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# Decamolybdodicobaltate(III) heteropolyanion: structural, spectroscopical, thermal and hydrotreating catalytic properties

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## Abstract

The ammonium decamolybdodicobaltate(III) salt:  $(\text{NH}_4)_6[\text{Co}_2\text{Mo}_{10}\text{O}_{38}\text{H}_4] \cdot 7\text{H}_2\text{O}$  (here in  $\text{Co}_2\text{Mo}_{10}$ ) has been prepared and characterized. Then, their structural, spectroscopic and thermal properties have been investigated by some physical–chemical techniques as XRD, FT-IR, Raman, DRS, SEM–EDAX, TG, DTA, and temperature programmed reduction (TPR). According to these properties, some  $\text{Co}_2\text{Mo}_{10}/\gamma\text{-Al}_2\text{O}_3$  catalysts have been prepared by equilibrium impregnation of the support with aqueous solution of ammonium salts. The  $\text{Co}_2\text{Mo}_{10}$  isothermal adsorption on  $\gamma\text{-Al}_2\text{O}_3$  at room temperature has been also investigated in the Mo range of 15–150  $\mu\text{mol Mo/ml}$ . The hydrotreating (HDS of thiophene and HYD of cyclohexene) catalytic activity has been compared to both  $\gamma\text{-Al}_2\text{O}_3$  supported Anderson phase  $[(\text{NH}_4)_3[\text{CoMo}_6\text{O}_{24}\text{H}_6] \cdot 7\text{H}_2\text{O}$  (here in  $\text{CoMo}_6$ )] and Co–Mo conventional catalysts. The improving of activity for the  $\text{Co}_2\text{Mo}_{10}$  and  $\text{CoMo}_6$  based catalysts is related to the heteropolyoxometalates adsorption process as to preparative conditions; whereas, the different activity between heteropoly-systems are undoubtedly related to the particular structure of the  $\text{Co}_2\text{Mo}_{10}$  heteropolyanion. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Co–Mo/ $\gamma\text{-Al}_2\text{O}_3$  hydrotreating catalysts; Heteropolyoxometalates; Ammonium; Decamolybdodicobaltate(III)

## 1. Introduction

The development, characterization and exploitation of new catalysts based on heteropolyoxocompounds are exceptionally active and of fast expansion fields. The recently observed interest in such compounds is mainly centered on Keggin or Dawson species and on their acids of great use in heterogeneous and homogeneous catalysts [1]. However, there is a long Anderson type heteropolymolybdate and tungstate species with important structural redox and thermal properties [2–5]. These structures have shown to be bi- or tri-metallic oxide-precursor and either supported or as

bulks they can be employed in some catalytic processes [6–11].

In a general project for HPAC and HPOMs study and their use in heterogeneous catalyst, the ammonium decamolybdodicobaltate(III) salt (here in  $\text{Co}_2\text{Mo}_{10}$ ) has been prepared. Its heteropolyanion structure is related to Anderson type hexamolybdocobaltate(III) anion whose planar anion of  $D_{3d}$  symmetry was previously described in literature [2].

The scarce information about  $\text{Co}_2\text{Mo}_{10}$  anion is limited to Evans and Showel study [12]. These authors described this structure as derived from Co(III) Anderson phase and formed by joining two planar  $\text{CoMo}_5$  species resulting from the remotion of two  $\text{MoO}_2$  groups from two  $\text{CoMo}_6$  Anderson planar rings. In this arrangement, two octahedral  $\text{CoO}_6$  groups occupy the

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center of the heteropolyanion. All these structural features seem to have promising catalytic properties since the Co:Mo ratio is higher for  $\text{Co}_2\text{Mo}_{10}$  than for  $\text{CoMo}_6$  which has been successfully used for the preparation of hydrotreating Co–Mo/ $\gamma\text{-Al}_2\text{O}_3$  type catalysts [6].

This last system has some advantages over the conventional hydrotreating catalysts such as the suppression of calcination steps during the activation process. It is well-known that  $\text{CoAl}_2\text{O}_4$  species is formed during the thermal process therefore the decrease of active Co occurs [13]. On the other hand, the planar ring adsorption is good, leading to a catalyst with 8% of Mo and 0.8% of Co adsorbed ( $\text{g Mo}/100 \text{ g Al}_2\text{O}_3$ ) and  $\text{Co}/[\text{Co} + \text{Mo}] = 0.14$  ratio [6]. This catalyst has an activity which can be compared to the conventional catalyst activity. The purpose of this paper is to study the  $\text{Co}_2\text{Mo}_{10}$  heteropolyanion from its structural spectroscopic properties and its adsorption in alumina to be used as a precursor on hydrotreating process. Since there are no previous works about  $\text{Co}_2\text{Mo}_{10}$  in the catalysis field, the comparative study on Anderson phase results has been made. An attempt to establish some type of correlations between hydrotreating activity of supported  $\text{Co}_2\text{Mo}_{10}$  and structural, spectroscopic and thermal properties, XRD, SEM–EDAX, DRS, FT-IR, Raman and DTA–TGA physical–chemical techniques were employed on bulk and/or supported samples. Taking all these properties into account, the isothermal adsorption and the hydrotreating activity (HDS, HYD here in  $\text{H}_\text{S}$  and  $\text{H}_\text{Y}$ , respectively) of  $\gamma\text{-Al}_2\text{O}_3$ -supported  $\text{Co}_2\text{Mo}_{10}$  have been studied.

The hydrodesulfurization activity for the system under study is higher than the same activity for the  $\text{CoMo}_6$  based system. In addition, the hydrogenation activity for  $\text{Co}_2\text{Mo}_{10}$  is higher than the same activity for commercial catalyst.

In this work, all these results are discussed on the basis of some important aspects: (a) heteropolyanion structural characteristics which give a higher reactivity to the catalyst surface; (b) catalysts preparation and activation.

