Influence of cobalt content on the hydrotreatment catalytic activity of $CoMo_6/\gamma\text{-}Al_2O_3$ heteropolyoxomolybdate-based catalyst

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The influence of Co content in the catalytic activity in hydrotreatment reactions (hydrodesulfurization (HDS) of thiophene and hydrogenation (HYD) of cyclohexene) using $CoMo_6/\gamma\text{-}Al_2O_3$-type catalysts, where the precursor is Co(III) heteropolymolybdate of $(NH_4)_3[CoMo_6O_{24}H_6]\cdot 7H_2O$ formula and Anderson-type planar structure, (hereafter $CoMo_6$) was investigated. The preparation of catalysts was carried out by the coimpregnation of γ-alumina with $CoMo_6$ and $(NH_4)_6[TeMo_6O_{24}]\cdot 7H_2O$ ($TeMo_6$) in order to obtain catalysts with variable amounts of Co(III) keeping about the same Mo amount. The Anderson phase of Te(VI), ($TeMo_6$) was chosen because of its good solubility and because no promoting effect of the Te was observed in hydrotreatment. Five catalysts were prepared by coimpregnation of $\gamma\text{-}Al_2O_3$ by using aqueous solutions of both phases in different proportions. Catalysts with a ratio $[Co]/([Co]+[Mo])$ between 0 and $\sim$0.14 and a Mo loading (wt% Mo) between 8 and 10 were obtained. The Raman and diffuse reflectance (DR) spectroscopies were used for the characterization of bulk and supported $CoMo_6$ phase. By analyzing the respective adsorption isotherms and parameters and according to the catalytic tests, it could be established that HDS as well as HYD activities of the catalysts increase as a function of the added Co.

KEY WORDS: Co-Mo/$\gamma\text{-}Al_2O_3$-hydrotreating catalysts; heteropolyoxomolybdates; Co and Te Anderson phases.

1. Introduction

In recent years, the heteropolyoxometalates of Mo and/or W have became of great importance in the catalytic area, showing high activity in different industrial processes [1–3]. The use of these species as precursors of heterogeneous catalysts is very interesting since, compared to other systems, they show some advantages mainly related to their structure. Thus, they generally present a regular order that allows matching of different metallic elements ensuring uniformity in their deposition and offering redox and acid properties associated to the presence of the heteroatoms, which can also produce synergetic effects in catalytic processes [4,5].

In our laboratory, we have been studying the spectroscopic, thermal and catalytic behavior features of different Anderson phases [6–9] as well as their interaction with different supports. Such phases have a general formula of type $[XM_6O_{24}H_6]^{n-}$ with M = Mo, W, and X = Co, Cr , Rh, Al, Te, Ni, etc. Results indicate that in the presence of any heteroatom, the heteropolyoxoanion, which has a planar structure, is adsorbed on the alumina following an isotherm model of Langmuir type. Lying planar on the support, such planar structure may interact with the support, which results in a deformation of its structure and in a certain level of interchange with Al(III) ions of alumina surface [10].

In literature, there is a great amount of work regarding the Co(Ni)-Mo(W) system as catalysts for hydrotreatment (HDT) reactions where the association among those elements produces a synergetic effect that enhances the activity in these processes [11,12].

In recent studies about the use of Anderson phases as catalysts for hydrotreatment reactions, it was observed that the HDS activity of a $CoMo_6/\gamma\text{-}Al_2O_3$ catalyst, which has a ratio $[Co]/[Co]+[Mo]=0.14$ that is comparable to the one of a Co-Mo/$\gamma\text{-}Al_2O_3$ catalyst prepared in a conventional route with a ratio $r=[Co]/([Co]+[Mo])=0.25$–0.4 [4,5]. It was also observed that the Te phase did not show any synergetic effect. This result is very important since the Co amount used in the preparation of conventional catalysts is higher than in catalysts whose precursor is the Co Anderson phase.

The influence of this relationship was also observed with prepared catalysts using as precursor the ammonium decamolybdodicobaltate (III) salt (Co_2Mo_{10}, a nonplanar heteropolyanion resulting from condensation of two planar anions of Anderson type and synthesized by solution reaction). Indeed, the catalytic performances were better than those of the Anderson-based catalysts [13].

