Journal of Catalysis **188,** 102–110 (1999)
Article ID jcat.1999.2633, available online at http://www.idealibrary.com on IDEAL®

Hydrotreatment Catalysts Prepared with Heteropolycompound: Characterisation of the Oxidic Precursors

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Received March 11, 1999; revised June 22, 1999; accepted July 12, 1999

Molybdenum-based catalysts were prepared by impregnation of γ-alumina with heteropolycompound (HPC) solutions: two salts were used, a nonreduced compound ($Co_{3/2}PMo_{12}O_{40}$) and a reduced one ($Co_{7/2}PMo_{12}O_{40}$). The dried and calcined solids were characterised with laser raman and diffuse reflectance spectroscopies. Extraction of the surface entities of the oxidic precursors was performed by washing them with various electrolytic solutions and the filtrates analysed by polarography. On the basis of these characterisations, a detailed description of the evolution of the entities during the preparation as well as the nature of the surface oxomolybdate species of the oxidic precursor have been deduced. It has been shown that the nonreduced HPCs were decomposed upon impregnation, whereas the reduced HPCs were preserved on the support after impregnation and drying. After calcination for 4 h at 673 K (in air for the nonreduced and in air or N_2 for the reduced compounds), the HPCs were decomposed. However, it appears that the nature of the surface oxomolybdenum phase of the calcined solids strongly depends on the nature of the starting material. This difference should explain the variation in the thiophene conversion. © 1999 Academic Press

1. INTRODUCTION

Innovation in the development of Co(Ni)–Mo–Al_2O_3 catalysts has been driven by the need to produce clean fuels, based on the pressing requirement for environmental protection. Most of the commercially available hydrodesulfurization (HDS) catalysts contain phosphorus as an additive. These catalysts are obtained by sulfidation of an oxidic precursor which is conventionally prepared by impregnation of a γ-alumina support with impregnating solutions containing the elements to be deposited. Ammonium heptamolybdate (AHM), cobalt or nickel nitrate, and phosphoric acid are used as the starting material for the preparation of these impregnating solutions.

Results about the effect of the support on the heteropolycompounds (HPCs) formation and changes during these conventional preparations has been previously reported in the literature (1–6), whereas interesting HDS activities were previously obtained with alumina-supported HPC (5–7). These HPCs have the advantage of associating all the elements to be deposited in the same entity which can then be used for the preparation of the impregnating solution. Recently, we reported the preparation of new HPC salts having the Keggin-type structure and their use for the preparation of HDS catalysts (8, 9). We showed that due to the absence of counterions (NH_4^+, NO_3^-), a strong interaction between the promoter atom and the HPC exists in the impregnating solution. It has also been shown that an increase of the thiophene conversion was obtained with solids prepared with reduced HPC. However, the exact nature of the supported oxomolybdate phase of these latter solids has never been clearly defined. The usual methods of characterisation have not allowed us to identify the species present on the support, particularly after calcination. The results obtained by ^{31}P MAS-NMR were complex and inconclusive because of the possible existence of NMR silent species (10, 11).

In the present work we have been interested in the genesis of the surface oxomolybdate phase obtained with these reduced HPCs. The solids were analysed by laser raman (LRS) and diffuse reflectance spectroscopies (DRS). Extractions of the species present on the support were performed by washing with electrolytic solution and the solutions were analysed by polarography.

2. EXPERIMENTAL

(a) Preparation

Impregnating aqueous solutions were prepared by dissolution of HPC cobalt salts, the preparation of which were described previously (8). Two salts were used, i.e., a nonreduced ($Co_{3/2}PMo_{12}O_{40}$) and a reduced ($Co_{7/2}PMo_{12}O_{40}$) one. The HPC concentrations of the solutions as well as

0021-9517/99 $30.00

those of the solutions for the preparation of the reference solids were chosen to prepare solids containing 14 wt% Mo as MoO_3. The Co/Mo (0.12 or 0.29) and the P/Mo (1/12) atomic ratio are imposed by the stoichiometry of the starting material. The oxidic precursors were prepared by incipient wetness impregnation of alumina extrudates with these solutions. The textural properties of the support, deduced from BET and BJH analysis, were 250 m^2/g for the specific surface area, 0.68 cm^3/g for the porous volume, and 12.1 nm for the mean pore diameter. The impregnated extrudates were dried at 383 K overnight and then calcined for 4 h at 673 K in air for the nonreduced compound and in air or nitrogen for the reduced compound. The following nomenclature will be used hereafter: for the solution stoichiometries, the term will be Cox, where x is the number of Co atoms for 12 Mo atoms, i.e., 3/2 or 7/2. By extension, the dried and calcined solids will be respectively denoted CoxDy and CoxCy, where y is the nature of the gas used for the treatment (i.e., a = air or n = N_2).

