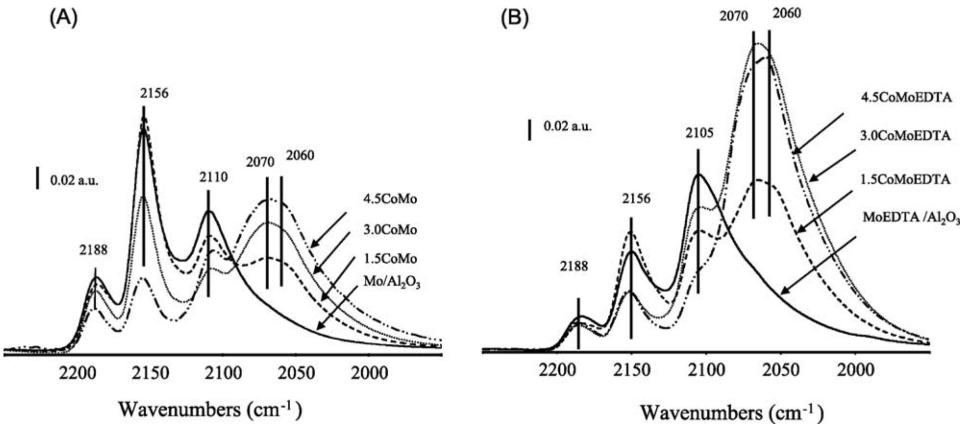

Fig. 7. IR spectra of CO adsorbed on (Co)Mo/Al$_2$O$_3$ and (Co)MoEDTA/Al$_2$O$_3$ catalysts.

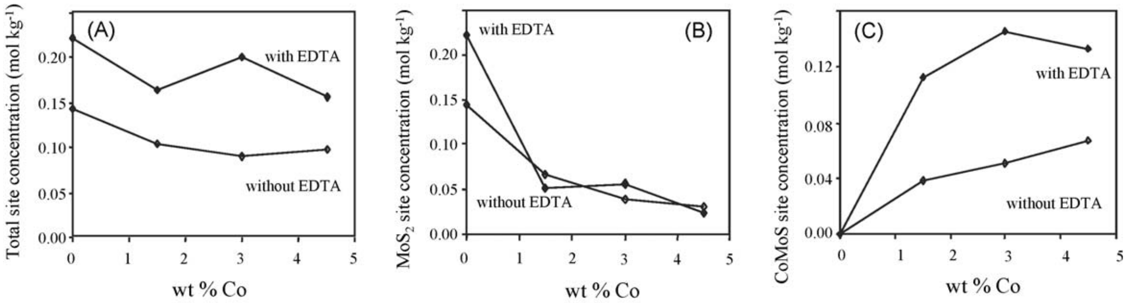

Fig. 8. Concentration of sites determined by CO adsorption after sulfidation and H_2 post-treatment. [A] Total sites, [B] MoS_2 sites and [C] CoMoS sites.

treated catalysts are presented in Fig. 8A, B and C, respectively. Similar trends are observed on sulfided catalysts.

For both series a slight decrease of the total amount of sites is observed for increasing Co content. However, the concentration of total sites is 50% higher when the catalyst is prepared with EDTA.

For MoS_2 sites, the effect of EDTA is mostly distinguishable for the unpromoted catalyst: the MoEDTA/Al_2O_3 catalyst has a 1.5-fold higher amount of MoS_2 sites (Fig. 8B). Concerning the promoted catalysts, EDTA seems to have no effect on the amount of unpromoted Mo sites.

As expected, the concentration of CoMoS sites increases with Co content whether the catalysts were prepared with EDTA or not (Fig. 8C). In the absence of chelating agent, this increase is proportional to the amount of Co, whereas for EDTA catalysts, a maximum is observed at 3 wt% Co content. This difference between the two series could indicate that the maximum of Co which can be anchored to the MoS_2 slabs is reached when the catalyst is prepared with EDTA. Moreover, it can be noticed that the EDTA catalysts have always a larger amount of CoMoS than the catalysts without EDTA: for each amount of Co, the concentration of CoMoS sites is at least multiplied by 2.