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The aim of the present work is to verify the promoting effect of Co in hydrotreatment reactions, analyzing catalysts with a Co amount adsorbed between 0 and 0.8% and a Mo amount around 8%, where the precursor is the heteropolymolybdate with "Anderson" planar structure.

2. Experimental part

2.1. Preparation of catalysts

The preparation of simple and mixed catalysts was carried out by coimpregnation in equilibrium of γ-Al_2O_3 (specific surface area: 226 m^2/g, pore volume: 0.36 cm^3/g and particle size: 200 μm) with aqueous solutions of $CoMo_6$ and $TeMo_6$ (pure or mixed). The mixed catalysts were prepared by using $TeMo_6$, which was chosen to keep a range of constant adsorbed Mo and to change the Co amount by varying the amounts of $CoMo_6$ in the mixed impregnating solutions. This procedure is based on the good water solubility of both phases and on the neutral character of Te in a hydrotreatment process.

The coimpregnation was carried out with a total volume of 6 cm^3 of solution per 0.5 g of alumina for each catalyst. The solution concentration varied from 15 to 120 μmol Mo/cm^3 for simple catalysts, whereas for mixed catalysts the solution concentration was 100 μmol Mo/cm^3. The solution volume composition for mixed catalysts (aCoMo$_6$ + bTeMo$_6$) was varied as indicated in table 1. Two simple catalysts based on $CoMo_6$ (No. 1) and $TeMo_6$ (No. 5) pure phases have been chosen with similar Mo loadings to compare the catalytic activity. The mixed catalysts (No. 2, 3 and 4) were prepared by using the solutions corresponding to $CoMo_6$ and $TeMo_6$ pure phases and were obtained with a concentration range of adsorbed Mo (C_a Mo) between 8 and 10% (g Mo/100 g γ-Al_2O_3). Such values correspond approximately to the monolayer values of both $CoMo_6$ and $TeMo_6$ supported on γ-Al_2O_3, and they come from the previous study of the respective adsorption isotherms on γ-Al_2O_3, which follow the Langmuir model. Basically, the process consists in the calculation of C_a (adsorbed concentration of Mo, expressed in g Mo/g support) by means of a simple mass balance equation using the values of C_i (initial impregnating solution) and C_f (final impregnating solution) concentrations, expressed in μmol Mo/cm^3 according to the expression: (I) $C_a = \{[(C_i - C_f) \times V]/m\}100$, where V is the initial impregnating solution volume and m is the γ-Al_2O_3 mass. C_i and C_f were obtained by means of atomic absorption spectrometry (AAS) of the initial and final solutions with a Spectrometer Il-457. The adsorbed Mo concentration C_a (expressed as monolayer (%) as well as g Mo/100 g γ-Al_2O_3) was plotted versus the Mo concentration in the solution in equilibrium (C_f). It was found that the shape of the curves follows the Langmuir model [10]. 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 was possible to calculate the total number of active sites (S), expressed in g Mo/g γ-Al_2O_3. The equilibrium adsorption constant (K_{ad}) expressed in mL/g Mo was also obtained from the line slope.

Table 1
Composition of impregnating solutions of (a) $CoMo_6$ and (b) $TeMo_6$ (in cm^3) used in the simple (No. 1 and No. 5) and mixed (No. 2 to No. 4) catalysts preparation

Catalyst	(a) $CoMo_6$ + (b) $TeMo_6$
1	6.0 $CoMo_6$ + 0.0 $TeMo_6$
2	4.5 $CoMo_6$ + 1.5 $TeMo_6$
3	3.0 $CoMo_6$ + 3.0 $TeMo_6$
4	1.5 $CoMo_6$ + 4.5 $TeMo_6$
5	0.0 $CoMo_6$ + 6.0 $TeMo_6$