For comparison purposes two reference catalysts with a Co/Mo atomic ratio of 3/2 or 7/2 and the same P/Mo ratio (1/12) as the HPC-based solids were prepared by impregnation of the same alumina with the solution obtained by the addition of phosphoric acid in an aqueous solution of ammonium heptamolybdate followed by the addition of cobalt nitrate. The impregnated extrudates were dried at 383 K overnight and then calcined for 4 h at 673 K in air. The notation used for these reference catalysts is CoxCy(AHM).

To study the influence of the presence of nitrate ions on the thiophene conversion, an oxidic precursor was prepared by impregnation of the same alumina with an impregnating solution obtained by the addition of cobalt nitrate in a reduced $H_7PMo_{12}O_{40}$ solution, the preparation of which is described in Ref. (12). For comparison purposes an oxidic precursor was prepared by impregnation of alumina with the $H_7PMo_{12}O_{40}$ solution. The impregnated extrudates were dried at 383 K overnight and then calcined for 4 h at 673 K in nitrogen. These solids are respectively designated hereafter as Co7/2Cn(H7) and H7Cn.

The Mo, Co, and P loadings were determined by X-ray fluorescence by the Service Central d'Analyses du C.N.R.S. (Vernaison, France).

(b) Physical Characterisations

The Raman spectra, with a resolution of 2 cm^{-1}, were recorded using a Raman microprobe (XY from Dilor), equipped with a photodiode array. The exciting light source was an Ar^+ laser emitting the 514.5-nm line with a power of less than 10 mW at the sample.

UV–visible diffuse reflectance spectra (DRS) of the finely grounded powders were recorded in the 200- to 1600-nm range on a Perkin-Elmer Lambda 19 spectrometer with a diffuse reflectance accessory. Samples were scanned against a barium sulphate background.

For the extraction the solids were placed in the electrolytic solution under stirring for 30 min. After filtration the solutions were studied by polarography. Two aqueous electrolytic solutions were used, i.e., CH_3CO_2H(1 M)/CH_3CO_2Na(1 M)/NaCl(1 M) and $HClO_4$(1 M)/CH_3CN (1 M). The polarographic measurements were performed on a Tacussel (Pol 150) electrochemical analyser monitored by a Tracemaster 5 programmer. A conventional single-compartment cell with a standard three-electrode configuration was used. Pt was used as an auxiliary electrode, while Ag/AgCl was used as a reference electrode. The working electrode was a glassy carbon disk and the rate of stirring of this electrode was equal to 2700 rpm. Deoxygenating of the solutions was carried out using N_2 as the inert gas. The concentration of the solutions in molybdenum atoms was equal to 12×10^{-3} M.

The X-ray photoelectron spectra (XPS) were recorded with a VG ESCALAB 220XL spectrometer equipped with a monochromatised Al source (Al $K\alpha = 1486.6$ eV). Charge compensation with an electron flood gun was needed. The analyser was operated in a constant pass energy mode ($E_{\text{pass}} = 30$ eV) using the electromagnetic mode for the lens. The resolution measured on the Ag $3d_{5/2}$ peak was 0.75 eV. Energy correction was performed by using the C 1S peak at 285 eV as a reference. The integrated intensity ratio of typical core levels ($I(\text{Mo } 3d_{3/2\text{-}5/2})/I(\text{Al } 2p)$) provides information on the surface repartition by comparison with the theoretical ratio calculated with the Kerkhof and Moulijn equation (13).

The high-resolution electron microscopy studies (HREM) were performed on a Philips EM 300 microscope. The sample was dispersed in heptane using an ultrasonic device and then deposited on carbon films supported on copper grids.

The oxidic precursor was also studied by analytical electron probe microanalysis (EPMA) using a LEICA Cambridge S360 scanning electron microscope equipped with a Tracor northern EDAX.

Catalytic activities for thiophene HDS were measured at atmospheric pressure in a flow-type reactor packed with 0.2 g of catalyst. The solids were first sulfided at 673 K for 2 h under a flow (100 ml/min) of a H_2S/H_2 (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). The reaction products were analysed by gas chromatography.

