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Modification of the preparation procedure for increasing the hydrodesulfurisation activity of the CoMo/γ-alumina catalysts

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Abstract

In this work we have examined whether the re-impregnation of CoMo/γ-alumina catalysts or the replacement of the conventional non-dry impregnation step by ''equilibrium deposition filtration'' (EDF) may be used for improving their surface characteristics and thus their catalytic activity.

Two samples were prepared. In the first sample (EDF) the molybdenum species were mounted by ''equilibrium deposition filtration'' whereas in the second sample these species were mounted by non-dry impregnation (NDI). In both cases the Co was deposited on the calcined Mo/γ-Al_2O_3 precursor solid by simple dry impregnation. An aliquot of each sample was impregnated again with an amount of pure water equal to its pore volume and then it underwent drying and calcination.

The catalysts prepared were characterized using N_2 adsorption measurements (BET), UV–vis diffuse reflectance spectroscopy (DRS), laser Raman spectroscopy (LRS) and NO chemisorption. The hydrodesulfurization (HDS) activities over the catalysts studied were determined using a continuous-flow tubular fixed-bed microreactor operating in a differential mode at atmospheric pressure.

It was confirmed that the replacement of the conventional impregnation by equilibrium deposition filtration results to catalysts with relatively high active surface and high portion of the well-dispersed octahedral cobalt and thus, to catalysts with 30% higher HDS activity. The re-impregnation resulted to partial dissolution and re-dispersion of the Mo and Co supported oxidic phases. Concerning the NDI catalyst re-impregnation resulted to an increase of the active surface and of the portion of the well-dispersed octahedral cobalt and thus to 25% higher catalytic activity. The opposite effects were observed for the EDF catalyst which exhibited almost 7% lower activity after re-impregnation.

Keywords: HDS catalysts; CoMo/alumina; DRS; LRS; Hydrodesulfurization

1. Introduction

Enhancement of the hydrodesulfurization (HDS) catalyst performances is prompted by the urgent need to improve fuel quality. Refineries have to face more and more stringent environmental regulations. These impose a progressive decrease in the sulfur content of commercial fuels.

To achieve even lower sulphur concentrations, the HDS units should operate at even higher temperatures and relatively low space velocities. However, under these working conditions the oil upgrading cost increases considerably. This is the reason for which several analysts agree that this is no longer a good approach for satisfying the new and very strict environmental regulations. The modification of hydrotreating catalysts seems to be more effective and cheaper approach because it could have a considerable effect on the catalytic activity [1–6].

Hydrotreating catalysts usually consist of molybdenum (Mo) supported on an alumina carrier with promoters such as cobalt (Co) or nickel (Ni). Three approaches are mainly used for improving the HDS activity of CoMo- and NiMo-type hydrotreating catalysts. The first one is based on the use of some additives in the catalyst formulations. Phosphorus [7,8] fluorine [8–11] and boron [12,13] are the three important additives that have been investigated extensively. It was found to have beneficial effects on HDS activity of both CoMo- and NiMo-type hydrotreating catalysts.

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The second approach is to use new supports. A large number of new materials with high surface area and other suitable properties have been developed and tested. These include TiO_2, ZrO_2, MgO, carbon, SiO_2, and zeolites [14–17]. Attempts have also been reported to modify the alumina and silica supports by zeolites and other metal oxides such as TiO_2 and ZrO_2 to take advantage of the favourable characteristics of both oxides. [18–21]

The third approach concerns the preparation procedure. This procedure involves impregnation, drying, calcination and activation; sometimes equilibration of the suspension and filtration. The most important step is the impregnation of the support particles or pellets with an aqueous solution containing species of the active and/or promoter ions. The impregnation step influences the structure and the dispersion of the active phase [22]. Different impregnation alternatives have been reported in the literature concerning the mounting of Mo and Co or Ni on the support surface. Among these, the incipient wetness (pore volume) impregnation and the non-dry (wet) impregnation are widely used. Recent studies have shown that remarkable improvements in HDS activity of CoMo and NiMo catalysts can be achieved by the addition of some chelating compounds to the impregnation solution. [23–31]