Likewise, the different concentrations of adsorbed Co (C_aCo$_e$) (with e = experimental) are obtained, varying between 0 and 0.8%. From these data and considering the following: (1) the Co/Mo mass ratio of $CoMo_6$ phase is about 0.1; (2) the phase adsorption occurs maintaining such ratio independently of Te presence; the cobalt amount that should be adsorbed in mixed catalysts was calculated (C_aCo$_c$ with c = calculated). Finally, the ratio [Co]/([Co] + [Mo]) was calculated with the experimental values C_aMo and C_aCo$_e$. In addition, it was possible to obtain the total Mo and Co content as C_t (g M/100 g γ-Al_2O_3) by taking into account the Anderson anion occluded in the pores (from the addition of adsorbed M(C_a) + occludedM(C_o) in the pores). This results in an increase of the active species after 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 [4,13].

After the impregnation process, the solids were separated by centrifugation and were dried in the heater at 80 °C. The calcination step was avoided to prevent the formation of $CoAl_2O_4$ spinel, which induces the presence of inactive cobalt [4].

2.2. Spectroscopic characterizations

Pure (as bulk and aqueous solution) and γ-Al_2O_3-supported Co Anderson phase were characterized by Raman microprobe and DR spectroscopies.

The Raman spectra were recorded in the range of 100 to 1600 cm^{-1} with a Raman LabRAM Infinity microprobe (Jobin Yvon) equipped with a liquid nitrogen-cooled detector and a frequency-doubled Nd:YAG laser supplying the excitation line at 532 nm. The power at the sample was below 5 mW.

DR spectra were recorded in the wavelength range by a UV–vis Varian Super Scan 3 spectrophotometer, with double beam and built-in recorder; γ-Al_2O_3 (support used in the catalyst preparation) was used as internal standard.

2.3. Catalytic activity measurements

The catalytic activity measurements were carried out with a high-pressure reactor fed with hydrogen and a liquid phase, which is formed by a mixture of thiophene (15 000 ppm) in cyclohexene (10%) and cyclohexane (90%), with a flow of 0.353 cm^3/min, the spatial speed expressed as LHSV = 56.3 L/h, the reactor temperature was of 280 °C and the total pressure 30 kg/cm^2. The conversion of thiophene and cyclohexene was obtained by gaseous chromatography, by analyzing the liquid reagents before and after the reaction. Each sample was presulphided *in situ* by means of the technique described in previous works [4,5,13], which consisted of heating the sample under a flow of H_2S/H_2 (volumetric ratio 1/10) gaseous mixture from room temperature to a temperature of 280 °C and kept at this temperature for 1 h. Immediately, the gas current was changed to the feed current.

3. Results and discussion

3.1. Spectroscopic characterization of both pure and γ-Al_2O_3-supported catalysts

The analysis of the Raman spectra of pure (bulk and impregnating solution) and γ-Al_2O_3-supported Co Anderson phases has been carried out on the basis of the properties of each fragment in the planar hexagonal configuration of D_3d symmetry [13]. Hence, three different types of Mo–O bonds can be distinguished; Mo–O_{2t} (dioxo-terminal bonds), and Mo–O_b and Mo–O_c bridge bonds: Mo–O–Mo and Mo–O–M, respectively. The corresponding stretching modes are observed between 1000 and 930 cm^{-1} for Mo–O_{2t}, between 750 and 500 cm^{-1} for both Mo–O_b and Mo–O_c stretching modes, respectively [14]. Upon dissolution, a broadening is observed, the Raman spectrum being characteristic of isolated $CoMo_6$ Anderson unit. Upon deposition on the alumina support, other modifications are observed. The comparison between both pure (bulk and impregnating solution) and supported $CoMo_6$ spectra, given in figure 1, reveals a general broadening of lines for the supported species. This effect can be attributed either to the XMo_6-support interaction that seems to produce a slight distortion of the symmetric planar structure [10,14,15] or to a partial decomposition with the formation of the corresponding $AlMo_6$ Anderson structure as suggested by the shoulder at 570 cm^{-1}, characteristic of the AlO(Mo) vibrational mode [14].