3. RESULTS

It has been shown previously that whether or not the salt is reduced, the structure of the HPC is preserved upon dissolution (8). It is well known that these Keggin structures possess several isomers (14). For the nonreduced compound the isomer form which is stable in solution is the α form, referred to here as 0α. Upon four-electron reduction the α form isomerises to give the β form. The two- or four-electron-reduced compound will be hereafter referred to as II or IV, respectively, followed by the nature of the isomer form, i.e., IIβ, IIα, IVα, or IVβ.

3.1. Study of Catalysts Prepared with Nonreduced HPC

(a) Dried solid. Figure 1b shows the Raman spectrum of the Co3/2Da solid. A careful monitoring of the power of the laser beam was used to avoid any degradation of the surface compound. The Raman features of the starting material (Fig. 1a) are no longer observed and the Raman spectrum exhibits a broad line at 952 cm^{-1} which characterises a polymolybdate phase on an alumina surface (15, 16). Thus, a decomposition of the HPC occurred during the impregnation. This has been ascribed to a buffer effect of the support (17, 18) and is in agreement with the pH range of stability of nonreduced Keggin anions which is lower than the pH at the zero point charge (ZPC) of alumina ($\approx$8). A broad line at 1100 cm^{-1} is also observed and could be assigned by comparison with the spectrum of the $AlPO_4$, $4H_2O$ (Fig. 1e) to phosphate entities in interaction with alumina, confirming the degradation of the HPC. The low intensity of the line is due to the very low P loading (0.1 wt%).

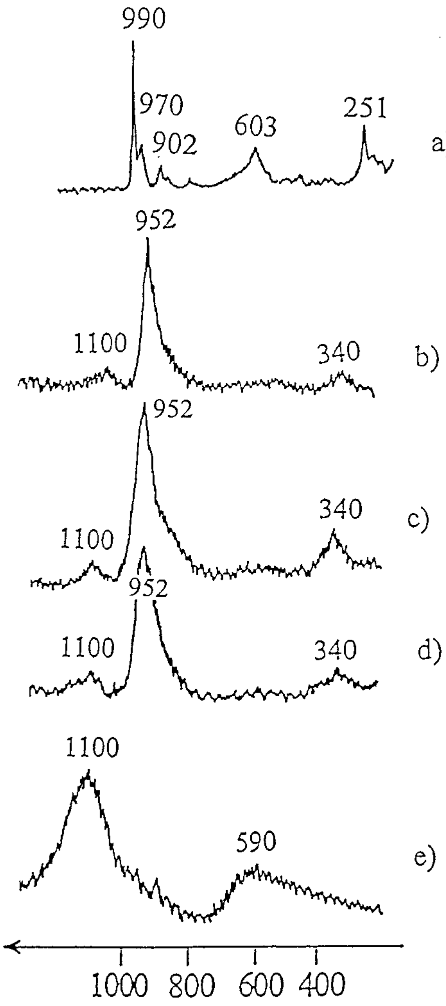

FIG. 1. Raman spectra of (a) $Co_{3/2}PMo_{12}O_{40}$, (b) Co3/2Da, (c) Co3/2Ca, (d) Co7/2Ca, and (e) $AlPO_4$, $4H_2O$ (checked by XRD).