In the last years, we have developed both theoretically and practically an alternative impregnation methodology, the equilibrium deposition filtration technique (EDF) (e.g. [32–35]), otherwise called equilibrium adsorption [36–38]. The term EDF stresses both the importance of the filtration step in the whole process and the fact that species are deposited not only by electrostatic adsorption but also by chemical adsorption (reaction) on the receptor sites developed on the support surface resulting to the formation of inner sphere surface complexes as well as by surface precipitation, namely precipitation in the 'impregnating solution/support' interface [22]. The application of this technique resulted to the improvement of the textural and structural properties and thus to the catalytic behaviour for several catalysts and catalytic reactions [39]. Specifically, previous studies [33,34,40–42] have shown that using EDF, hydrodesulfurization catalysts with relatively high activity can be prepared. More precisely, CoMo/γ-Al_2O_3 catalysts prepared by EDF were proved to be about 30–43% more active in HDS than the corresponding catalysts prepared following the conventional impregnation techniques. The relatively high HDS activity of the EDF catalyst was attributed to the relatively large number of active HDS sites formed on its surface. This has been attributed to the fact that the deposition of the Mo species by EDF results to a relatively high coverage of the support surface by the supported molybdenum phase. This inhibits the formation of the catalytically inactive $CoAl_2O_4$ favouring the dispersion of octahedral cobalt on the molybdenum phase.

However, the industrial preparation procedure involves conventional impregnation and not the application of the EDF technique. Thus, one may wonder whether it would be possible to approach the improved physicochemical features and the catalytic behaviour obtained by EDF through a simple modification of the usual preparation scheme. In this context the re-dispersion of the Mo and Co oxidic phases stabilized on γ-alumina after calcination by re-impregnation of the CoMo/γ-Al_2O_3 precursor solids with pure water seems to be an attractive eventuality. The examination of this possibility is the main target of the present work. A second goal of this work is to compare the improvement achieved by performing the aforementioned modification of the preparation scheme to that achieved by the replacement of the conventional impregnation by EDF.

2. Experimental

2.1. Preparation of the specimens

Two CoMo/γ-Al_2O_3 samples were prepared using gamma alumina as support (Houdry, Ho 415, 90–150 mesh, $125\ m^2\ g^{-1}$, $0.45\ mL\ g^{-1}$). In the first sample the molybdenum species were first mounted by EDF. Specifically, 5 g of γ-Al_2O_3 powder were suspended in a $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ solution of 2.5×10^{-2} mol Mo dm^{-3}, totalling 2.0 dm^3. The ionic strength of the solution was adjusted to 0.1 M using NH_4NO_3. The pH of the suspension was regulated at pH = 4.5 using HNO_3. Preliminary experiments have shown that under these conditions molybdic acid precipitation does not take place and the impregnating solution remains stable for several days. The suspension was kept under stirring at constant temperature (25 °C) for 20 h and then it was filtered through membrane filters (Millipore, 0.22 μm). The resulting solid was dried at 120 °C for 2.5 h. Then it was calcined in air at 500 °C for 5 h. The MoO_3 loading of the calcined solid was determined using AAS (Hewlett–Packard A Analyst 300). The Co was deposited on the calcined Mo/γ-Al_2O_3 precursor solid by simple dry impregnation using a $Co(NO_3)_2$ aqueous solution. The final sample underwent the above-described thermal treatment. We symbolize this sample as EDF.

In the second sample the molybdenum species was deposited on the alumina surface by non-dry impregnation. The impregnating solution contained suitable amount of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in order to obtain the same loading as that of the above prepared EDF sample. The volume of the solution was 20 times larger than the total volume of the carrier's pores. No pH regulation took place. The suspension remained under stirring for 4 h at room temperature and pressure in a rotary evaporator and then the water was removed at 40 °C and 30 mbar. The prepared solid was dried and calcined as described previously. The Co phase was deposited as in the case of the EDF sample. We denoted this sample as NDI.

An aliquot of each of the above prepared samples was impregnated again with an amount of pure water equal to its pore volume and then it underwent the aforementioned thermal treatments for one more time. The re-impregnated samples are denoted as EDF-r and NDI-r. The catalysts in their oxidic form contained 8.3 wt% MoO_3 and 2.08 wt% CoO.