## 2. Experimental

### 2.1. Synthesis and characterization of pure phase

The synthesis of the ammonium salt of decamolybdocobaltate(III) ( $\text{Co}_2\text{Mo}_{10}$ ) was carried out by the

slow precipitation from ammonium heptamolybdate (hereafter AHM) solutions and  $\text{Co}(\text{NO}_3)_2$  in stoichiometric amounts and oxidant appropriate conditions, according to the general method previously described [12]. The characterization of the species was carried out by X-ray powder diffraction (XRD), by means of a Philips PW 1714 diffractometer ( $\text{Cu K}\alpha$  radiation, Ni filter), and by infrared and Raman spectroscopy by means of a Bruker IFS 66 FT-IR spectrophotometer (KBr pellet technique) and a Bruker FTIFS interferometer (Nd-YAG laser,  $1064 \mu\text{m}$ ), respectively. Samples were also observed by scanning electron microscopy SEM using a Philips 505 electron microscope with an EDAX 9100 microsonde and energy dispersive detector.

### 2.2. Thermal analysis

TG and DTA measurements were carried out on a Shimadzu Thermoanalyzer (TGA-50 and DTA-50) working in an  $\text{N}_2$  stream. The heating rate was  $10^\circ\text{C min}^{-1}$  and the temperature was raised up to  $1000^\circ\text{C}$ .

Additional thermal studies were carried out in a furnace, using similar conditions to those of the DTA–TG measurements. These experiments provide a characterization of intermediate and pyrolysis residues.

### 2.3. Analysis by TPR

The TPR patterns of the ammonium salt of  $\text{Co}_2\text{Mo}_{10}$  were obtained by means of a home-made equipment. The reactor was fed with 10% of  $\text{H}_2$  reducing agent in  $\text{N}_2$  ( $100 \text{ cm}^3 \text{ min}^{-1}$ ) from 20 to  $1000^\circ\text{C}$ . The heating rate was  $10^\circ\text{C min}^{-1}$ . Similar TPR conditions were used in order to compare the present results with those previously obtained for pure  $\text{CoMo}_6$  Anderson phases [5]. The consumed  $\text{H}_2$  was detected by a conductimetric cell.

### 2.4. Adsorption isotherm and catalysts preparation

The adsorption isotherm of  $\text{Co}_2\text{Mo}_{10}$  ammonium salt on  $\gamma\text{-Al}_2\text{O}_3$  supports was obtained by the equilibrium impregnation of the support from salt aqueous solutions with concentrations from  $15\text{--}150 \mu\text{mol Mo/ml}$ .

The  $\gamma$ - $\text{Al}_2\text{O}_3$  powder support presents superficial area of  $226 \text{ m}^2/\text{g}$ , pore volume of  $0.65 \text{ cm}^3/\text{g}$  and a grain size of  $200 \mu\text{m}$ . The impregnation was performed at room temperature with excess of solution, in a continuous stirring for 24 h. Then, the solid was separated by centrifugation and it was dried in the heater at  $80^\circ\text{C}$ . The chemical analysis of the solutions before and after the impregnation were made by IL-457 atomic absorption spectrometer. With these results, the  $C_i$  (initial impregnant solution) and  $C_f$  (final impregnant solution) concentrations, expressed in mg metal/ml of solution were calculated. From these values and by means of a simple matter balance equation, it was possible to calculate  $C_a$  (adsorbed concentration of metal, such as Mo or Co) expressed in g M/g support. In addition, it was possible to obtain the total Mo and Co content as  $C_t$  (g M/100 g  $\gamma$ - $\text{Al}_2\text{O}_3$ ) from the addition of adsorbed  $M(C_a)$  + occluded  $M(C_o)$  in the pores where  $C_o$  is the M amount could result in an increase of the active species in the drying stage.  $C_o$  was evaluated according to a theoretical model as  $C_o = C_f \times V_o$ , where  $V_o$  is the pore volume.

The adsorbed Mo concentration  $C_a$ , [expressed as monolayer (%)] is plotted versus the Mo concentration in the solution in equilibrium ( $C_f$ ). It was found that the shape of the curve follows the Langmuir model [14,15]. Thus, by plotting the linearized form of the Langmuir equation [ $C_f/C_a = (1/K_{ad}S) + (C_f/S)$ ] and by extrapolating the subsequent straight line, it is possible to calculate the total number of active sites ( $S$ ), expressed in g Mo/g  $\gamma$ - $\text{Al}_2\text{O}_3$ . The equilibrium adsorption constant ( $K_{ad}$ ) expressed in ml/g Mo may also be obtained from the slope of the line.

Similar studies have been performed with AHM (AHM(VI) tetrahydrate Aldrich) with comparative purposes.

## 2.5. Analysis by diffuse reflectance spectroscopy (DRS)

The characterization of the pure and supported phases as well as of the pyrolysis remainders and intermediates was carried out by a UV–VIS Varian Super Scan 3 spectrophotometer, with double beam and built-in recorder. The  $\gamma$ - $\text{Al}_2\text{O}_3$  (support used in the catalyst preparation) was used as internal standard.

## 2.6. Catalytic activity measurements

The thiophene hydrodesulfurization and cyclohexene hydrogenation activity of the catalysts were measured in a high pressure reactor. The selected feedstock composition was cyclohexane (90%), cyclohexene (10%) and thiophene (15,000 ppm). The experimental conditions for the activity runs were: liquid flow rate  $0.353 \text{ ml min}^{-1}$ ; LHSV =  $56.3 \text{ l/h}$ ; total pressure:  $30 \text{ kg cm}^{-2}$  and reaction temperature:  $280^\circ\text{C}$ . The analysis of the product has been made by gas chromatography by means of a Varian Start 3400 Chromatograph, with FID detector. The catalytic activity was expressed as  $H_S$  (%) of thiophene and  $H_Y$  (%) cyclohexene conversion and calculated as the ratio from their final to the initial concentration. The samples were previously presulfurized, in situ, by using a mixture of thiophene and cyclohexene heated from RT up to  $300^\circ\text{C}$  for 1 h and then the temperature was lowered to  $280^\circ\text{C}$  using the technique previously described [6].

