

Preparation of (Co)–Mo-based hydrodesulphurization catalysts: characterizations of deposited species on lanthanum modified γ -alumina

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Received 18 March 1997; accepted 21 November 1997

Abstract

The preparation of La-doped hydrodesulphurization (HDS) catalysts is investigated by deposition of Mo and Co from solutions containing their salts on a gamma alumina previously modified by impregnation with lanthanum nitrate solutions and further calcined at 773 K. Whatever the pH of the impregnating solution, the $n_{\text{Mo}}/n_{\text{La}}$ atomic ratio in the oxide precursor always governs the nature of the adsorbed oxomolybdenum entities and a model of Mo distribution on the surface of the support is proposed. The Mo surface distribution is mainly attributed to the selective adsorption of monomeric MoO_4^{2-} species on sites associated with La whereas poly-oxomolybdates adsorb on the alumina sites. Presence of the promotor (Co) does not modify the Mo distribution. In addition, it is shown that the presence of La in the catalyst formulation induces a decrease of the thiophene HDS conversion due to the preferential adsorption on the lanthanum hydroxyl groups of the oxomolybdate species present in the impregnating solution as isolated monomeric entities which are less easily sulphided, when deposited on the support, than the poly-oxomolybdates. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Co–Mo-based catalysts; Alumina modified by La; Hydrodesulphurization

1. Introduction

Innovation in the development of Co–Mo– Al_2O_3 and Ni–Mo– Al_2O_3 catalysts has been driven by the need to produce clean fuels, based on the pressing requirement for environmental protection. Extensive studies on these hydro-treating (HDT) catalysts [1] revealed that a high dispersion of MoS_2 nanocrystallites on alumina and a precise location of Co or Ni promotor

atoms on these crystallites is required for a good HDS activity. Although alumina is the most widely used support, in the last few years much attention has been paid on the beneficial role of other supports. Indeed, other solids such as carbon [2], silica [3], zeolites [4], titania [5] or zirconia [6] have been proposed as carriers of the active HDS phase. Some studies have revealed that some of them could be an interesting alternative to alumina. For example, compared to alumina, the HDS intrinsic activity of Mo/ ZrO_2 based catalysts was higher. Neverthe-

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less, these carriers have textural properties (i.e., specific surface area, pore volume, density and mechanical properties) which are not always well adapted for their use in industrial HDT plants. So researches on alumina modified with various doping agents have been undertaken and many elements such as phosphorus, halogens, zirconium, have been tried to be incorporated in the catalysts formulations. However, the results are not always clear. If in some cases the use of a given modifier has a beneficial effect [7], the same element can be considered as an inhibitor in other studies [8]. Indeed, the modifications of the catalytic performances drastically depend on the method of preparation and on the amount of introduced modifier. Much less attention has been paid to the use of lanthanide elements as possible alumina modifiers in HDS catalysts formulation whereas these elements are well known for their ability to stabilise γ -Al₂O₃ at very high temperatures [9], in particular in the preparation of car exhaust catalysts. In the present study, the preparation and characterisation of Mo/La–Al₂O₃ and Co–Mo/La–Al₂O₃ catalysts have been undertaken and these solids have been tested in HDS of thiophene. Based on their spectroscopic characterisations, a detailed description of the interactions between the molybdate entities and the La-doped supports is proposed which allows to explain the variation in thiophene conversion.

2. Experimental

2.1. Preparation of the supports

The supports were prepared by the incipient wetness impregnation method of a commercial γ -Al₂O₃ (pore volume: 1 cm³ g⁻¹; specific surface area: 350 m² g⁻¹) with solutions containing the appropriate amounts of lanthanum nitrate [La(NO₃)₃ · 6H₂O from Fluka]. The impregnated extrudates were dried at 393 K overnight and then calcined in air at 773 K for 4 h. The nomenclature of the studied samples is

La(*T*) where *T* is the La loading calculated in wt.% of La₂O₃.

2.2. Preparation of the catalysts

The (Co)–Mo based oxide precursors were prepared by the incipient wetness impregnation method of the doped La- γ -Al₂O₃ supports with ammonium heptamolybdate (AHM) and cobalt nitrate solutions containing the appropriate amounts of the active metals. In these solutions, ethylenediamine (En) was added to modify the solution pH and also to complex the Co species. The use of En allows to prepare Co–Mo based solids with rather high metal loadings as previously discussed [10]. [Co(NO₃)₂ · 6H₂O], [Mo₇O₂₄(NH₄)₆ · 4H₂O] and En are commercial products from Fluka. For comparison purposes, some Mo/Al₂O₃ solids were synthesised without En in the impregnating solution. The impregnated extrudates were dried at 383 K overnight and then calcined in air at 773 K for 4 h.

The nomenclature of the samples recalls the main parameters of the synthesis. Designation as α CoMo(X)[En]/La(*T*) concerns a sample where α is the atomic ratio $n_{\text{Co}}/(n_{\text{Co}} + n_{\text{Mo}})$, X the Mo loading in wt.% as MoO₃, *T* the La loading in wt.% as La₂O₃ and En when present in the impregnating solution. Co or En are omitted respectively for samples prepared without these species. A solid was prepared with nitric acid instead of the En and will be referred hereafter as Mo(X)[HNO₃]/La(*T*).