In conclusion, the presence of EDTA on CoMo catalysts increases the amount of CoMoS sites without modifying the amount of unpromoted MoS_2 sites, thus the total number of sites increases with EDTA.

4. Discussion

From a comparison between catalytic tests and IR characterization results, we aim to determine whether addition of EDTA has only an effect on the concentration of active sites or also an effect on their intrinsic activities, i.e. on the structure of active sites.

4.1. Site concentrations and HDS of thiophene and HYD of DMA activity

Figs. 9 and 10 show the evolutions of activity for HDS of thiophene and HYD of DMA versus the amount of CoMoS sites on the two series of catalysts, with or without EDTA, respectively. For series of (Co)Mo catalysts supported on Al_2O_3, correlations between activity and concentration of MoS_2 and CoMoS sites were previously reported by Dujardin et al. both in the HDS of thiophene and the HYD of DMA in presence of H_2S [21]. These correlations have allowed the TOF values to be determined for both types of sites in these two reactions (Table 2). In this previous work, it was supposed that activity of MoS_2 sites was independent of the one of CoMoS: i.e. that the TOF value for MoS_2 sites was the same on a Mo/Al_2O_3 series and a CoMo/Al_2O_3 series. The good correlation obtained for CoMoS site concentration and activity validated this hypothesis.

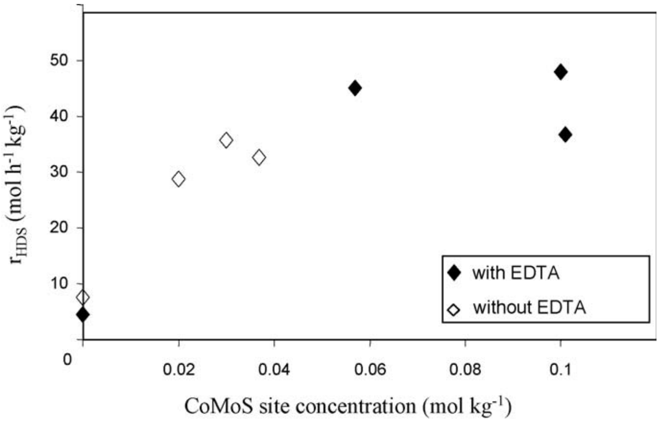

Fig. 9. Comparison between IR results and thiophene HDS activity.

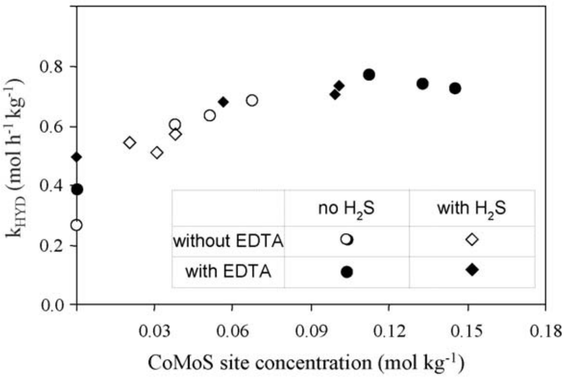

Fig. 10. Comparison between IR results and DMA HYD activity.

In the same way, in this study, we have first estimated the TOF value for MoS_2 sites from the activity of Mo/Al_2O_3 without EDTA. Then for the CoMo catalysts, the activity of CoMoS sites was estimated by subtracting from the total activity of CoMo catalysts the activity of MoS_2 sites obtained by multiplying the TOF value of MoS_2 by the concentration in MoS_2 sites. The resulting HDS and HYD activities of DMA showed satisfactorily linear correlations (not shown) with the CoMoS site concentrations ($R^2 > 0.9$) in the absence of EDTA and presence of H_2S.

Moreover, the TOF values obtained for CoMoS sites are in the same order of magnitude than the ones reported by Dujardin et al.

Table 2
TOF of CoMoS sites for thiophene HDS and HYD of DMA of CoMo/Al_2O_3 catalysts without EDTA.

Catalyst series	TOF HDS (h^{-1}) [reaction *T*]	TOF HYD (h^{-1}) with H_2S
Dujardin, 2007	1080 [673 K]	16
This work	880 [623 K]	13

taking into account the change in reaction temperature (673 K in [21] and 623 K in this study) for thiophene HDS (Table 2). Thus, it can be concluded that for the series without EDTA, the catalytic activity is well explained by the concentration of CoMoS and MoS_2 sites.