The DR spectra of bulk and γ-Al_2O_3-supported $CoMo_6$, reported in figure 2, show a typical band in the

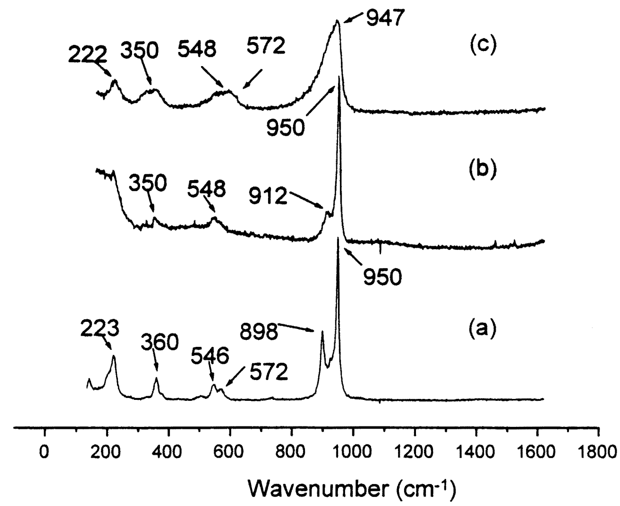

Figure 1. Raman spectra of (a) $CoMo_6$ pure, (b) $CoMo_6$ aqueous solution and (c) $CoMo_6/\gamma$-Al_2O_3 [8% Mo-supported catalyst (No. 1)].

270-nm spectral range, which is characteristic of the Mo ← $O^=$ charge transfer in $Mo(VI)O_6$ octahedra. In the visible region (350–800 nm), there are two spin-allowed d–d transition bands typical for a regular octahedral configuration Co(III) (d^6) ion: $^1A_{1g}$ ground state to the $^1T_{1g}$ and $^1T_{2g}$ higher states, falling in the 700–550 and 500–400 nm ranges respectively [16,17]. These bands, characteristic of the Co(III), are still observed on the spectra of the bulk and supported phase. This clearly shows that the heteropolyanionic species is mainly preserved upon deposition even if some modifications are observed in the low spectral range characteristic of the Mo(VI) octahedral configuration.

3.2. Physicochemical features of the γ-Al_2O_3 adsorption process

Figure 3 shows the molybdenum adsorption isotherms for γ-Al_2O_3-supported Co and Te Anderson phases, where the adsorbed molybdenum is expressed as

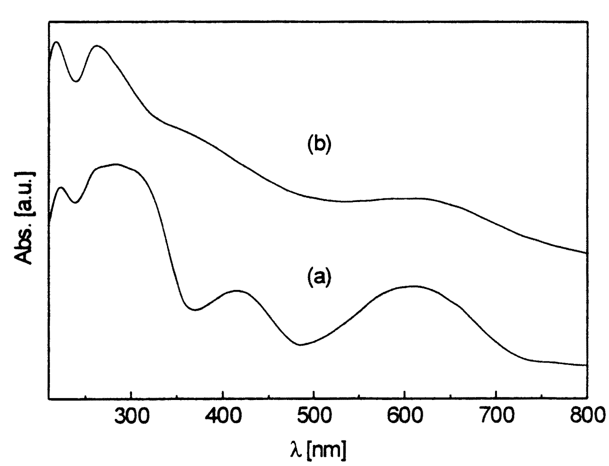

Figure 2. Diffuse reflectance spectra: (a) $CoMo_6$ pure and (b) $CoMo_6/\gamma$-Al_2O_3 [8% Mo-supported catalyst (No. 1)].

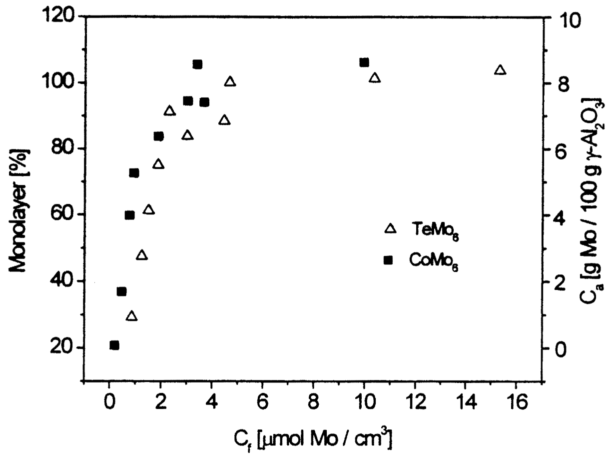

Figure 3. Molybdenum adsorption isotherms for XMo_6/γ-Al_2O_3 samples (where X = Co and Te) as determined at room temperature.

monolayer (%) as well as C_a (g Mo/100 g γ-Al_2O_3). The shape of the resulting curves was found to follow the Langmuir model.