The Mo, Co and La contents were determined by X-ray fluorescence on the calcined samples by the ‘Service Central d’analyses du CNRS’ (Vernaison, France). For the XPS characterisation and before the catalytic tests, the calcined extrudates were sulphided in a flowing feed containing 10% of H₂S in H₂ (v/v) at 673 K for 2 h.

2.3. Characterisations

Laser Raman Spectroscopy (LRS) was performed using a Raman microprobe (XY from

Dilor) equipped with a photodiode array, which allows the analysis of selected particles. The exciting light source was an Ar⁺ laser emitting the 488 nm line with a power at the sample of ~ 10 mW.

X-ray Photoelectron Spectra (XPS) were recorded by using an AEI ES200B spectrometer equipped with an aluminium X-ray source working at 300 W. The binding energies BE have been measured by reference to the Al 2p peak of the support at 74.8 eV, a value generally encountered for γ -Al₂O₃. The surface atomic ratio $n_{\text{Mo}}/n_{\text{Al}}$, $n_{\text{Co}}/n_{\text{Al}}$ or $n_{\text{La}}/n_{\text{Al}}$ have been calculated from the XPS intensity ratio of the typical core levels (Mo 3d_{3/2-5/2}, Co 2p_{1/2-3/2}, La 3d_{3/2-5/2} and Al 2p_{1/2-3/2}). Since different Mo oxidation states may exist on the sulphided catalysts, a decomposition procedure to calculate the extent of molybdenum sulphidation has been used [11,12].

Ultra-Violet Spectra were obtained by Diffuse Reflectance Spectroscopy (DRS) in the 250–1100 nm spectral range with a diffuse reflectance accessory. Samples were placed in quartz cuvettes and were scanned against a pure alumina background.

Specific Surface Area (SSA) of the prepared samples were evaluated by the single point BET method using a Quantasorb Jr equipment. SSA accuracy is about 10%.

High resolution electron microscopy pictures were obtained on a Philips EM30 electron microscope. The powder, after sulphidation, was dispersed in alcohol for the preparation of the

grid. Based on the detection of more than 400 crystallites on several micrographs, the distribution of lengths of the elemental layers as well as their stacking can be obtained.

Catalytic activity for thiophene HDS was measured at atmospheric pressure in a flow-type reactor packed with 0.2 g of catalyst. The solids were first sulphided at 673 K for 2 h under a flow (100 ml min⁻¹) of a H₂S/H₂ (10/90) mixture and then cooled down to 573 K. After purification by vacuum distillation, thiophene was introduced in the reactor at constant pressure (50 Torr) in a flow of purified hydrogen (20 ml min⁻¹). The reaction products were analysed by gas chromatography.

3. Results

3.1. Supports

The first part of Table 1 presents the SSA results of the La–alumina supports. It shows that SSA remain quite constant at La₂O₃ loadings up to 25 wt.%, then a decrease is observed. This could be assigned to the formation of bulk La₂O₃ which has a very low specific area in accordance with literature data [13–15]. Nevertheless, at these high loadings, the SSA values correspond mainly to the one of the bare alumina if a correction is made to take into account the ‘dilution’ of alumina by more heavier La oxo-species. For example, sample La(35) has an effective SSA of 240 m² g⁻¹ with 228 m² g⁻¹

Table 1
Specific surface area (SSA) of La–Al₂O₃ based solids

Supports	SSA (m ² g ⁻¹)	Mo-based catalysts	SSA (m ² g ⁻¹)	Co–Mo-based catalysts	SSA (m ² g ⁻¹)
Al ₂ O ₃	350	Mo(20)[En]	310	0.28CoMo(20)[En]	256
La(2)	324	Mo(20)[En]/La(5)	272	0.28CoMo(20)[En]/La(1)	234
La(5)	346	Mo(20)[En]/La(8)	297	0.28CoMo(20)[En]/La(1.5)	259
La(10)	326	Mo(20)[En]/La(16)	248	0.28CoMo(20)[En]/La(2)	254
La(15)	310	Mo(20)/La(16)	228	0.28CoMo(20)[En]/La(3)	247
La(20)	330	Mo(30)[En]/La(5)	238	0.28CoMo(20)[En]/La(3.5)	246
La(25)	320	Mo(30)[En]/La(7)	253	0.28CoMo(20)[En]/La(4)	245
La(35)	240	Mo(30)[En]/La(14)	215	0.28CoMo(20)[En]/La(10)	230
La(43)	220	Mo(30)[En]/La(20)	241	0.28CoMo(20)[En]/La(20)	270

being estimated for the contribution of not modified alumina. This shows that if bulk lanthanum oxide is formed at these high La loadings, it has not a perturbing influence on the pore texture of the alumina support.