## 3. Results and discussion

### 3.1. Morphological and structural features

Fig. 1 shows the structure of the decamolybdodicobaltate(III) and Anderson heteropolyanions. The  $[\text{CoMo}_6\text{O}_{24}\text{H}_6]$  group is made up of a compact package of six  $\text{MoO}_6$  octahedra which are surrounding one  $\text{XO}_6$  in a planar hexagonal configuration, with approximative overall  $D_{3d}$  symmetry. According to Evans and Showell [12], the heteropoly-molecule ion

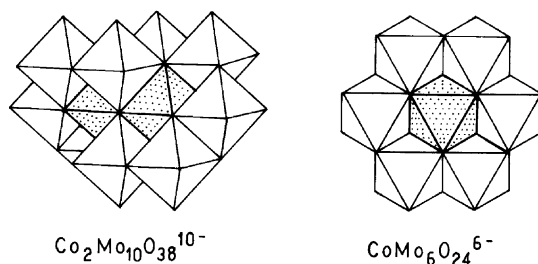


Fig. 1. Structure of the decamolybdodicobaltate (III),  $[\text{Co}_2\text{Mo}_{10}\text{O}_{38}]$  and Anderson hexamolybdocobaltate (III)  $[\text{CoMo}_6\text{O}_{24}]$  heteropolyanions.

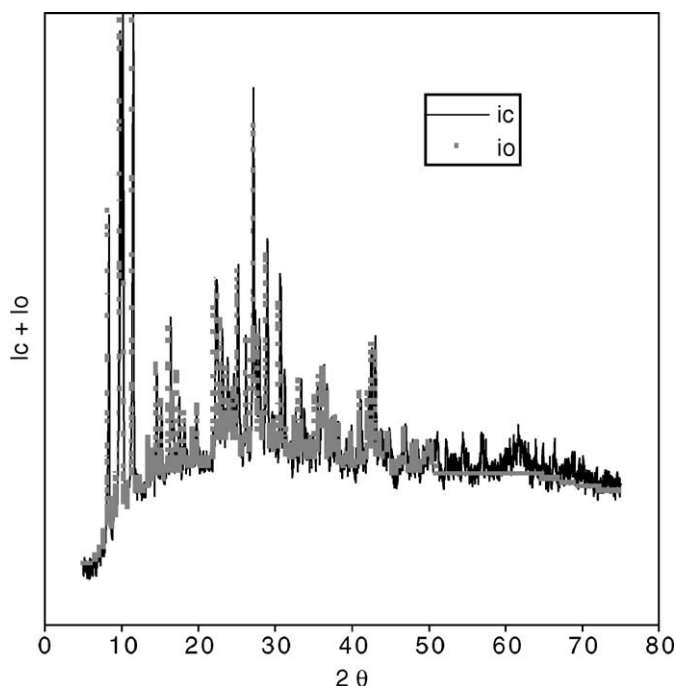


Fig. 2. Comparative XRD patterns of: ( $I_o$ ) observed and ( $I_c$ ) calculated for  $\text{Co}_2\text{Mo}_{10}$  ammonium salt powder.

$[\text{H}_4\text{Co}_2\text{Mo}_{10}\text{O}_{38}]$  conforms closely to an ideal point symmetry 222 ( $D_2$ ) and it may be considered as being derived from the Anderson ion by removing one  $\text{MoO}_2$  group from each of two hexa molecules, turning one  $180^\circ$  around  $\text{CoO}_6$  octahedron diagonal, and joining them so that the two  $\text{CoO}_6$  octahedra come together at the center sharing an edge. Fig. 2 shows the XRD pattern matching the observed ( $I_o$ ) and calculated ( $I_c$ ) spectra for  $\text{Co}_2\text{Mo}_{10}$  ammonium salt powder. The calculated data has been obtained by means of the FullProf 3.0.0 Apr 95-LLB-JRC Program [16] and the best adjustment between  $I_o$  and  $I_c$  has been obtained by using the crystallographics parameters for the form A, monoclinic, space group  $C2c$  or  $Cc$ ;  $a = 44.18 \pm 0.03 \text{ \AA}$ ;  $b = 12.60 \pm 0.01 \text{ \AA}$ ;  $c = 15.36 \pm 0.01 \text{ \AA}$ ;  $\beta = 106.89 \pm 0.02^\circ$ ;  $Z = 8$ ;  $V = 4 \times 2044 \text{ \AA}^3$  [12]. Fig. 3 shows the SEM micrographs of  $\text{Co}_2\text{Mo}_{10}$  and  $\text{CoMo}_6$  crystals. A clear difference in the morphology of the samples can be appreciated. The electron microprobe analysis by EDAX for  $\text{Co}_2\text{Mo}_{10}$ , reveals a Co:Mo ratio of 1:8.5 according to the theoretical value of 1:8.14.

### 3.2. Spectroscopic characterization

#### 3.2.1. Vibrational spectrum

In Table 1, it is shown the data for FT-IR and Raman vibrational spectra for  $\text{Co}_2\text{Mo}_{10}$  in  $4000\text{--}400 \text{ cm}^{-1}$  range. The assignment has been carried out taking into account the presence of different molecular unities. The spectrum can be divided into the following typical regions: (1)  $3600\text{--}2800 \text{ cm}^{-1}$  corresponding to the O–H and N–H stretchings; (2)  $1700\text{--}1400 \text{ cm}^{-1}$  the region of the O–H and N–H bendings; (3)  $1000\text{--}850 \text{ cm}^{-1}$  assignable to the Mo– $\text{O}_2$  terminal stretchings; (4)  $750\text{--}550 \text{ cm}^{-1}$  assignable to the Mo–O–Mo bridge stretchings (the vibrations of the Co– $\text{O}_6$  bonds and the water librations are also located in this last region). Between 550 and  $500 \text{ cm}^{-1}$ , it is possible to observe some bands attributable to the water librations. Below  $450 \text{ cm}^{-1}$ , the spectrum is rather difficult to analyze, the bending of the Mo–Ot and Mo–Ob bonds can be mixed with the Mo–Oc stretching vibrations. Likewise, the lattice modes are located below  $300 \text{ cm}^{-1}$ .