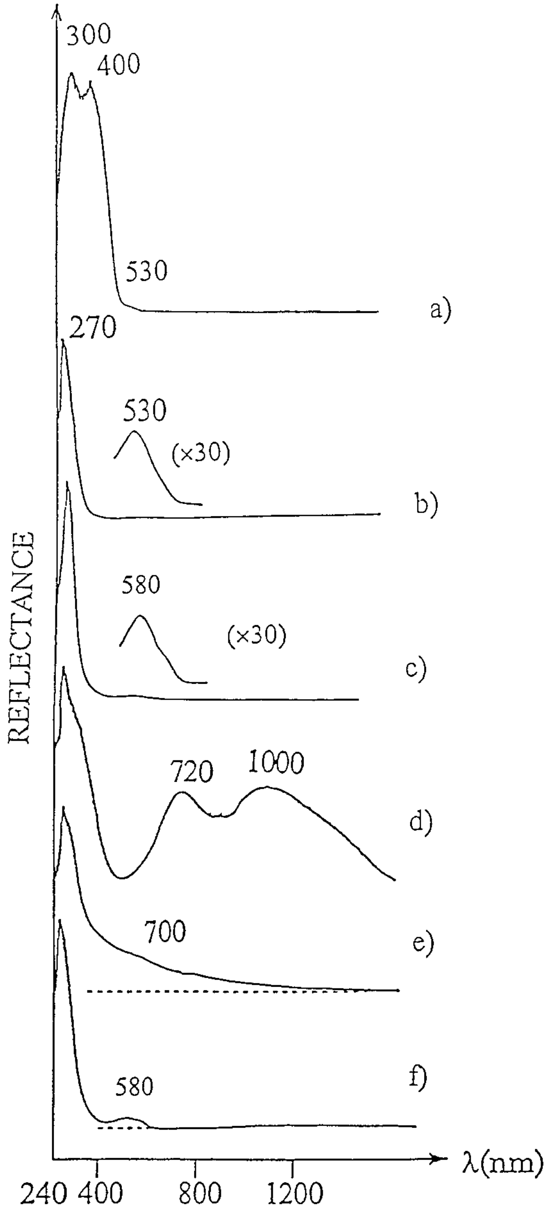

FIG. 2. DRS spectra of (a) $Co_{3/2}PMo_{12}O_{40}$, (b) Co3/2Da, (c) Co3/2Ca, (d) Co7/2Dn, (e) Co7/2Cn, and (f) Co7/2Ca.

Figure 2b shows the DRS spectrum of the Co3/2Da solid that confirms the decomposition. Indeed, the features of the starting phosphomolybdic anion are no longer observed and the spectrum exhibits a main band at 270 nm, characteristic of a polymolybdate structure on alumina (19, 20). A broad band at 530 nm is also present which characterises the

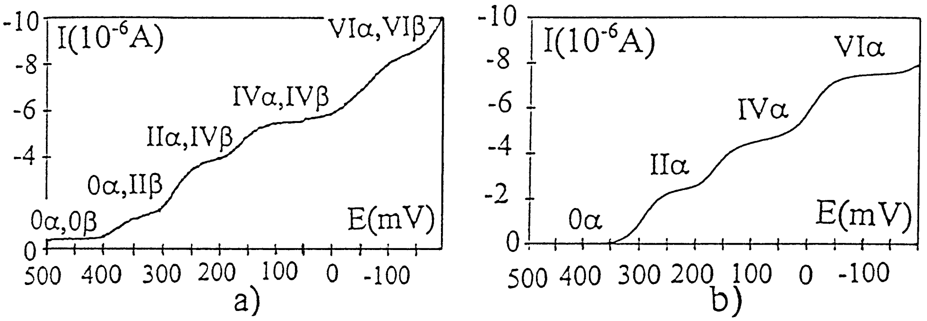

FIG. 3. Polarograms in a $HClO_4/CH_3CN$ medium of (a) a washing solution of a Co3/2Da solid and (b) a Co3/2 impregnating solution ($[Co_{3/2}PMo_{12}O_{40}] = 10^{-3}$ M).

presence of a cobalt aquocomplex (21, 22), i.e., $Co(H_2O)_6^{2+}$ in agreement with the pink colour of the sample.

Extraction of the species present on the support was performed with a mixed aqueous solution of $HClO_4/CH_3CN$ in which the formation of the nonreduced HPC from polymolybdate entities did not occur (23). Figure 3a shows the polarogram of the solution obtained after the washing of 10 g of the Co3/2Da solid with 20 ml of electrolytic solution. For comparison purposes the polarogram of the HPC impregnating solution is reported on the same figure (Fig. 3b). By comparing the wave height of the traces and taking into account the elementary analysis of the washed extrudates showing that about 15 wt% of the initial loading remains on the support after the extraction, one can deduce that 97% of the HPC is decomposed into isopolymolybdate entities upon impregnation on the support. On the basis of the half-wave potential, it can be deduced that the polarogram of the washing solution that is representative of only 3 wt% of the nondegraded Keggin unit characterises a mixture of the two 0α and 0β isomer forms of the nonreduced $PMo_{12}O_{40}^{3-}$ (12, 24) in almost equal proportions. This implies that a partial degradation into the lacunary $PMo_9O_{34}^{9-}$ entity occurred during the impregnation, from which the $PMo_{12}O_{40}^{3-}$ anion (0β and 0α) could be restored in the electrolytic solution according to the literature data (23, 25, 12).