Fig. 1 shows the evolution of the XPS intensity ratio $I_{\text{La}}/I_{\text{Al}}$ (La 3d and Al 2p core levels) vs. the bulk atomic ratio $n_{\text{La}}/n_{\text{Al}}$. Until 35 wt.% La as La_2O_3 (Fig. 1a), the evolution of the ratio $I_{\text{La}}/I_{\text{Al}}$ characterises a good La dispersion on the alumina surface with a monolayer-like coverage. A similar evolution was already reported in literature for solids prepared by a dry impregnation followed by a calcination at rather moderate temperatures [14–20].

For all the solids, the La 3d_{5/2} binding energy (BE) characterises La(III) species well dispersed in/on the alumina matrix ($835.9 \text{ eV} \leq \text{La } 3d_{5/2} \text{ BE} \leq 836.6 \text{ eV}$) [14,18,19]. Bulk La_2O_3 (La 3d_{5/2} BE = 833.2 eV by reference to the Al 2p BE at 73.5 eV [14]) is never observed, even at 43 wt.% of La_2O_3 . At this loading, this oxide is likely present but in a non-detectable amount by XPS or XRD. Indeed, only the features of $\gamma\text{-Al}_2\text{O}_3$ are detected by XRD on the La(43) support. By comparison with literature data (La 3d_{5/2} BE = 833.8 eV by reference to Al 2p BE at 73.5 eV [14]), the BE observed do not characterise the existence of LaAlO_3 , the formation of which is not evidenced by XRD.

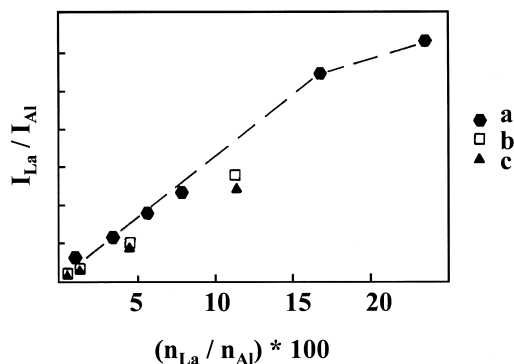


Fig. 1. XPS analysis of La based solids: $I_{\text{La}}/I_{\text{Al}}$ vs. the atomic ratio $n_{\text{La}}/n_{\text{Al}}$, (a) $\text{La}/\text{Al}_2\text{O}_3$ supports, (b) $\text{CoMo}[\text{En}]/\text{La}-\text{Al}_2\text{O}_3$ oxide catalysts, (c) $\text{CoMo}[\text{En}]/\text{La}-\text{Al}_2\text{O}_3$ sulphide catalysts.

From the aforementioned results, it can be deduced that dry impregnation of alumina by La^{3+} containing solutions conducts to a good dispersion of the La atoms up to $\sim 35 \text{ wt.}\%$ La as La_2O_3 without formation of well defined compounds such as LaAlO_3 or La_2O_3 . The observed SSA decrease is only due to the lowering of the relative proportion of alumina in the prepared solids.

3.2. Characterisations of $\text{Mo}/\text{La}-\text{Al}_2\text{O}_3$ catalysts

Table 1 (second part) also shows that the SSA of the Mo-based oxide precursors decrease with the Mo loading, a phenomenon generally reported in the literature [21]. The use of En which allows to deposit large amounts of Mo, confirm this trend. However, similarly to what was observed with La deposition, the SSA mainly corresponds to the dilution of alumina with more heavier Mo-oxo species.

Fig. 2 reports the Raman spectra of the calcined $\text{Mo}/\text{La}-\text{Al}_2\text{O}_3$ samples with various Mo and La contents. The observed features are assigned by reference to the literature data [22] on the species usually observed on Mo-based catalysts, i.e., adsorbed monomeric tetrahedral entities (main lines at 920 and 320 cm^{-1}) or the polymolybdate phase (main lines at 950 and 340 cm^{-1}). The identification of the supported species, reported in Table 2, shows that the nature of the adsorbed species mainly depends on the relative amount of Mo and La.

Whatever the pH of the impregnating solution which contains the monomeric MoO_4^{2-} ions at pH above 8 and mainly the polymeric oxomolybdate entities at lower pH, polymolybdates are observed on the prepared solids with high $n_{\text{Mo}}/n_{\text{La}}$ ratio as usually observed in classical Mo–alumina catalysts. When the $n_{\text{Mo}}/n_{\text{La}}$ ratio decreases, the relative amount of monomeric entities increases and for $n_{\text{Mo}}/n_{\text{La}} \approx 1$, only monomolybdates are observed on the calcined precursors. In addition to the characteristic lines