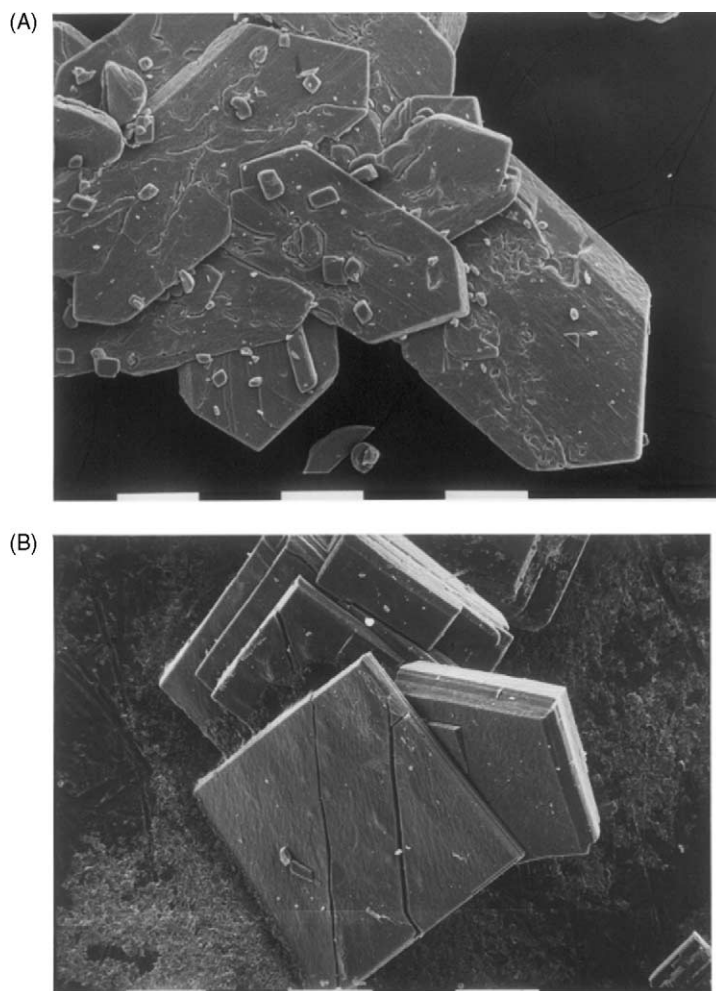


Fig. 3. SEM micrographs of ammonium salts of (A)  $\text{Co}_2\text{Mo}_{10}$  (magnification:  $140\times$ ; scale bar:  $100\text{ }\mu\text{m}$ ) and (B)  $\text{CoMo}_6$  (magnification:  $200\times$ ; scale bar:  $100\text{ }\mu\text{m}$ ).

In Fig. 4, both FT-IR and Raman spectra, are shown. These are identical to those obtained for the  $\text{CoMo}_6$  structure [3] and the FT-IR spectra are compared in Fig. 5. This study has been demonstrated that the  $\text{Co}_2\text{Mo}_{10}$  anion structure is related to the Anderson type structure which has the similar angular and bond lengths.

### 3.2.2. Diffuse reflectance spectra (DRS)

In Fig. 6, it is shown the DRS spectra for (a) pure specie and (b)  $\gamma\text{-Al}_2\text{O}_3$  supported specie of  $C_t = 7.03\text{ g Mo}/100\text{ g }\gamma\text{-Al}_2\text{O}_3$  from an aqueous solution

of the  $\text{Co}_2\text{Mo}_{10}$  ammonium salt (initial concentration  $C_i = 150\text{ }\mu\text{mol Mo}/\text{ml}$ ). The spectra show typical bands, on the UV region (200–350 nm):  $\text{Mo}\leftarrow\text{O}$  charge transfer bands characteristic for octahedral  $\text{Mo(VI)}$  centred around 270 nm. On the visible region (350–800 nm), there are two spin-allowed d–d transition bands typical for a regular octahedral configuration  $\text{Co(III)} (d^6)$  ion:  ${}^1\text{A}_{1g}$  ground state to the  ${}^1\text{T}_{1g}$  and  ${}^1\text{T}_{2g}$  higher states, falling in the 700–550 and 500–400 nm ranges, respectively [17]. The (b) spectrum shows clearly that the heteropolyanion is adsorbed on the  $\gamma\text{-Al}_2\text{O}_3$  without degradation since



Table 1  
Vibrational spectrum of  $\text{Co}_2\text{Mo}_{10}$  ammonium salt

FT-IR	Raman	Assignment
3650 m	3200 w	$\nu_1, \nu_3 \text{H}_2\text{O}$
3484 sh		
3421 s		
3172 vs		$\nu_1, \nu_3 \text{NH}_4$
3024 sh		$2\nu_4$
(a) 1600 s		(a) $\delta \text{H}_2\text{O}(\nu_2)$
(b) 1404 vs		(b) $\delta \text{NH}_4(\nu_4)$
(a) 942 vs	(a) 944 vs	(a) $\nu \text{S-Mo-Ot}$
(b) 899 vs	(b) 901 m	(b) $\nu \text{a-Mo-Ot}$
858 sh		
(a) 560 sh	(a) 410 sh	(a) Lib- $\text{H}_2\text{O}$
(b) 442 w	(b) 398 w	(b) $\nu \text{Mo-Oc}$
366 w		$\delta \text{M-O}$ ,
319 m	295 m	Lib- $\text{NH}_4$
265 sh	253 w	Lattice modes
230 sh		

Key: vs: very strong; s: strong; m: medium; w: weak; vw: very weak; sh: shoulder; br: broad.

$\text{Co(III)}$  does not change their electronic configuration and  $\text{Mo(VI)}$  species seem to have their original octahedral coordination for the typical polymeric species.

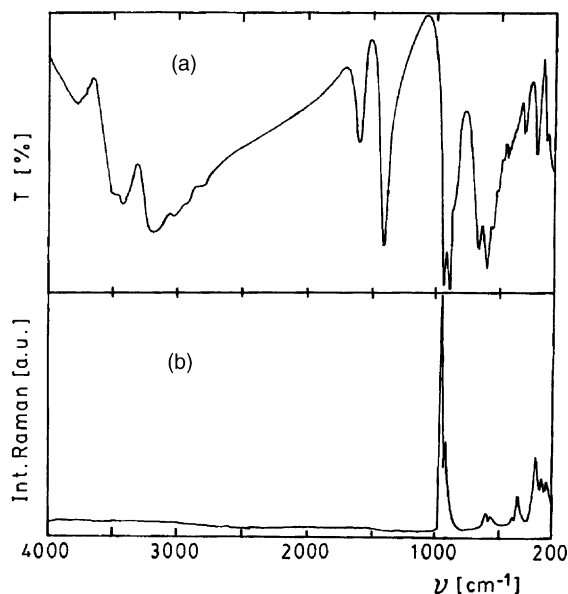


Fig. 4. (a) FT-IR and (b) Raman spectra of  $\text{Co}_2\text{Mo}_{10}$  ammonium salt (between 4000 and  $200 \text{ cm}^{-1}$ ).