(b) Calcined solid. As for the dried solid, the calcined catalyst was washed with the same electrolytic solution [$HClO_4/CH_3CN$] and the filtrate was analysed by polarography. No polarogram was observed that indicates a total decomposition of the HPC upon calcination.

Figures 1c and 2c show respectively the Raman and the DRS spectra of the Co3/2Ca solid. The features of the aforementioned polymolybdate phase (main Raman line at 952 cm^{-1} and DRS band at 270 nm) observed on the spectra of the dried solid are still observed on the spectrum of the calcined solid. However, upon calcination a broad band at about 580 nm appears in the DRS spectrum which can be assigned to the presence of cobalt atoms in the tetrahedral sites of the alumina by reference to literature data (26–28). These LRS and DRS features are similar to those observed for catalysts conventionally prepared with AHM and cobalt nitrate as starting materials (28). Indeed, the Co3/2Da sample is blue as the conventional oxidic precursor.

3.2. Study of Catalysts Prepared with Reduced HPC

(a) Dried solid. The DRS spectrum of the dried Co7/2Dn solid shown in Fig. 2d exhibits a broad band at 720 nm which is characteristic of the four-electron-reduced β form of the HPC (14). A broad band is also observed at about 1000 nm that characterises the charge transfer Mo^{V} to Mo^{VI} due to the mobility of the electrons in the reduced polyanion (intervalence band). This shows that the reduced HPC is at least partly preserved on the dried catalyst. Indeed, the dark blue colour of the starting salt is maintained after impregnation and drying. However, the band at 270 nm, characteristic of a polymolybdate structure on alumina, indicates that a partial degradation of the reduced HPC occurred upon impregnation on the alumina.

The $CH_3CO_2H/CH_3CO_2Na/NaCl$ electrolytic solution in which the formation of the reduced HPC from polymolybdate entities cannot occur (23) was used for the extraction of the Co7/2Dn solid. Figure 4 shows the polarogram of this filtrate (trace b) and of the impregnating solution (trace a). The two polarograms are quite similar and are characteristic of the β form of the four-electron-reduced HPC (12). This is consistent with the preservation of the starting reduced

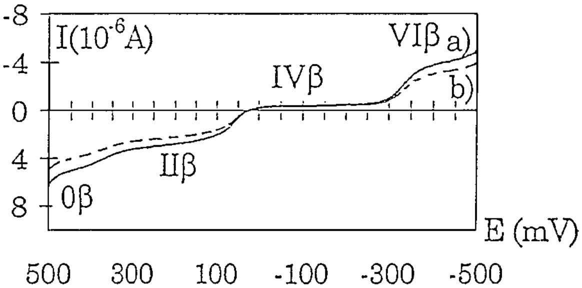

FIG. 4. Polarograms in a $CH_3CO_2H/CH_3CO_2Na/NaCl$ medium of (a) a reference solution, Co7/2 ($[Co_{7/2}PMo_{12}O_{40}] = 10^{-3}$ M), and (b) a washing solution of Co7/2Dn.

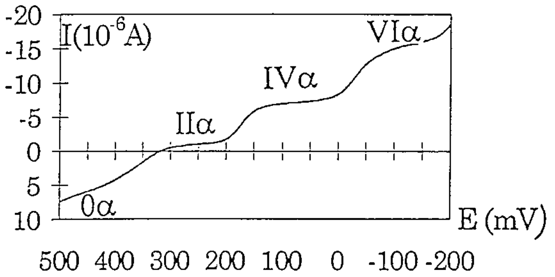

FIG. 5. Polarogram in a $HClO_4/CH_3CN$ medium of the washing solution of Co7/2Cn.

Keggin unit. The polarogram (Fig. 4b) was obtained from 0.25 g of dried solid in 20 ml of electrolytic solution. By comparison of the wave height of the traces a and b, it can be deduced that 85 wt% of the four-electron-reduced HPC was preserved on the support after impregnation and drying and was released after washing. Quantitative analysis shows that the HPC was mainly preserved after impregnation on alumina and drying in N_2. This result is consistent with the stability of the four-electron-reduced compound at high pH up to 7–8 (14). However, elemental analysis shows that about 15 wt% remained on the support after the washing. This could correspond to a partial transformation into isopolymolybdate entities as shown by the DRS spectrum (band at 270 nm) of the dried solid (Fig. 2d).