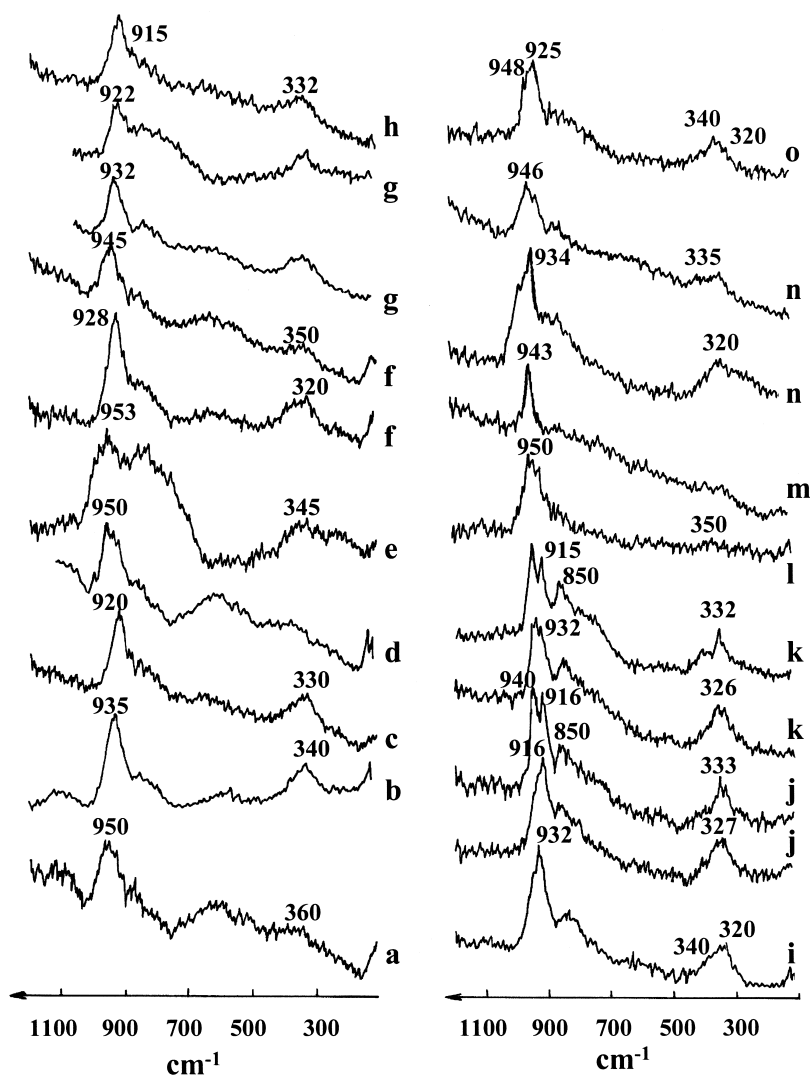


Fig. 2. Raman spectra of calcined Mo/La-Al₂O₃: (a) Mo(17)[En]/La(4); (b) Mo(17)[En]/La(12); (c) Mo(17)[En]/La(20); (d) Mo(20)[En]/La(4); (e) Mo(20)[En]/La(5); (f) Mo(20)[En]/La(8); (g) Mo(20)[En]/La(16); (h) Mo(20)[En]/La(20); (i) Mo(20)/La(16); (j) Mo(20)/La(20); (k) Mo(20)[HNO₃]/La(20); (l) Mo(30)[En]/La(5); (m) Mo(30)[En]/La(8); (n) Mo(30)[En]/La(16); (o) Mo(30)[En]/La(20).

of molybdates (monomeric and polymeric species), Raman features of a well defined compound are observed for solids prepared without En whereas such features are never evidenced when impregnation is performed with En. In such cases, the spectra of some catalyst particles show new sharp lines (915, 940 cm⁻¹) which are characteristic of a well defined compound. In spite of some differences, these lines could be assigned to La molybdate by reference to

literature data [23] obtained on a crystalline bulk oxide. When this compound exists on the oxide form of the catalysts, it could only be present in a small amount in an amorphous state as it is not detected by XRD. Therefore the differences noted by reference to the spectrum of the well crystallized La molybdate could be assigned to crystal field effects in the crystalline compound which induces a splitting of the Raman lines. Formation of La molybdate should be due to a

Table 2
Raman analysis of calcined Mo/La–Al₂O₃ with various Mo and La contents

Catalysts	$n_{\text{Mo}}/n_{\text{La}}$ bulk ratio	ν (cm ⁻¹) ^a	Adsorbed species ^b
Mo(17)[En]/La(4)	4.8	950(st), 580(br), 360(br)	pMo
Mo(17)[En]/La(2)	1.6	935(st), 925(sh), 340(br)	mMo + pMo
Mo(17)[En]/La(20)	1.0	920(st), 330(br)	mMo
Mo(20)[En]/La(4)	5.6	950(st), 580(br), 360(br)	pMo
Mo(20)[En]/La(5)	4.5	953(st,br), 345(br)	pMo
Mo(20)[En]/La(8) ^c	2.8	(1) 945(st), 350(br) (2) 928(st), 320(br)	pMo mMo + pMo
Mo(20)[En]/La(16) ^c	1.4	(1) 932(st), 340(br), 320(br) (2) 922(st), 320(br)	mMo + pMo mMo
Mo(20)[En]/La(20)	1.1	915(st), 332(br)	mMo
Mo(20)/La(16)	1.4	932(st), 340(br), 320(br)	mMo + pMo
Mo(20)/La(20) ^c	1.1	(1) 940(st,Sh), 916(Sh), 850(br), 330(br) (2) 916(st), 326(br)	mMo + pMo + La molybdate ^d mMo
Mo(20)[HNO ₃]/La(20) ^c	1.1	(1) 948(Sh), 915(Sh), 850(br), 332(br) (2) 932(st), 326(br)	mMo + pMo + La molybdate ^d mMo + pMo
Mo(30)[En]/La(5)	6.8	950(st), 350(br)	pMo
Mo(30)[En]/La(8)	4.8	943(st)	pMo
Mo(30)[En]/La(16) ^c	2.4	(1) 946(st), 335(br) (2) 934(st), 320(br)	pMo mMo + pMo
Mo(30)[En]/La(20)	1.7	948–925(st), 340–320(br)	mMo + pMo