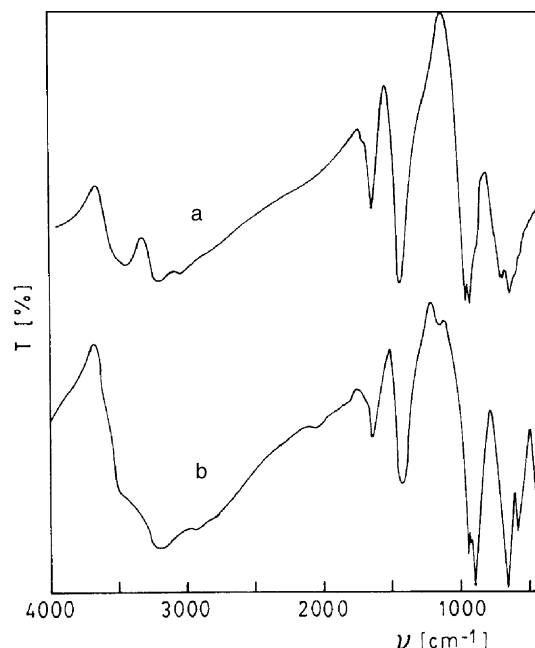


Fig. 5. Comparative FT-IR spectra of (a)  $\text{Co}_2\text{Mo}_{10}$  and (b)  $\text{CoMo}_6$  ammonium salts.

### 3.3. Thermal behavior

#### 3.3.1. TGA and DTA analysis

Fig. 7 shows the TG and DTA curves. It can be observed that the process occurs in five endothermic effects. The loss of crystallization water and ammonia molecules is lower compared to the analogous Anderson salt which has shown a four-step degradation thermal process [5].

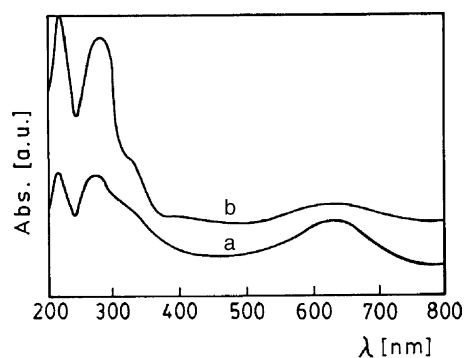
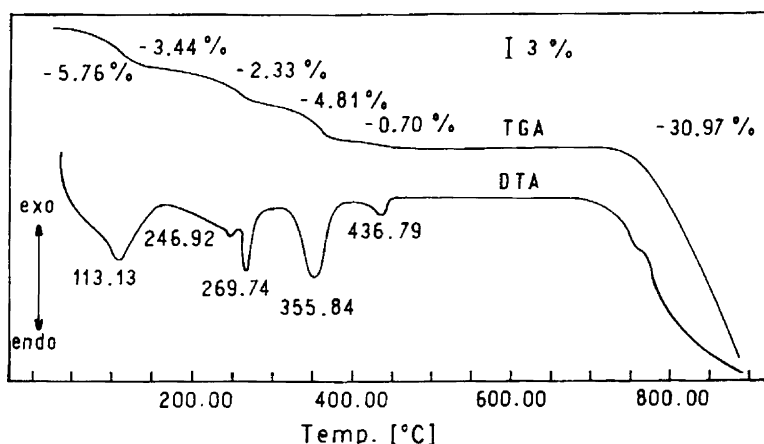
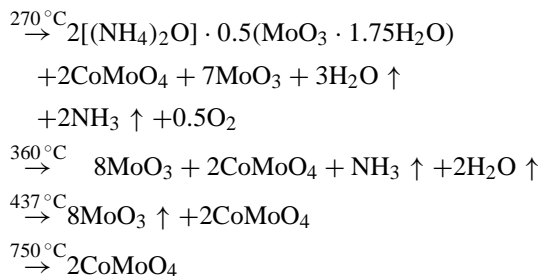
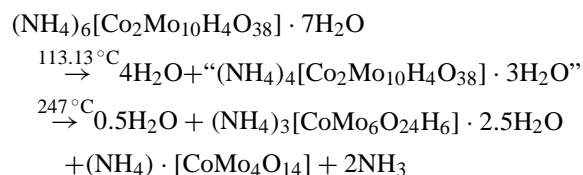


Fig. 6. Comparative DRS spectra for (a)  $\text{Co}_2\text{Mo}_{10}$  and (b)  $\gamma\text{-Al}_2\text{O}_3$  supported  $\text{Co}_2\text{Mo}_{10}$  (between 200 and 800 nm).

Fig. 7. TG and DTA curves for  $\text{Co}_2\text{Mo}_{10}$  ammonium salt.

In the first step, only 6.3 molecules of water are lost. The second endothermic peak at  $247^\circ\text{C}$  is correlated to the loss of 3.6 molecules of water and the formation of two different species: dehydrated  $[(\text{NH}_4)_3(\text{CoMo}_6\text{H}_6\text{O}_{24})]$  Anderson phase and incipient intermediated  $[(\text{NH}_4)_2\text{O}]_x\text{MoO}_3 \cdot z\text{H}_2\text{O}$  molybdic phase (PDF 23–0786). These results have been confirmed by FT-IR, XRD and SEM–EDAX complementary analysis for the sample treated in a crucible furnace at the appropriate temperature. Below  $360^\circ\text{C}$ , the thermal behavior is similar to the one observed later for the Anderson phase and involves the bond rupture and the loss of both crystallization and intramolecular water. The subsequent event involves the  $\text{MoO}_3$  and  $\text{CoMoO}_4$  formation, this last specie remains as final residue of decomposition. The vibrational spectroscopy study of intermediate and pyrolysis residue show that all these are crystalline compounds. As it is observed in Fig. 8, it is revealed the presence of bands corresponding to  $\text{Mo}=\text{O}$  and  $\text{Mo}-\text{O}-\text{M}$  bonds throughout all the thermal process, starting from the  $\text{Co}_2\text{Mo}_{10}$ , following the typical  $\text{MoO}_3$  and finishing with  $\text{CoMoO}_4$  spectra.