2.2. Characterization of the specimens and determination of their catalytic activity

The catalysts prepared were characterized using N_2 adsorption measurements (BET), UV–vis diffuse reflectance spectroscopy (DRS), laser Raman spectroscopy (LRS) and NO chemisorption. Full experimental details concerning the above characterization techniques have been reported elsewhere [43,44].

The HDS activities over the catalysts studied were determined using a continuous-flow tubular fixed-bed microreactor operating in a differential mode at atmospheric pressure [45]. The catalyst samples (50 mg) were presulfided in situ, with a stream of 15% (v/v) hydrogen sulfide in hydrogen, for 2 h at 400 °C. The reaction mixture was prepared by passing hydrogen through a flow evaporator filled with liquid thiophene at 0 °C. After an aging period of 15 h under the stream of the reaction mixture the rate of thiophene HDS was determined over each catalyst at 320 °C. A gas chromatograph (Pye Unicam) equipped with a flame ionization detector and a column (8 m × 1/8 in. o.d.) filled with carbowax 20 M on chromosorb P A.W. was used for analyzing of the effluent of the reactor. HDS rate was defined as r = Fx/W, where F is the molar flow-rate (mol min^{-1}) of thiophene at the reactor inlet, x the conversion measured and W the weight (g) of catalyst used. Under our experimental conditions the rate-determining step was the surface reaction for all catalysts studied.

3. Results

3.1. Catalytic activity

The rates of HDS determined over the catalysts studied are presented in Fig. 1. These are expressed as the mol of thiophene converted per minute and gram of catalyst. It may be seen that the catalytic activity of the EDF sample is higher than that of the NDI one. This confirms our previous findings that EDF provides more active catalysts as compared to those prepared following conventional impregnation [33,34,40–42]. Moreover, it may be observed that the re-impregnation of the above catalysts with pure water influences their activity. More precisely, the NDI-r sample exhibited higher activity than that exhibited by its parent sample. This is the most important finding of the present work. In contrast, the activity of the EDF-r sample is lower than that of the corresponding parent sample.

Taking into account that under our experimental conditions the surface reaction is the HDS rate-determining step, the differences in activity mentioned above should be related with the different surface characteristics achieved using the different preparation techniques or treatments. Therefore, in the following sub-sections we deal with the influence of the re-impregnation on important surface characteristics of the catalysts studied.

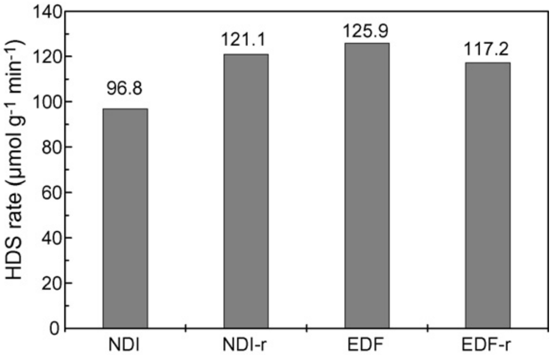

Fig. 1. Rates of thiophene hydrodesulfurization achieved over the catalysts studied.

3.2. Specific surface area (SSA)

Inspection of Table 1 shows that the SSAs of the catalysts prepared are similar and too close to the SSA of the alumina support. This indicates that relatively small supported crystallites are formed on the support surface. These cannot provoke a high extent plugging of the carrier thin pores and thus a considerable decrease in SSA, irrespectively of the preparation procedure followed. However, the impregnation of the parent samples with pure water seems to provoke a slight increase in their SSAs. This result provides the first, indeed too weak, evidence that re-dispersion of supported phases takes probably place upon re-impregnation.

3.3. NO chemisorption

The values achieved for the NO uptake by the sulfided CoMo/γ-Al_2O_3 catalysts are compiled in Table 1. It is known that the NO uptake is a good estimate of the concentration of sulfur vacancies. These are considered to be responsible for the acceleration of various hydrotreatement reactions [46,47]. Assuming constant density for the sulfur vacancies the NO uptake may be used as an approximate measure of the Mo-phase surface and thus of the Mo dispersion. On the other hand, NO is also adsorbed, in addition, on the supported cobalt and thus NO uptake would be used for estimating the supported Co surface and Co dispersion. Therefore, the NO uptake would be used for estimating the dispersion of the total active phase provided that a constant stoichiometry is assumed concerning the NO adsorption. Taking into account the above and the values compiled in Table 1 it may be inferred that the EDF sample exhibit higher dispersion of the active phase than the NDI one. Moreover, it may be concluded that the re-impregnation of the NDI (EDF) sample provoked an increase (decrease) in the dispersion of the active phase. These results confirm the above mentioned evidences for a re-dispersion of the supported phases brought about by the re-impregnation of the parent samples.