(b) Calcined solids: Co7/2Ca and Co7/2Cn. The same [$CH_3CO_2H/CH_3CO_2Na/NaCl$] electrolytic solution was used for the extraction after calcination. Whether air or N_2 was used as the calcination gas, no polarogram was observed. This result indicates a transformation of the reduced HPC upon calcination at 673 K, but the exact nature of the decomposition products is still not known. The extraction experiments were also performed with an $HClO_4/CH_3CN$ aqueous solution, an electrolytic medium from which the Keggin unit can only be recovered if reduced polymolybdate entities are present (23). The polarographic study of the filtrate shows the presence of a two-electron-reduced heteropolyanion (α form), referred to here as IIα, when the solid was calcined under nitrogen but no polarogram is observed when the solid was calcined in air (Fig. 5). The presence of these IIα entities observed in the Co7/2Cn washing solution can be interpreted as evidence of the existence of reduced and nonreduced polymolybdate species, whilst a total re-oxydation occurred upon calcination in air.

This re-oxydation is confirmed by LRS as well as by DRS. Indeed, the Raman spectra of the solid calcined in air or N_2 exhibit the same main features characteristic of the supported polymolybdate phase (Fig. 1d). The DRS features of the four-electron-reduced β form of the HPC are no longer observed on the spectra of the calcined solids shown in Figs. 2e and 2f that exhibit a band at 270 nm, characteristic of a polymolybdate phase. After calcination in the air the DRS spectrum (Fig. 2f) exhibits also the broad band at 580 nm, characteristic of the cobalt atoms in the tetrahedral sites of the alumina (29). Only a large shoulder on the main peak is observed on the DRS spectrum of the Co7/2Cn in that spectral range. Whatever the nature of the gas, a decomposition of the HPC is observed that induces a more or less pronounced migration of the cobalt atoms in the tetrahedral sites of the alumina in agreement with the colour of the samples that is grey and blue for respectively Co7/2Cn and Co7/2Ca.

3.3. Dispersion of the Active Phase

The dispersion of the elements inside the extrudates was evaluated by EPMA. A typical X-ray micrograph is shown in Fig. 6. Regardless of whether the calcined catalysts were prepared with nonreduced or reduced HPA, the results are in general agreement and show that the elements Co, Mo, and P are well dispersed inside the extrudates after

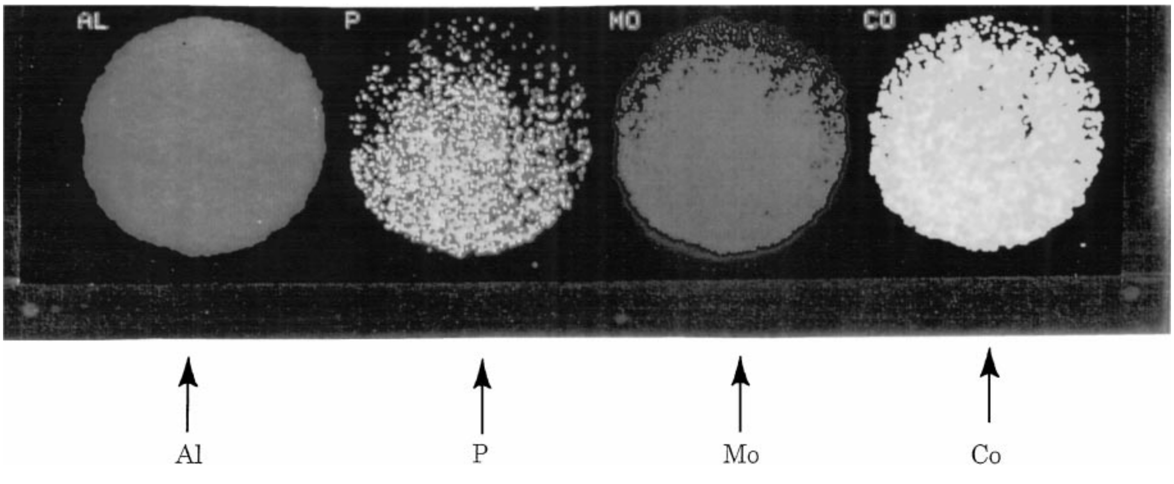

FIG. 6. X-ray micrograph of Co7/2Cn.

calcination. This result is in agreement with the size of the Keggin unit (12 Å) which is far smaller than the pore size diameter of the support.