^a(br) = broad; (sh) = shoulder; (Sh) = sharp; (st) = strong.

^bpMo = polymolybdate; mMo = monomeric molybdate.

^cAs some heterogeneity is detected on some selected particles, two sets of results are sometimes presented.

^dPresence of La molybdate is discussed in the text.

partial redissolution of the La during Mo impregnation without En in the solution and further precipitation of a precursor which will conduct to this compound after calcination.

3.3. Characterisations of CoMo[En] / La–Al₂O₃ catalysts

3.3.1. Oxide catalysts

As for the Mo-based catalysts, Table 1 (third part) confirms that the decrease of the SSA of the Co–Mo catalysts is the result of the alumina support dilution by heavier elements.

Fig. 3 shows the Raman spectra of some CoMo(20)[En]/La–Al₂O₃ calcined catalysts with various La loadings. At low La loading (1 wt.% La₂O₃), the spectrum exhibits a line at 950 cm⁻¹ which characterises adsorbed polymolybdates. Upon increasing the La loading, this line shifts to 920 cm⁻¹. As for the solids without promotor (Co), it appears that the nature of the Mo adsorbed species depends on the

La loading with preferential formation of monomolybdates at high La loadings.

XPS characterisation of 0.28CoMo[En]/La–alumina catalysts in the oxide form indicates that both the La 3d_{5/2} and Mo 3d_{5/2} BE are constant at 853.6 (±0.2) and 233.1 (±0.2) eV, respectively, whatever the La and Mo contents. These values correspond to the presence of well dispersed La(III) species on alumina and Mo(VI) oxo species respectively. The intensity ratios $I_{\text{La}}/I_{\text{Al}}$ (Fig. 1, part (b)) are not very much modified after impregnation with the solution containing the elements constituting the promoted active phase (Mo + Co) and En. The Co 2p_{3/2} BE at 781.8 (±0.3) eV characterise Co(II) species in oxide environment as currently observed in commercial catalysts. It is not possible to state on the presence of a small amount of well dispersed Co(III) entities. Indeed Grimblot [24] have shown that the ratio $I_{\text{sat}}/I_{\text{pp}}$ (sat: satellite peak; pp: principal peak) drastically decreases if some octahedral Co(III) species are

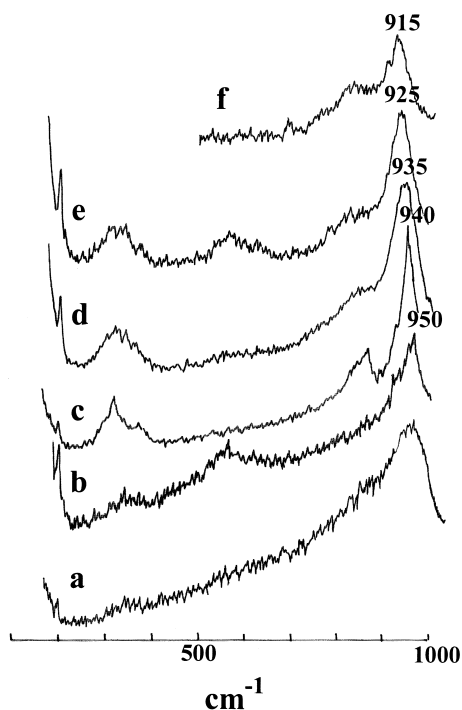


Fig. 3. Raman spectra of $\text{CoMo(20)[En]/La-Al}_2\text{O}_3$ calcined catalysts: (a) $0.28\text{CoMo(20)[En]/La(1)}$; (b) $0.28\text{CoMo(20)[En]/La(1.5)}$; (c) $0.28\text{CoMo(20)[En]/La(2)}$; (d) $0.28\text{CoMo(20)[En]/La(3)}$; (e) $0.28\text{CoMo(20)[En]/La(10)}$; (f) $0.28\text{CoMo(20)[En]/La(20)}$.

present on the solid. Indeed, all the spectra have intense satellite peaks and no significant difference is observed when comparing the ratios $I_{\text{sat}}/I_{\text{pp}}$ (0.85 to 1.10). The presence of Co(II) entities is confirmed by DRS of the calcined solids, the spectra of which show the triplet (540, 580, 630 nm) characteristic of the surface ' CoAl_2O_4 ' species [25]. The features of LaCoO_3 , of bulk Co_3O_4 or of CoMoO_4 are not observed by XPS nor by XRD and the atomic ratio $n_{\text{Co}}/n_{\text{Al}}$, as determined by XPS, of the same order or higher than the bulk $n_{\text{Co}}/n_{\text{Al}}$ ratio, shows that Co is well dispersed in/on the alumina lattice.