Table 1
Catalysts prepared, specific surface areas (SSA), uptake of chemisorbed NO, fraction of tetrahedral Mo (R_1) and octahedral Co (R_2) formed on the catalytic surfaces

Catalyst	SSA ($\text{m}^2\ \text{g}^{-1}$)[a]	NO uptake[b] (μmol g^{-1})	R_1[a]	R_2[b]
NDI	113	35.6	0.55	0.20
NDI–r	116	51.8	0.51	0.28
EDF	112	57.2	0.56	0.31
EDF–r	117	50.2	0.54	0.26

[a] values obtained in the oxide state.
[b] values obtained in the sulfide state.

The plausible question is whether the re-impregnation changes exclusively the dispersion of the active phase not affecting the structural characteristics of the Mo and Co supported species. In this respect it would be useful to study the influence of the re-impregnation on these characteristics using diffuse reflectance and laser Raman spectroscopies.

3.4. Diffuse reflectance spectroscopy (DRS)

Supported Mo: The DR spectra of the CoMo/γ-Al_2O_3 catalysts are illustrated in Fig. 2. Inspection of these spectra in the region 200–400 nm, where the supported Mo species absorb [37,48–50], demonstrates that both the impregnation method followed and the re-impregnation with pure water somewhat influence the symmetry of the supported molybdenum. This is manifested by the values of the ratio R_1 ($R_1 = F(R)_{265}/[F(R)_{265} + F(R)_{305}]$) compiled in Table 1.

In the above ratio by $F(R)_{265}$ and $F(R)_{305}$ we denote the values of the Kubelka–Munk functions of the bands at 265 and 305 nm attributed, respectively, to monomeric tetrahedral and polymeric octahedral Mo-oxo species. Thus, R_1 can be considered as a measure of the fraction of the tetrahedral Mo-oxo species. The relatively high R_1 ratio observed in the EDF sample shows that this method leads to catalyst with relatively high amount of tetrahedral Mo. This may be easily explained taking into account the selective adsorption of the monomeric, versus the polymeric, species on the γ-alumina surface during the equilibration step of the EDF [51]. On the other hand, the impregnation of the parent samples with pure water diminishes slightly the above ratio.

Supported Co: According to the literature [52,53] the triple band centred at about 600 nm is attributed to tetrahedral Co^{2+}. This presumably indicates the presence of the catalytically inactive $CoAl_2O_4$. On the other hand the absorption at 425 nm is attributed to cobalt species in octahedral symmetry. Thus, the following ratio of the Kubelka–Munk functions of the corresponding bands $R_2 = F(R)_{425}/[F(R)_{425} + F(R)_{600}]$ can be considered as a measure of the fraction of the octahedral cobalt species in the samples. The values of this ratio are compiled in Table 1.

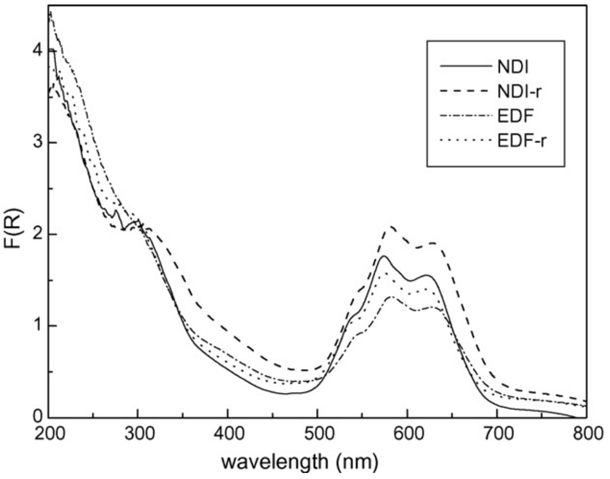

Fig. 2. DR spectra of the CoMo/γ-Al_2O_3 catalysts recorded in the range 200–800 nm.