All these conclusions lead us to formulate the following scheme:



These results are in agreement with the  $\text{Co}_2\text{Mo}_{10}$  structural properties and confirm their Anderson structural relation.

### 3.4. TPR analysis

Because of the structural characteristics of the studied phase, the  $\text{Co}_2\text{Mo}_{10}$  TPR pattern, shown in Fig. 9, is compared with those of  $\text{CoMo}_6$  and AHM. In general, the TPR behavior of the condensed molybdates exhibits two typical regions of  $\text{H}_2$  consumption with increasing temperature. These regions correspond to  $\text{Mo(VI)} \rightarrow \text{Mo(IV)}$  and  $\text{Mo(IV)} \rightarrow \text{Mo(0)}$ , respectively [18]. However, it will be seen from the figure that the peak temperatures and the shapes of the patterns for the Co heteropolycompounds, differ appreciably from that of AHM. The main reason for differences is related with the presence of the  $\text{Co(III)}$  ion. In fact, the TPR patterns of HPOMs show some weak bands in the region of  $300\text{--}700^\circ\text{C}$  (close to an intense band of total reduction of  $800^\circ\text{C}$ ), assigned to the reduction of  $\text{Mo(VI)}$  to  $\text{Mo(V)}$  and  $\text{Mo(IV)}$  and



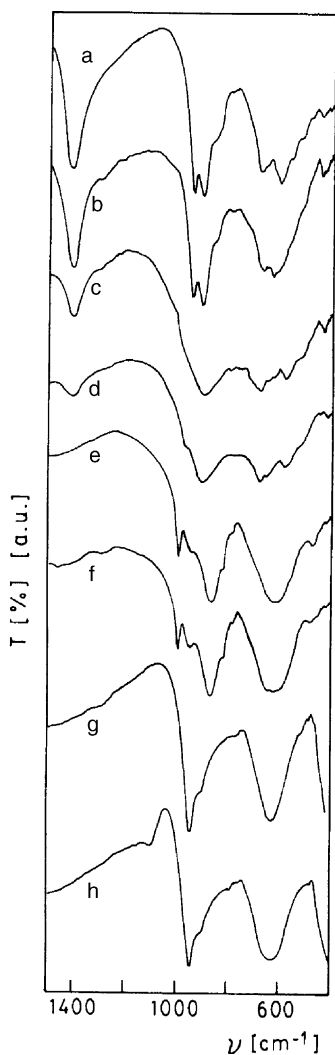


Fig. 8. Comparative FT-IR of samples of  $\text{Co}_2\text{Mo}_{10}$  corresponding to several stages of thermal treatment (in air atmosphere) from 1500 to  $400\text{ cm}^{-1}$ . Sample heated at: (a) room temperature; (b)  $120^\circ\text{C}$ ; (c)  $240^\circ\text{C}$ ; (d)  $270^\circ\text{C}$ ; (e)  $360^\circ\text{C}$ ; (f)  $440^\circ\text{C}$ ; (g)  $750^\circ\text{C}$ ; and (h)  $800^\circ\text{C}$ .

Co(III) to Co(II). Early studies about reducibility of some Anderson Phases as well as AHM, have shown that the first stage involves the formation of  $\text{Mo}_4\text{O}_{11}$  (Mo(V) containing mixed oxide) as an intermediate process which can be observed by ESR spectroscopy [5]. On the other hand, this study has clearly demonstrated that the Co ion produces a promoting effect by decreasing the reduction temperature of Mo(VI).

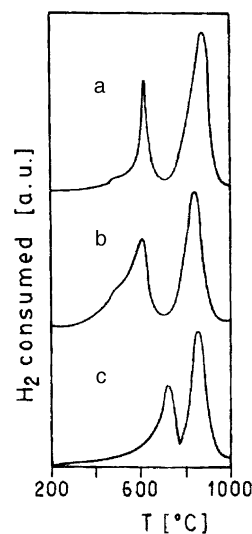


Fig. 9. TPR profiles of (a)  $\text{Co}_2\text{Mo}_{10}$ , (b)  $\text{CoMo}_6$ , (c) AHM.

### 3.5. Catalysts preparation and adsorption isotherms

The preparation of  $\text{Co}_2\text{Mo}_{10}/\gamma\text{-Al}_2\text{O}_3$  catalysts were made by equilibrium impregnation of the support with aqueous solution of the ammonium salts of  $\text{Co}_2\text{Mo}_{10}$  with a  $\text{Co}/[\text{Co} + \text{Mo}]$  ratio ( $r$ ) = 0.20. Fig. 10 shows the experimental results for adsorption. This isotherm shape responds to the Langmuir

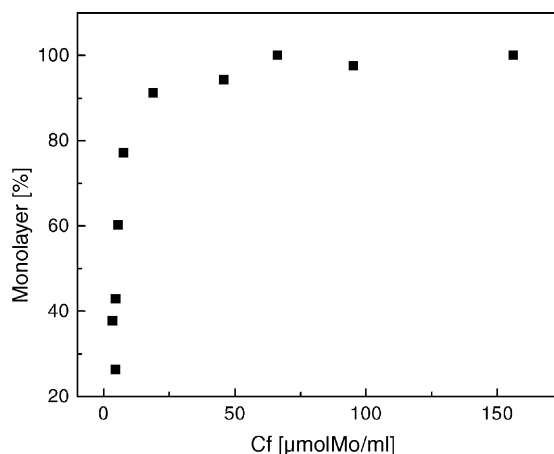


Fig. 10. Mo adsorption isotherm for  $\text{Co}_2\text{Mo}_{10}/\gamma\text{-Al}_2\text{O}_3$  samples as determined at room temperature.