Figure 7a shows the Mo 3*d* XPS spectrum of the starting salt Co7/2 that exhibits the lines characteristic of the Mo^{V} and Mo^{VI} species. But the broadening of the Mo 3*d* peak that is always observed with alumina-supported solids induces a collapse of the Mo^{V} and Mo^{VI} peaks of the dried solid (Fig. 7c). This broadening can be ascribed either to the interaction of the Keggin entities with the support or to a charge effect as discussed previously by authors (30). Indeed, upon calcination in air the valley between the two peaks is more pronounced. Whatever the solids, the Co 2*p* peaks are characteristic of the Co^{2+} entities. However, no information can be deduced on the localisation of the promotor atom.

Whether reduced or nonreduced HPC was used as the starting material, the XPS intensity ratio $I(\mathrm{Mo})/I(\mathrm{Al})$ is always about 0.9, a value corresponding to the theoretical value deduced from the Kerkhof and Moulijn model (13). This shows that there is a good repartition of the elements as a monolayer at the alumina surface.

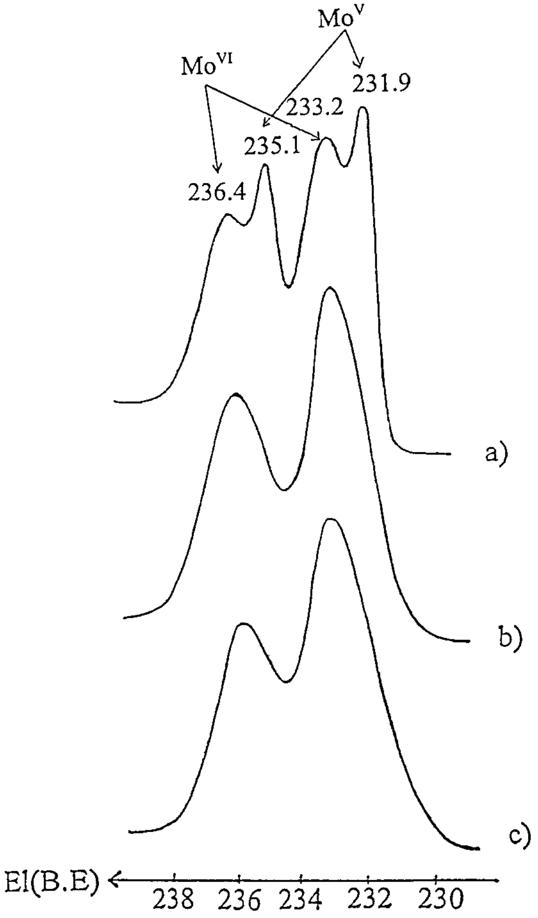

FIG. 7. XPS spectra of the Mo 3*d* level of (a) $Co_{7/2}PMo_{12}O_{40}$, (b) Co7/2Ca, and (c) Co7/2Dn.

TABLE 1

Conversion (%) of Thiophene

Catalyst	Conversion (%)
H3Ca	4
H7Cn	5
Co3/2Ca(AHM)	14
Co3/2Ca	15
Co7/2Ca(AHM)	22
Co7/2Ca(H7)	27
Co5/2Cn[a]	24
Co7/2Ca	30
Co7/2Cn	32

[a] See Ref. (8).

High-resolution electron microscopy (HREM) was used to evaluate the morphology of the disulfide crystallites obtained after sulfidation. Typical HREM micrographs are shown in Fig. 8. Regardless of the nature of the starting material, the mean length, similar for both samples, is about 30 Å. A similar value is generally observed for conventional catalysts prepared by impregnation with AHM as the starting material (31, 32). An increase of the stacking is however observed ($\bar{N} = 2.7$) in comparison with conventional catalysts. Such a variation has never been observed with different alumina supports. Hence, this stacking can be considered to arise as a consequence of the starting material used. XPS analysis of the sulfided catalyst showed that the monolayer coverage is preserved upon sulfidation and that the binding energy difference $E(\mathrm{Co}_{2p})-E(\mathrm{Mo}_{3d})$ (550.2 eV) characterises cobalt atoms in a decoration position according to the model of Topsoe (33).