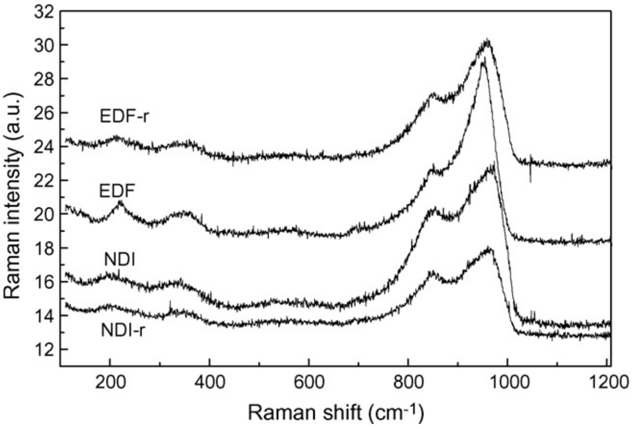

Fig. 3. LR spectra of the CoMo/γ-Al_2O_3 catalysts.

It may be seen that the magnitude of the triple band (Fig. 2) and the aforementioned ratio (Table 1) are changed with the impregnation method and the re-impregnation with pure water of the parent samples as well. More specifically, it may be observed that the EDF sample exhibited the maximum fraction of the octahedral cobalt and the minimum concentration of the tetrahedral cobalt species. Moreover, it may be seen that the re-impregnation of the NDI (EDF) sample brings about an increase (decrease) of the fraction of the octahedral cobalt and thus a decrease (increase) of the concentration of the tetrahedral cobalt species.

3.5. Laser Raman spectroscopy (LRS)

The LR spectra of the catalysts studied are presented in Fig. 3. According to the literature, the monomeric Mo species exhibit LR bands at about 320 and 920 cm^{-1}, whereas the well-dispersed polymeric ones (identified as hepta- or octamolybdates) exhibit bands at about 220, 360, and 960 cm^{-1} under ambient conditions. A band centred at ca. 870 cm^{-1} is attributed to the Al–O–Mo bridges [54–57]. In contrast, bands at ca. 820, 945, and 952 cm^{-1} are attributed to the bulk $CoMoO_4$, while a band at ca. 696 cm^{-1} and a sharp peak at ca. 820 cm^{-1} are characteristic of bulk cobalt and molybdenum oxides, respectively [58,59]. Inspection of Fig. 3 shows that formation of bulk cobalt oxide, molybdenum oxide and $CoMoO_4$ should be excluded on the catalysts studied.

4. Discussion

4.1. Impregnation technique and surface characteristics of the catalysts studied

The replacement of the NDI by EDF technique causes three important effects: (a) the considerable increase of the dispersion of the active phase (results of NO uptake), (b) the increase of the tetrahedral Mo (DRS) and (c) the remarkable increase of the octahedral cobalt at expense of the tetrahedral one, presumably at expense of the $CoAl_2O_4$ (DRS). The following picture may be used for interpreting these effects. Following EDF the deposition of the Mo species take places, upon the equilibration of the suspension, through adsorption of the monomeric and polymeric Mo species. It is well-established that this deposition mode results to catalysts with better dispersion than that achieved by bulk precipitation of the Mo phase as it is the case, at least partly, for the catalyst prepared by NDI [22].

The different modes of deposition related with EDF and NDI explain, moreover, the relatively high portion of tetrahedral Mo in the EDF sample. Following NDI a considerable portion of the Mo supported phase is deposited by precipitation of the octahedral polymeric species. This is because these species predominate in the concentrated Mo solution resulted due to the progressive evaporation of the initial impregnation solution [51]. In contrast, following EDF a considerable portion of the Mo supported phase is deposited by adsorption of the monomeric, tetrahedral, Mo species though at pH = 4.5, where the equilibration of the suspension takes place, the polymeric Mo species predominate. In fact, the selective adsorption of the monomeric Mo species on the γ-alumina surface has been well-established [51].