In contrast, for the catalyst series with EDTA, no good linear relationship was obtained whatever the activity test: the increase of concentration of CoMoS sites does not lead to activity as high as expected from the TOF values in absence of EDTA. It has to be mentioned that for the EDTA series, calculations were done either considering that MoS_2 sites have the same intrinsic activity with or without EDTA or with TOF for MoS_2 calculated from MoEDTA/Al_2O_3 activity results. None of these options give satisfying results. Thus it appears that the nature of CoMoS sites is somewhat modified by EDTA addition. Accordingly, EDTA would essentially increase the concentration of CoMoS promoted sites to the detriment of their intrinsic activities.

4.2. Site concentrations and DDN route of DMA HDN

The activity for the DDN route of DMA HDN has been previously attributed to highly unsaturated MoS_2 sites [18]. On the Mo/Al_2O_3 catalyst, EDTA addition not only leads to an increase of MoS_2 site concentration (Fig. 8) but also increases the amount of unsaturated MoS_2 sites characterized by a band at 2098 cm^{-1} (Fig. 6), thus explaining the strong increase of the DDN activity in HDN of DMA (Fig. 5).

The CoMo catalysts prepared with EDTA present an extra DDN activity – similar for the three Co levels – as compared to the catalysts prepared without EDTA. The concentrations of MoS_2 sites determined by IR spectroscopy being similar with or without EDTA (Fig. 8), the extra DDN activity could account for a higher intrinsic activity of unpromoted Mo sites. IR spectra in Fig. 7 show that EDTA addition leads to a downward shift of the band assigned to unpromoted sites (2105 cm^{-1} vs. 2110 cm^{-1}), which could be accounted by the increase of unsaturated sites (2098 cm^{-1}, Fig. 6), active for DDN. The strong overlap of these bands with those due to CoMoS sites, however, prevents any assessment of these sites (Fig. 7).

Alternatively, assuming CoMoS sites present a much lower DDN activity as compared to unpromoted Mo sites, the small extra DDN activity observed for CoMoEDTA catalysts could be due to the strong increase of CoMoS sites induced by EDTA.

4.3. Influence of EDTA on the structure of sulfide sites

Addition of EDTA clearly increases the amount of CoMoS sites, which leads to a marked enhancement of the HDS and HDN activity of the catalysts. However, the results presented in the previous section does not allow to calculate a TOF in presence of EDTA. Moreover, DDN results suggests a change in sulfide site structure. These observations can be interpreted as the formation of new types of sites. Two models are tentatively proposed:

- EDTA could favor the formation of sulfide slabs of type II instead of type I. Note that type II sites are generally considered as more active than type I. However, this is not in contradiction if we consider that the amount of CoMoS sites has been overestimated in the present study (because of the use of absorption coefficient for 'conventional' CoMoS sites) and thus that the TOF value has been underestimated.
- EDTA leads to the formation of "CoMoSN" sites. The interaction between Co and EDTA leads to the insertion of some nitrogen into the sufide slab which could generate some nitrogeno-sulfide Co-promoted sites at the edges of the MoS_2 slabs.

Similar models were proposed to account for the effect of other chelating agents such as NTA, on the structure of the sulfide sites [17].

5. Conclusion

IR spectroscopy reveals that on unpromoted Mo/Al_2O_3 catalysts, EDTA increases the amount of Mo-edge unpromoted sites (2110 cm^{-1}) and, in a larger extent, unsaturated Mo sites (2098 cm^{-1}) active for the DMA DDN route. These findings account for the much higher activity of Mo/Al_2O_3 prepared with EDTA towards all DMA HDN routes. Surprisingly, these changes are not reflected in thiophene HDS for which activity is decreased by addition of EDTA.

For promoted CoMo catalysts, EDTA addition also leads to a change in unpromoted Mo sites distribution (Mo-edge vs. unsaturated), without affecting much their total amount. Consequently, CoMo catalysts prepared with EDTA present a limited extra DDN activity as compared to catalysts prepared without EDTA.