3.3.2. Sulphided catalysts

High Resolution Electron Microscopy pictures of some sulphided $\text{CoMo[En]/La-Al}_2\text{O}_3$ samples indicate the presence of well dispersed MoS_2 crystallites as single layers whatever the

$n_{\text{La}}/n_{\text{Mo}}$ ratio. It was not possible to detect amorphous grains almost completely covered by MoS_2 layers in all the cases. The quantitative analysis in term of density of crystallites, as described by Eijsbouts et al. [26], has not been undertaken.

The XPS data obtained on the sulphided catalysts do not provide evidence of La sulphidation as already observed by Mauchausé [27] on bulk La_2O_3 or by Cui et al. [17] on La-doped alumina. The XPS ratios $I_{\text{La}}/I_{\text{Al}}$ do not change after sulphidation (Fig. 1c), confirming that this activation procedure does not modify the La dispersion. Fig. 4 shows the XPS spectra of the Mo 3d level of some sulphided catalysts. At low La loading, the well resolved Mo 3d doublet is characteristic of the presence of MoS_2 as currently observed for $(\text{Co})\text{Mo}/\text{Al}_2\text{O}_3$ catalysts. At high La loading a broadening of this doublet is observed. Spectrum broadening in XPS may have different origins, one being due to differential charging effects. In the present study, all

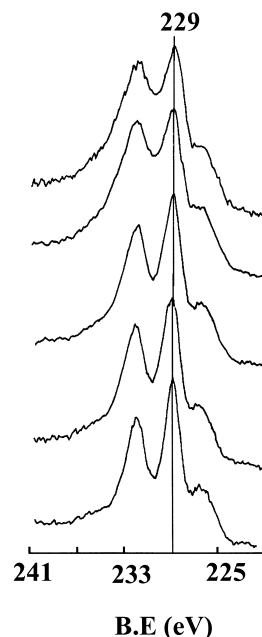


Fig. 4. XPS spectra of the Mo 3d level for some sulphided catalysts: (a) $0.28\text{CoMo(20)[En]/La(1)}$; (b) $0.28\text{CoMo(20)[En]/La(2)}$; (c) $0.28\text{CoMo(20)[En]/La(3)}$; (d) $0.28\text{CoMo(20)[En]/La(10)}$; (e) $0.28\text{CoMo(20)[En]/La(20)}$.

the samples are rather similar in terms of electrical conductivity as alumina is the main component and, therefore, the Mo 3d doublet broadening is assigned to the presence of different Mo chemical states. In addition to Mo(IV) of MoS₂, it remains Mo(VI) species showing that a non negligible amount of Mo is not sulphided. The sulphidation level of the 0.28CoMo(20)[En] solids, determined by decomposition of the Mo 3d feature into three doublets varies from $\approx 85\%$ to $\approx 45\%$ upon increasing the La loading up to 20 wt.% as La₂O₃. The difference between the Co 2p_{3/2} BE and the Mo 3d_{5/2} BE is 550.1 eV. This value is characteristic of the well known CoMoS phase [28]. At high La loading, an increase of the Co 2p_{3/2} full width at half maximum (FWHM) is observed. Such a broadening could be due to the X-ray induced emission of Auger electrons from La which have similar kinetic energies. However, as such Auger emission is low for La, this broadening could be

also assigned to the presence, after sulphidation, of several Co entities sulphided or not [10].

3.4. Thiophene conversion

In Table 3 are reported the thiophene HDS conversion of some catalysts. Upon increasing the La loading and whatever the Mo loading, a decrease of the activity is observed. This effect is more important for the solids prepared without En in the impregnating solution. If Mo and CoMo catalysts at equivalent La loading are compared, the promotion factor (conversion ratio between promoted and unpromoted catalysts at the same Mo loading) remains constant at about 6. Table 3 also shows that the activity of the Mo[En] catalysts at constant $n_{\text{Mo}}/n_{\text{La}}$ ratio is the same whatever the Mo loading. So the most important effect of La is to inhibit the thiophene HDS conversion by limiting the level of Mo sulphidation. For samples prepared without En, the lowering of activity has also to be related to the presence on the oxide precursor of a well defined compound identified by LRS as being probably La molybdate.