Table 2

Adsorption parameters for  $\text{Co}_2\text{Mo}_{10}$  and  $\text{CoMo}_6/\gamma\text{-Al}_2\text{O}_3$  systems<sup>a</sup>

	$S$ (g $\text{Mo}_{\text{ads}}$ per g support)	$K_{\text{ads}}$ (ml/g Mo)	(at. wt Mo)/(nm <sup>2</sup> support)	$10^{23}S$ (at. wt Mo/g support)
$\text{Co}_2\text{Mo}_{10}$	0.065	1635	1.93	4.03
$\text{CoMo}_6$	0.09	1374	3.2	5.6
AHM	0.10	290	2.5	6.3

<sup>a</sup> AHM/ $\gamma\text{-Al}_2\text{O}_3$  included for reference purposes;  $K_{\text{ad}}$  = molybdenum adsorption constant;  $S$  = number of active sites on alumina surface.

model [14,15] and such shape indicates that there is an interaction between the heteropoly anion and the support as found for the  $\text{CoMo}_6$  case [6]. It can be noted that the Co content is slightly higher for the  $\text{Co}_2\text{Mo}_{10}/\gamma\text{-Al}_2\text{O}_3$  than for  $\text{CoMo}_6/\gamma\text{-Al}_2\text{O}_3$  where  $r = 0.14$  and the adsorbed Mo content in the monolayer is lower for the first system than for the Anderson system. Then, the obtained adsorption parameters are slightly different from those of  $\text{CoMo}_6$  Anderson specie. The adsorption parameters from the corresponding isotherms are given in Table 2, including the AHM/ $\gamma\text{-Al}_2\text{O}_3$  data with comparative purposes. Nevertheless, the observed differences reveal that the heteropolyanions adsorption process is not so simple, involving a complex equilibrium as it has been demonstrated recently for a series of Ni(II), Co(III), Cr(III), Al(III), and Te(VI) Anderson phases [19]. These species are adsorbed as monolayer and the deposition of the  $\text{D}_{3d}$  Anderson anion is an ideal quasi planar deposition for Co(III) specie and a convex distortion of this symmetry for NiMo<sub>6</sub>. For the  $\text{Co}_2\text{Mo}_{10}$  heteropolyanion, the symmetry ( $\text{D}_s$ ) is lower than for  $\text{CoMo}_6$ . According to the  $K$  data for the specie under study, its deposition process seems like the corresponding Anderson anion and it is probable that

the adsorption process occurs as a preferential event through any of the  $\text{D}_s$  symmetry planes of  $\text{Co}_2\text{Mo}_{10}$  heteropolyanion as it is shown in the model of Fig. 11. In addition, the lower  $S$  data indicates the lower Mo/Co stoichiometry ratio compared to the analogous  $\text{CoMo}_6$  value. Likewise, the monolayer corresponds to  $C_t$  values close to 7.03 g Mo/100 g  $\gamma\text{-Al}_2\text{O}_3$  (equivalent to 1.93 at. w Mo/nm<sup>2</sup>  $\gamma\text{-Al}_2\text{O}_3$ ). All these values are lower than those of  $\text{CoMo}_6/\gamma\text{-Al}_2\text{O}_3$  [6] as it is observed in Table 2.

### 3.6. Catalytic activity

The operative conditions for the hydrodesulfurization of thiophene and hydrogenation of cyclohexene activity measurements, have been selected according to the recent experience about the Anderson based systems because of the common structural and thermal properties between  $\text{Co}_2\text{Mo}_{10}$  and  $\text{CoMo}_6$  heteropolyanions. Therefore, the reaction temperature was 280 °C and all catalysts were presulfidate in situ at 320 °C for 1 h as it was previously established for different Anderson phases. These conditions have been established on the base of the results obtained from the thermal in both oxidizing and reducing

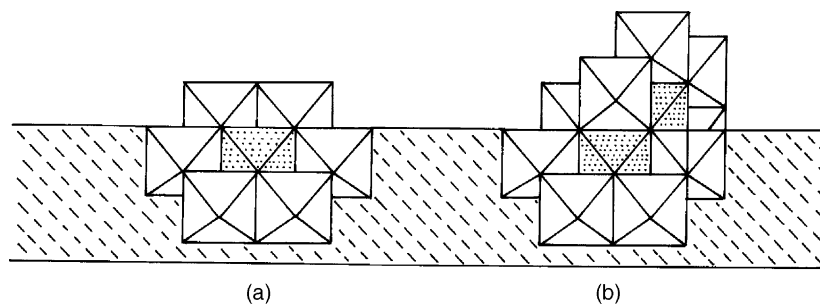


Fig. 11. Model for the ideal deposition of heteropolyanions on the support surface: (a)  $\text{CoMo}_6$ ; (b)  $\text{Co}_2\text{Mo}_{10}$  structures.

Table 3

Chemical; H<sub>S</sub>, H<sub>Y</sub> conversion and Mo and Co specific activity data for different catalysts

Catalysts	C <sub>t</sub> Co (%)	C <sub>t</sub> Mo (%)	H <sub>S</sub> (%)	H <sub>S</sub> /[Mo]	H <sub>S</sub> /[Co]	H <sub>Y</sub> (%)	H <sub>Y</sub> /[Mo]	H <sub>Y</sub> /[Co]
(1) Co <sub>2</sub> Mo <sub>10</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	1.05	7.03	75	10.67	71.43	30.90	4.40	29.43
(2) CoMo <sub>6</sub> /γ-Al <sub>2</sub> O <sub>3</sub>	0.84	8.75	68	7.77	80.95	25	2.85	29.76
(3) CoMo/γ-Al <sub>2</sub> O <sub>3</sub>	1.80	9.30	71	7.63	39.44	28	3.01	15.55

atmospheres [5]. After the reaction temperature is reached, steady state is rapidly achieved and activity was constant in the following 8 h of reaction for both systems.

In Fig. 12a and b, it can be observed that both H<sub>S</sub> and H<sub>Y</sub> conversions for the Co<sub>2</sub>Mo<sub>10</sub> system have a linearly increase from C<sub>t</sub> = 1.70 g Mo/100 g γ-Al<sub>2</sub>O<sub>3</sub> up to C<sub>t</sub> = 7.03 g Mo/100 g γ-Al<sub>2</sub>O<sub>3</sub>.