More strikingly, EDTA also leads to a strong increase of promoted CoMoS sites and significant increase in thiophene HDS (up to 1.6×) and DMA HDN (HYD up to 1.4×) activities. The relative increase of catalytic activities, however, is somewhat lower than that expected from the increase of CoMoS sites, suggesting that EDTA chiefly increases the amount of promoted sites having lower average intrinsic activities. This should be due to a change in the structure of promoted sites.

References

[1] H. Topsøe, R. Candia, N.-Y. Topsøe, B.S. Clausen, Bull. Soc. Chim. Belg. 93 (1984) 783.

[2] H. Topsøe, B.S. Clausen, N.-Y. Topsøe, E. Pederson, Eng. Chem. Fundam. 25 (1986) 25.

[3] J.A.R. van Veen, E. Gerkema, A.M. van der Kraan, P.A.J.M. Hendriks, H. Beens, J. Catal. 133 (1992) 112.

[4] J.A.R. van Veen, E. Gerkema, A.M. van der Kraan, A. Knoester, J. Chem. Soc., Chem. Commun. (1987) 1684.

[5] A.M. de Jong, V.H.J. de Beer, J.A.R. van Veen, J.W. Niemantsverdriet, J. Phys. Chem. 100 (1996) 17722.

[6] L. Medici, R. Prins, J. Catal. 163 (1996) 38.

[7] K. Hiroshima, T. Mochizuki, T. Honma, T. Shimizu, M. Yamada, Appl. Surf. Sci. 121/122 (1997) 433.

[8] K. Inamura, K. Uchikawa, S. Matsuda, Y. Akai, Appl. Surf. Sci. 121/122 (1997) 468.

[9] T. Shimizu, K. Hiroshima, T. Honma, T. Mochizuki, M. Yamada, Catal. Today 45 (1998) 271.

[10] L. Coulier, V.H.J. de Beer, J.A.R. van Veen, J.W. Niemantsverdriet, Topics Catal. 13 (2000) 99.

[11] L. Coulier, V.H.J. de Beer, J.A.R. van Veen, J.W. Niemantsverdriet, J. Catal. 197 (2001) 26.

[12] E.J.M. Hensen, P.J. Kooyman, Y. van der Meer, A.M. van der Kraan, V.H.J. de Beer, J.A.R. van Veen, R.A. van Santen, J. Catal. 199 (2001) 224.

[13] T. Kubota, N. Hosomi, K.K. Bando, T. Matsui, Y. Okamoto, Phys. Chem. Chem. Phys. 5 (2003) 4510.

[14] S.L. Gonzales-Cortes, T.-C. Xiao, P.M.F.J. Costa, B. Fontal, M.L.H. Green, Appl. Catal. A 270 (2004) 209.

[15] M.S. Rana, J. Ramírez, A. Gutiérrez-Alejandre, J. Ancheyta, L. Cedeño, S.K. Maity, J. Catal. 246 (2007) 100.

[16] M.A. Lelias, J. van Gestel, F. Maugé, J.A.R. van Veen, Catal. Today 130 (2008) 109.

[17] M.A. Lélias, P.J. Kooyman, L. Mariey, L. Oliviero, A. Travert, J. van Gestel, J.A.R. van Veen, F. Maugé, J. Catal. (2009), in press, doi:10.1016/j.jcat.2009.07.006.

[18] J. van Gestel, C. Dujardin, F. Maugé, J.C. Duchet, J. Catal. 202 (2001) 78.

[19] F. Maugé, A. Vallet, J. Bachelier, J.C. Duchet, J.C. Lavalley, J. Catal. 162 (1996) 88.

[20] F. Maugé, J.C. Lavalley, J. Catal. 137 (1992) 69.

[21] C. Dujardin, M.A. Lelias, J. van Gestel, A. Travert, J.C. Duchet, F. Maugé, Appl. Catal. A: Gen. 322 (2007) 46.

[22] Y. Zhao, R. Prins, J. Catal. 222 (2004) 532.

[23] A. Travert, C. Dujardin, F. Maugé, E. Veilly, S. Cristol, J.F. Paul, E. Payen, J. Phys. Chem. B 110 (2006) 1261.