Table 3
Thiophene conversion (mol%) of some (Co)Mo/La–Al₂O₃ sulphided catalysts

Catalysts	Conversion (%)
La(20)	0
Mo(17)[En]/La(4)	4.3
Mo(17)[En]/La(12)	3.0
Mo(17)[En]/La(20)	3.0
Mo(20)/En	6.1
Mo(20)(En)/La(5)	4.9
Mo(20)[En]/La(8)	3.9
Mo(20)[En]/La(16)	3.0
Mo(20)	6.0
Mo(20)/La(16)	2.0
Mo(20)[HNO ₃]/La(20)	2.4
Mo(30)/En	7.0
Mo(30)[En]/La(5)	5.0
Mo(30)[En]/La(8)	4.4
Mo(30)[En]/La(16)	3.5
Mo(30)[En]/La(20)	3.3
0.28CoMo(20)/En	38
0.28CoMo(20)[En]/La(1)	35
0.28CoMo(20)[En]/La(1.5)	35
0.28CoMo(20)[En]/La(2)	34
0.28CoMo(20)[En]/La(3)	34
0.28CoMo(20)[En]/La(3.5)	36
0.28CoMo(20)[En]/La(10)	22
0.28CoMo(20)[En]/La(20)	18

4. Discussion

4.1. Supports

This study confirms that the impregnation of alumina with a La nitrate solution induces a good dispersion of La in a monolayer structure on the alumina surface. The formation of the well defined LaAlO₃ compound is not evidenced and bulk La₂O₃ is not detected up to 35 wt.% La as La₂O₃. The presence of this oxide has been sometimes reported in the literature at very high La loading [14,15], but it appears that the preparation method as well as the calcination temperature have a great influence on its formation [14]. Some authors have also evidenced the presence of LaAlO₃, which induces a good thermal stability of γ -Al₂O₃. Neverthe-

less, its formation is generally not observed on solids calcined at temperatures below 500°C [15,29,30]. The limit of good dispersion of La on alumina observed in this study (≈ 35 wt.% of La_2O_3) corresponds to a mean occupied surface area of 19.3 \AA^2 per La atom, a value already obtained by Xie and al. [16]. Some authors proposed that the adsorption of La occurs via a condensation reaction of La oxyhydroxyls species with the Al-OH surface groups [17]. With further condensation, it is inferred that a fraction of the alumina surface is covered by La oxo species whereas the remaining part is free of La; their relative proportion is dependent on the La loading.

4.2. Catalysts in the oxide form

The impregnation of La modified alumina with Mo or Co + Mo solutions induces a completely different distribution of the molybdenum species from the one usually observed on alumina supported oxomolybdates. It is shown that the relative amount of polymolybdates and monomolybdates present on the calcined catalysts depends drastically on the $n_{\text{Mo}}/n_{\text{La}}$ atomic ratio (Table 2). The presence of La induces an increase of the adsorption of Mo as monomeric entities. In most of preparations, the impregnating solution contains MoO_4^{2-} ions and $\text{Co}(\text{En})_3^{3+}$ complexes. Two hypotheses can be proposed to explain the obtained results.

1. La_2O_3 by itself is a basic oxide with an isoelectric point (IEP) of about 10. Moreover, Subramanian et al. [13] have shown that the alumina IEP increases with impregnation of La. So, it could be supposed that the IEP of alumina modified by La impregnation becomes higher than the pH of the solutions (about 9.5) containing Mo, Co and En. An electrostatic interaction between monomolybdates in the impregnating solution and the support should therefore occur. At low La loading, the IEP of the support is likely to be lower than the pH of the solution in the pore of the modified alumina carrier and such an electrostatic interaction should not occur.

In that case, the adsorption mechanism corresponds to the one described for pure alumina [10], i.e., polymerisation of MoO_4^{2-} into $\text{Mo}_7\text{O}_{24}^{6-}$ before interaction with the support during the drying step; the polymerisation which occurs during the drying step is due to the increase of Mo concentration and to the lowering of the pH induced by ammonia vaporisation.

2. The second hypothesis is based on the ionic exchange between the oxomolybdate entities present in the solution and the basic La-OH groups. Cui and al. [17] have indeed shown that the deposition of La on alumina induces the formation of hydroxyl groups different from those present on the pure alumina surface. They proposed a model in which each monomolybdate entity is linked to two La-OH groups. If such an adsorption process is occurring, polymolybdates would be detected by Raman spectroscopy on all the prepared oxide precursors as the atomic ratio $n_{\text{Mo}}/n_{\text{La}}$ is always higher than one (see Table 2). Adsorbed monomeric entities are observed for a ratio $n_{\text{Mo}}/n_{\text{La}} = 1$, while upon increasing this ratio, polymolybdates are identified by LRS. This allows to conclude to the adsorption of one monomeric entity on one surface La atom as schematically shown in Fig. 5. Monomolybdate in excess will then polymerise and adsorb on the free alumina surface upon drying as suggested by the first hypothesis (Fig. 5, parts A and B). On the other hand, for the solids prepared with an acid solution containing only polymolybdates; the Raman spectra indicate the presence of both isolated molybdates and polymolybdates. This observation implies partial transformation of heptamolybdate into monomeric molybdate in the pores of the support which has to be assigned to its basic character. Nevertheless under these impregnating conditions, a partial dissolution of the La atom likely occurs and the formation of a well defined compound, analogous to La molybdate is observed (Fig. 5, part C).