Finally, we have to justify the remarkable increase of the octahedral cobalt at expense of the $CoAl_2O_4$. This may be easily attributed to the relatively large surface coverage of the support surface by the supported Mo phase achieved in the EDF sample. This inhibits the contact of the Co species with the support surface somewhat preventing the formation of the $CoAl_2O_4$.

4.2. The influence of the re-impregnation on the surface characteristics of the catalysts studied

The re-impregnation of the NDI sample causes two important effects: the considerable increase of the dispersion of the active phase (results of NO uptake) and the remarkable increase of the octahedral cobalt (DRS). The following picture may explain both effects. Re-impregnation causes the selective dissolution of the badly dispersed (and not so strongly interacted with the support surface) Mo and Co species. In fact, it was confirmed experimentally that upon re-impregnation with pure water a fraction of the initially precipitated Mo- and Co-phase is dissolved (14.6% of the Mo and 4.3% of the Co). Similar results have been reported by Cordero and Agudo who studied the effect of water extraction on the surface properties of Mo/Al_2O_3 and $NiMo/Al_2O_3$ hydrotreating catalysts [60]. The re-deposition of Mo species is then followed mainly, but not exclusively, through adsorption leading to an increasing coverage of the support surface by the Mo supported phase. In fact, the Mo adsorption is favoured as the pH of the solution developed into the pores of the catalyst upon re-impregnation is expected to be acidic provoking thus a positive charging of the alumina surface. In this acidic pH the adsorption of Co cations, being in the solution upon re-impregnation, is prohibited. Therefore, the Co cations are deposited mainly by precipitation upon the subsequent step of drying. However, the above mentioned increase of the support coverage by Mo phase inhibits the contact of the precipitated Co species with the support surface preventing thus the high extent formation of the $CoAl_2O_4$. Thus, the deposition of octahedral Co on the molybdena surface is favoured.

The re-impregnation of the EDF sample caused the opposite effects, namely a decrease in the dispersion of the active phase (results of NO uptake) and an increase of the tetrahedral cobalt at expense of the octahedral one (DRS). Keeping the aforementioned picture we may rather easily explain these effects: In the EDF sample the Mo phase had been deposited *exclusively* by adsorption which had provided the maximum coverage of the support surface by the Mo phase and a relatively large portion of octahedral cobalt supported on this phase. Again, it was found experimentally that upon re-impregnation with pure water a fraction of the initially precipitated Mo- and Co-phase is dissolved (8.2% of the Mo and 10.6% of the Co). The re-impregnation of this sample caused a partial decrease of this very high surface coverage. This is, presumably, because the re-deposition of the Mo phase has taken place partially by precipitation in the re-drying step. The aforementioned reduction is rather expectable if one takes into account that precipitation is related to relatively low dispersion compared to the adsorption imposed by EDF. The decrease of the surface coverage favoured the contact of the dissolved Co species with the bear support surface and thus the increasing formation of $CoAl_2O_4$.

4.3. Surface characteristics and catalytic behaviour

The change of the impregnation technique or the modification of the preparation procedure brought about changes in the dispersion of the active phase and in the portion of the supported octahedral cobalt as well. The above considerations indicated that these effects are closely related. This is clearly visualized in Fig. 4 which illustrates the linear relationship between the NO uptake and the ratio R_2.

In view of the above it is plausible to attribute the changes in the catalytic activity described in the sub-section 3.1 to the aforementioned changes in the surface characteristics. The linear increase of the HDS activity with the dispersion of the

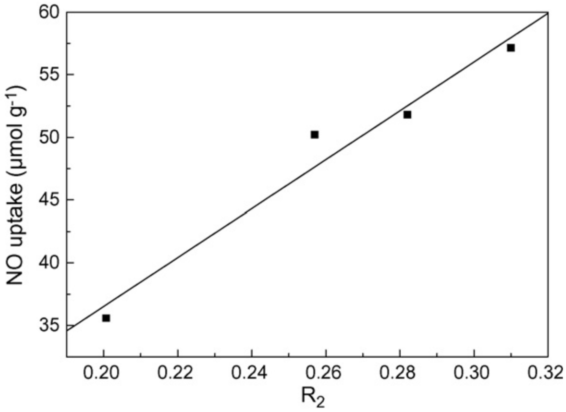

Fig. 4. The linear relationship obtained between the NO uptake of the CoMo/γ-Al_2O_3 catalysts and their fraction of octahedral Co estimated by the R_2 ratio (see Table 1).