As it is observed, the monolayer (%) is close to C_aMo = 8% for either Co or Te simple catalysts.

Besides, by plotting the linearized form of the Langmuir equation and by extrapolating the subsequent straight line, it was possible to calculate the adsorption parameters for Co and Te phases as exposed in table 2. It is possible to observe that the Co phase has a slightly higher support affinity than the Te phase. For the mixed catalysts, the Mo loading increases from No. 2 to No. 4 catalysts ranging between 8.50 to 10% as observed in table 3. The possible explanation for this effect is that a partial "bilayer" occurs in such mixed catalysts, probably related to a complex equilibrium involving adsorption, dissolution and cationic-replacement reactions. These processes provoke the formation of the $AlMo_6$ phase, as was mentioned above, which was widely discussed in previous works [10–14]. Nevertheless, the amount of this "bilayer" is small and does not exceed 10%.

Consequently, it is possible to consider that the total amount of adsorbed precursor is practically constant. Besides, it is possible to note that the relationship between the calculated and the experimental adsorbed Co (C_aCo$_c$ and C_aCo$_e$ respectively) is linear, as shown in table 3, thus indicating that the adsorption of $CoMo_6$ and $TeMo_6$ takes place independently. This fact also suggests that there is no preferential adsorption by the species, which keeps the relationship of original composition (X : Mo = 1 : 10 with X = Co and/or Te), as verified in the final solutions and in the metal-adsorbed content.

Table 2
Adsorption parameters for XMo_6/γ-Al_2O_3 (X = Co and Te) systems

Phase	K_{ad} (mL/g Mo)	S (g Mo/g γ-Al_2O_3)	10^{20} (atoms Mo/g γ-Al_2O_3)
$TeMo_6$	980	0.09	5.6
$CoMo_6$	1374	0.09	5.6

3.3. Hydrotreatment catalytic activity

In figures 4 and 5, the conversion of the thiophene or the cyclohexene versus the r' = [Co]/[Mo] ratios are reported respectively. They show the increase of both thiophene and cyclohexene conversions as a function of Co loading on the catalysts. A practically linear behavior for HYD activities is observed, which is in agreement with the literature data. However, if data corresponding to catalyst No. 5 (table 3) (C_aMo = 8.46 and C_aCo = 0.00) is included in figure 4, it is observed that the HDS conversion increases with a higher function than the linear one with $CoMo_6$ content. This is interesting provided that such a catalyst, having a comparable Mo loading, has HDS almost similar to catalyst No. 4 (with the lowest Co amount). This suggests that in order to form an active sulphided phase, several neighboring $CoMo_6$ entities are needed, that is to say, isolated $CoMo_6$ entities could not lead to an active phase and this effect may also indicate that the active phase of these catalysts results from an assembly of $CoMo_6$ phases.

Thus, this behavior, either in the HDS or HYD activities, suggests a synergetic effect of Co on the

Table 3
Chemical data of both Co and Mo concentrations in impregnating solutions and adsorbed metal contents for No. 1 to No. 5 catalysts

Catalyst	C_iMo	C_fMo	C_aMo	C_tMo	C_iCo	C_fCo	C_aCo$_e$	C_aCo$_c$	r	r'
1	104.30	33.60	8.50	8.83	10.40	3.70	0.80	0.80	0.133	0.152
2	126.30	54.80	8.50	9.05	7.60	3.50	0.50	0.60	0.087	0.096
3	138.70	48.90	9.50	9.98	5.00	2.40	0.30	0.40	0.049	0.050
4	131.20	47.00	10.00	10.50	2.50	0.80	0.20	0.20	0.032	0.032
5	113.20	46.50	8.00	8.46	0.00	0.00	0.00	0.00	0.000	0.000