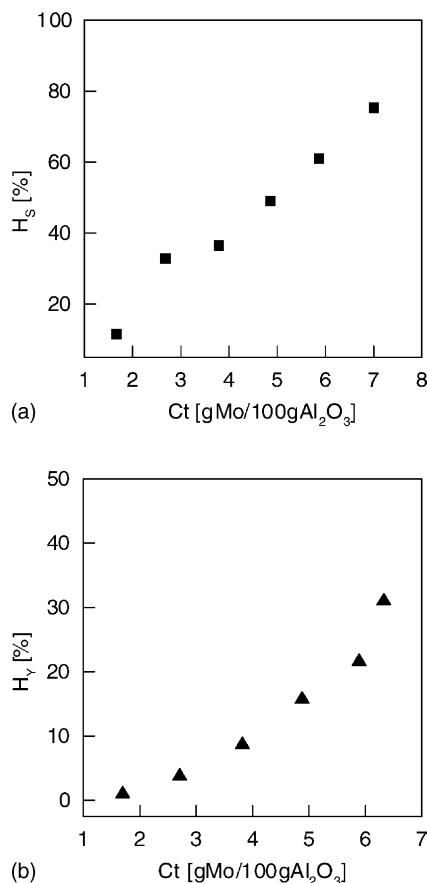


Fig. 12. Activity of the Co<sub>2</sub>Mo<sub>10</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalysts in the (a) H<sub>S</sub>; and (b) H<sub>Y</sub> reactions.

Table 3 shows the thiophene and cyclohexene conversion and H<sub>S</sub>/[M] and H<sub>Y</sub>/[M] specific activity (% conversion per Co or Mo amounts) obtained by (1) γ-Al<sub>2</sub>O<sub>3</sub> supported Co<sub>2</sub>Mo<sub>10</sub>; (2) γ-Al<sub>2</sub>O<sub>3</sub> supported CoMo<sub>6</sub>; and (3) γ-Al<sub>2</sub>O<sub>3</sub> supported Co–Mo conventional catalysts and both Co and Mo concentration data for the compared samples. It is interesting to remark that the conventional catalyst has over 50% Mo loading than the Mo value for (1) and over 100% Co loading than the Co values for (2) system. However, it is observed the unexpected H<sub>S</sub> and H<sub>Y</sub> catalytic behavior which can be summarized by the expression (a) and (b):

$$H_S(1) > H_S(3) > H_S(2) \quad (a)$$

$$H_Y(1) > H_Y(3) > H_Y(2) \quad (b)$$

However, if the behavior of different catalysts are analyzed taking into account the specific activity, the arrangement given in (a) and (b) can be changed especially for the H<sub>S</sub>/[Mo] and for H<sub>Y</sub>/[Co] by the following expressions:

$$\frac{H_S}{[Mo](1)} > \frac{H_S}{[Mo](2)} \cong \frac{H_S}{[Mo](3)} \quad (c)$$

$$\frac{H_Y}{[Co](1)} \cong \frac{H_Y}{[Co](2)} > \frac{H_Y}{[Co](3)} \quad (d)$$

The (c) and (d) expressions show an undoubtedly better performance for the heteropolymetallates catalytic systems which have lower metal content. This advantage seems to be related with the adsorptive interaction process which directly depends on the HPOMs structure properties.

The impregnation process of γ-Al<sub>2</sub>O<sub>3</sub> by means of heteropolymolybdate of planar or rather symmetric structure, results in a good interaction with the support leading to a uniform coverage on the surface as in CoMo<sub>6</sub> case. Also, the availability of metallic sites has been proved in our recent work about planar

D<sub>3d</sub> symmetry CoMo<sub>6</sub> [19]. Despite the fact that in Co<sub>2</sub>Mo<sub>10</sub>, the molecule (D<sub>2</sub> symmetry) is not planar, it has some symmetric planes through which an adsorptive interaction could be carried out as it is shown in the model of Fig. 11. This interaction, as explained above, could be performed preferentially throughout a molecular plane being one part of the molecule without direct interaction with the support and mostly exposed to the environment.

The little symmetry of Co<sub>2</sub>Mo<sub>10</sub> causes a steric effect that may enable the formation of small molybdenite crystals, which is the active phase of the catalysts. It is well-known that this specie grows lamellarly and it is even more active when the crystal is “decorated” at the edge sites by Co or Ni [20–23]. These characteristics give a greater reactivity to this catalyst surface, thus the Mo is easily sulfated, even though it has a lower Mo content compared to (2) and (3) catalysts. This result confirms the (c) expression for the hydrodesulfurization process.

As regards Co content, it can be observed that this is lower for heteropolyanion systems than for conventional catalysts with a similar Co:Mo ratio. Moreover  $H_Y/[Co]$  for (1) and (2) catalysts respectively are almost equal, which indicate that Co sites have similar accessibility for both catalysts in this process. This implies that even if there is a lower Co loading, the promoter effect is very important in the new catalysts, especially on the hydrogenation process. This fact may be due not only to above mentioned structural aspects, but also to the preparative conditions that involve the suppression of the calcination step. This enables, as it is well-known, the cobalt aluminize phase. All these aspects suggest that the obtained result for the hydrogenation process expressed in (d) is a consequence of the Co sites distribution in the new sulfide phases showing a synergic effect [24,25].

#### 4. Conclusions

- The  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support impregnation by HPOMs seems like an alternative method for hydrotreating catalysts preparation where HPOMs structure produces a good adsorptive interaction with the support and a uniform distribution of active sites on the catalysts surface.
- The catalytic activity for the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supported HPOMs is similar to that of conventional hydrotreating catalysts where  $r_{\text{Commercial}} = (0.25\text{--}0.4) > r_{\text{HPOMs}} = (0.14\text{--}0.2)$  (where  $r = [Co]/([Co] + [Mo])$ ). This fact involves the low consumption of Co but a high synergetic effect of this specie from HPOMs.
- It is observed a steric effect from the low symmetry molecules of the particular Co<sub>2</sub>Mo<sub>10</sub> catalytic systems which shows an unexpected reactive surface.
- The suppression of the calcination steps prevents the formation of CoAl<sub>2</sub>O<sub>4</sub> spinel and then the inactive cobalt.

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