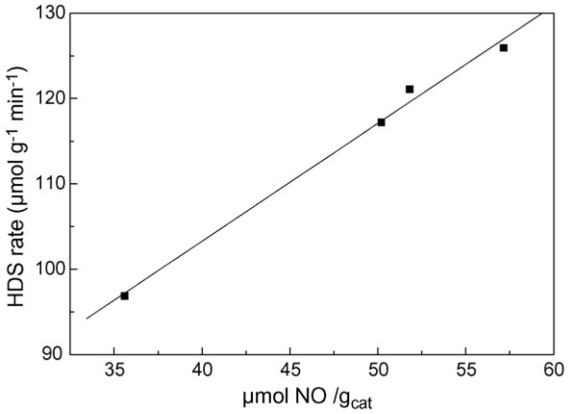

Fig. 5. The linear relationship of the HDS activity of the catalysts studied with the NO chemisorbed on their surfaces.

active phase is illustrated in Fig. 5. The interpretation is rather obvious: the increase of the active surface brings about an increase in the population of active sites (sulphur vacancies) and thus in the catalytic activity.

As the active surface is related linearly with the portion of the octahedral cobalt (Fig. 4) one may expect a linear relation between the latter parameter and the catalytic activity. This is illustrated in Fig. 6. This could imply the participation of the well-dispersed octahedral Co in the active sites. The literature corroborates this possibility. In fact, it is well known that well-dispersed octahedral cobalt on γ-alumina and/or molybdena surfaces is relatively easily reduced and/or sulfided. It is considered to participate in the formation of the active sites for HDS [3,61–64]. In fact, according to several investigators the cobalt ions have octahedral symmetry in the CoMoS phase considered as the active one [3]. Alternatively, according to Prins et al. [65,66], the sulfided species of the Co^{2+} in octahedral symmetry constitute the HDS active sites, whereas the supported molybdena simply *modifies* the support surface, inhibiting the formation of the catalytically inactive $CoAl_2O_4$. In view of the above considerations, which imply that the fraction of octahedral Co species remains virtually unchanged along the sulfidation process, the correlation obtained between the HDS activity and the fraction of the Co^{2+} in octahedral symmetry seems to be rather functional and not simply statistical.

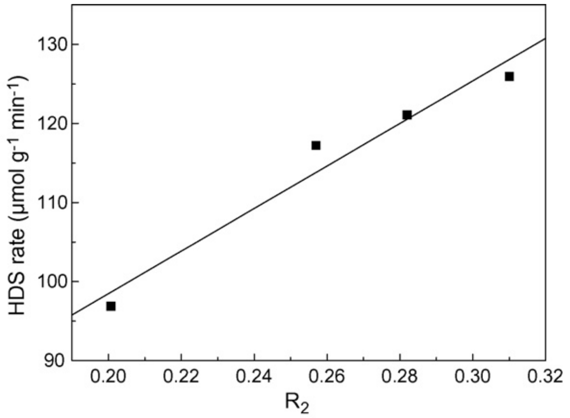

Fig. 6. The linear dependence of the HDS activity of the catalysts studied on the fraction of the supported Co in octahedral symmetry.

5. Conclusions

The following conclusions may be drawn from the present work:

1. The re-impregnation of two CoMo/γ-alumina catalysts, prepared by non-dry impregnation (NDI) or equilibrium deposition filtration (EDF) for depositing the Mo phase and dry impregnation for depositing the Co phase, with pure water resulted to partial dissolution and re-dispersion of the Mo and Co supported oxidic phases.
2. Concerning the catalyst prepared following the conventional preparation methodology (NDI), re-impregnation resulted to an increase of the active surface and of the portion of the well-dispersed octahedral cobalt and thus to relatively high catalytic activity.
3. The opposite effects were observed for the EDF catalyst.
4. For the parent samples it was confirmed that the replacement of the conventional impregnation (NDI) by equilibrium deposition filtration results to catalysts with relatively high active surface and high portion of the well-dispersed octahedral cobalt. Thus, to catalysts with relatively high HDS activity.

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