Note: C_iMo or Co and C_fMo or Co is the concentration of metal in the initial (C_i) and final (C_f) impregnating solution in μmol/cm^3.
C_t is the total content of Mo in g Mo/100 g of γ-Al_2O_3.
C_aM with M = Mo or Co is the adsorbed metal content expressed in g M/100 g γ-Al_2O_3.
C_aCo$_e$ and C_aCo$_c$ are adsorbed both experimental and calculated Co contents expressed in g Co/100 g γ-Al_2O_3.
r = [Co]/([Co] + [Mo]).
r' = [Co]/[Mo].

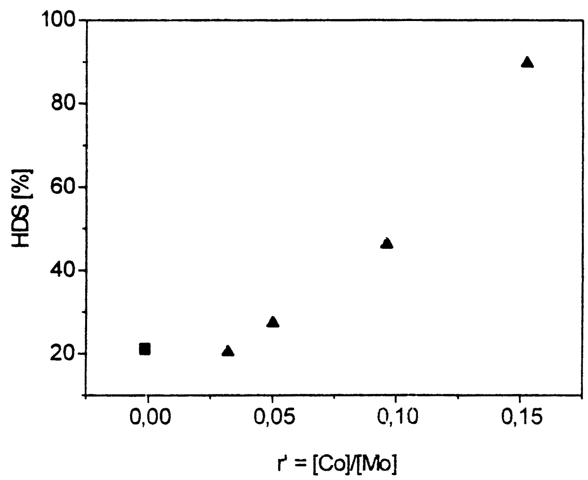

Figure 4. HDS activity as a function of $r' = [Co]/[Mo]$. (■) Data corresponding to catalyst No. 5.

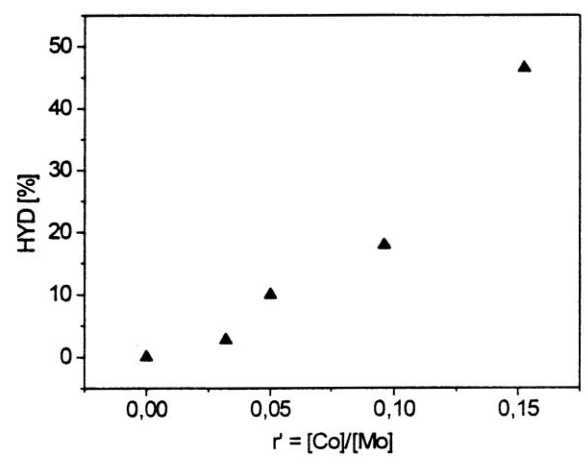

Figure 5. HYD activity as a function of $r' = [Co]/[Mo]$.

hydrotreating process for the Anderson phase-based catalysts. These results are very significant if it is considered that the higher value of the ratio $r = [Co]/([Co] + [Mo]) = 0.133$ used in this work is lower than the optimum value of 0.25 normally used in conventional catalysts [11,12]. Likewise, in a recent report, it has been shown that the HDS activity of the $CoMo_6$-based catalyst is similar to that of Co-Mo/γ-Al_2O_3 commercial catalyst (with $r = 0.25$), whose HDS activity in the same conditions corresponds to 80% of thiophene conversion [4,13].

4. Conclusions

The main findings of this work can be summarized as follows:

1. The heteropolyoxomolybdates with Anderson-type structure are adsorbed independently on γ-Al_2O_3 when an equilibrium impregnation of the support with mixed aqueous solutions of $CoMo_6$ and $TeMo_6$ is carried out.
2. The increase of the $[Co]/([Co] + [Mo])$ and $[Co]/[Mo]$ ratios induces an increase of HDT activities. Indeed, an important synergetic effect of the Co heteroatom is observed, which is higher than the one observed with classical preparation.
3. This work shows that Anderson heteropolyanions containing the Co promoter atom are convenient starting materials for the preparation of HDS catalyst.

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