The simultaneous introduction of the promoter atom has apparently no effect on the nature of the surface oxomolybdate. Co is mainly pre-

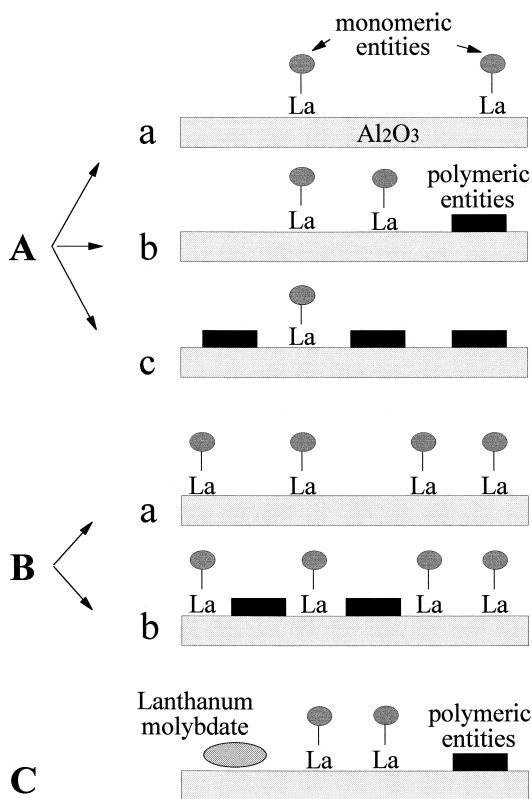


Fig. 5. Schematic description of the interactions between Mo-oxo species and the alumina surface modified by La as a function of the $n_{\text{Mo}}/n_{\text{La}}$ atomic ratio: (A) low La content: (a) low $n_{\text{Mo}}/n_{\text{La}}$ ratio; (b) intermediate $n_{\text{Mo}}/n_{\text{La}}$ ratio; (c) high $n_{\text{Mo}}/n_{\text{La}}$ ratio; (B) high La content: (a) low $n_{\text{Mo}}/n_{\text{La}}$ ratio; (b) intermediate $n_{\text{Mo}}/n_{\text{La}}$ ratio; (C) acid pH.

sent as Co(II) entities on the calcined solids and, due to the use of En, bulk Co_3O_4 or CoMoO_4 are not formed. As what was observed during impregnation of pure alumina [10], reduction of the Co(En)_3^{3+} entities occurs upon impregnation and calcination. However, the presence of Co(III) species in small amount could not be excluded definitively as the formation of a LaCoO_3 surface phase could occur. This has been suggested previously by Ledford et al. [20] for samples prepared by impregnation of Co on a La modified alumina support. However presence of LaCoO_3 , if it is formed, is in a very small amount as it has not been evidenced by spectroscopic characterisations. Presence of molybdate entities likely avoids its formation.

4.3. Sulphided catalysts and HDS activity

It appears that the deposition of a (Co)Mo phase on La– Al_2O_3 supports does not allow to increase the thiophene HDS conversion. This is mainly due to the presence, on calcined catalysts, of isolated monomolybdates adsorbed on La sites which are more difficult to sulphide than the polymolybdates, as evidenced by the XPS (Fig. 4).

At high La loading, the increase of the FWHM of the Co $2p_{3/2}$ level is characteristic of the presence of several Co entities [10] which are likely formed by the sulphidation of the well dispersed Co atoms as no Co_3O_4 nor CoMoO_4 are evidenced on the oxide precursor. The chosen Co loading corresponds to the optimum promotion currently observed for HDS catalysts, the sulphidation extent of which is high [10]. Due to the low Mo sulphidation level observed for the samples with high La loading, there should exist an excess of promotor atom which, therefore, is transformed into Co_9S_8 during the sulphidation step. Taking into account the CoMoS model and due to the low Mo sulphidation level, one may consider that Co is in excess to fully decorate the MoS_2 platelets because of the poor sulphidation of monomeric entities.

If impregnation is performed without En, a decrease of thiophene conversion is observed, which is also correlated to the presence on the oxide precursor of isolated tetrahedral entities poorly sulphided after activation. Moreover, a partial dissolution of La of the support occurs with concomitant formation of La molybdate which conducts to a lower activity for these solids.

5. Conclusion

We have shown that, whatever the pH of the impregnating solution, the final atomic ratio $n_{\text{Mo}}/n_{\text{La}}$ always governs the nature of the adsorbed oxomolybdenum entities in the oxide

precursors. The Mo surface distribution has been attributed to the selective adsorption of monomeric entities (MoO_4^{2-}) on basic La-OH groups whereas polymeric entities adsorb on the alumina surface sites. The surface monomeric La-Mo oxo-entities are not easily sulphided which induces a decrease of the thiophene HDS conversion. Moreover, upon impregnation with acid solution, a part of La is extracted to form of a well defined compound similar to La molybdate. The presence of the promoter (Co) does not modify these results which show that the HDS conversion is also governed by the Mo/La ratio.

Acknowledgements

The authors are pleased to acknowledge both TOTAL Petroleum and the 'Conseil Régional de la Région Nord-Pas de Calais' for their financial support.

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