3.4. *Activity Measurements*

The thiophene conversions of the HPC-based catalysts are reported in Table 1. They are compared with the activities of reference samples having the same metal loadings. The catalytic behaviour of these new solids is similar to that of the reference solids. A linear relationship is obtained between the thiophene conversion and the Co/Mo atomic ratio as evidenced in Fig. 9. The synergy effect between cobalt and molybdenum, usually observed on conventional catalysts (34), is also observed for heteropolycompound-based catalysts. It appears that the activity is dependent on the nature of the starting material used for the preparation of the oxidic precursor. If the activity of the catalysts prepared with nonreduced HPC is similar to those of the reference ones, an improvement is observed with the catalysts obtained with reduced HPC as starting materials.

4. DISCUSSION

It clearly appears that the use of nonreduced HPC has no beneficial effect at the metal loading studied in this

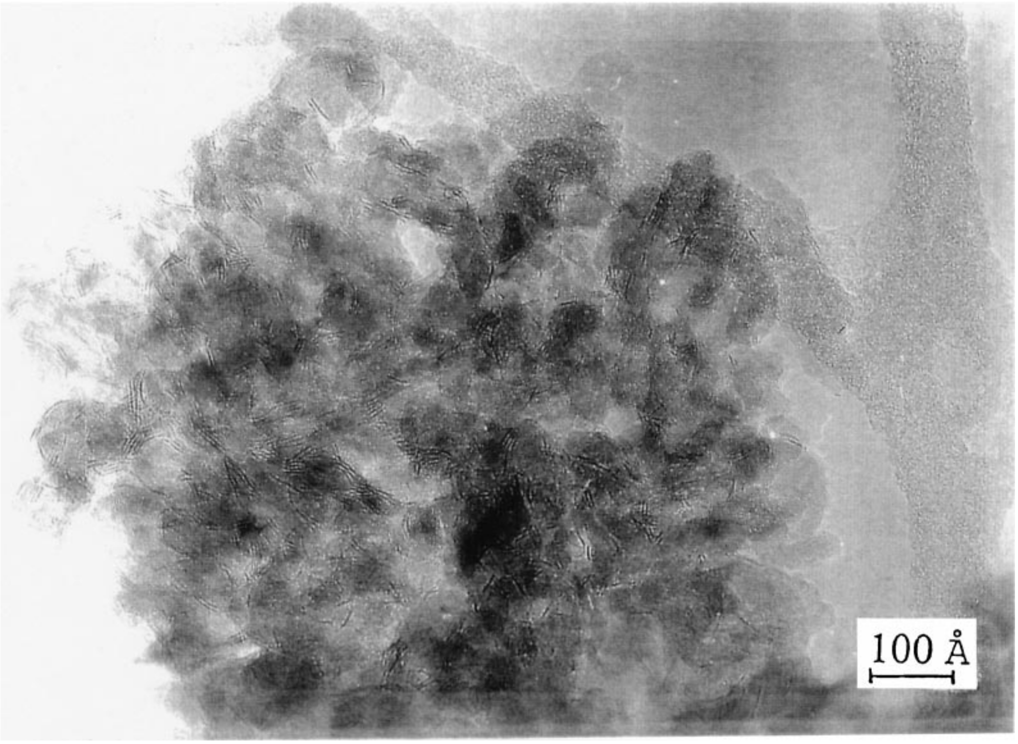

FIG. 8. HREM pictures of a Co7/2Cn sulfided catalyst.

work. The activity of the Co3/2Ca catalyst is similar to the one of the reference catalyst (Co3/2Ca(AHM)). This is in agreement with the similar nature of the supported oxomolybdate phase of these two oxidic precursors prepared with nonreduced HPC or with AHM. Indeed, it has been clearly shown that the nonreduced HPC is decomposed upon impregnation on the alumina. This has been ascribed to the buffer effect of the alumina that induces a decomposition into isopolymolybdates giving the classical surface polymolybdate, the formation of which should occur in the solution in the pore of alumina. The phosphorus atoms of the decomposed HPC then give an amorphous aluminophosphate as shown by LRS and suggested by other authors for conventionally prepared oxidic precursors (35, 36). The absence of counterions (NH_4^+, NO_3^-) that allows a better interaction of the promotor atoms with the oxomolybdate entities in the impregnating solution does not affect the thiophene conversion. But this can have a beneficial effect at higher Co loading at which the formation of microcrystalline $CoMoO_4$ or Co_3O_4 has been evidenced with a conventional method of preparation (37).

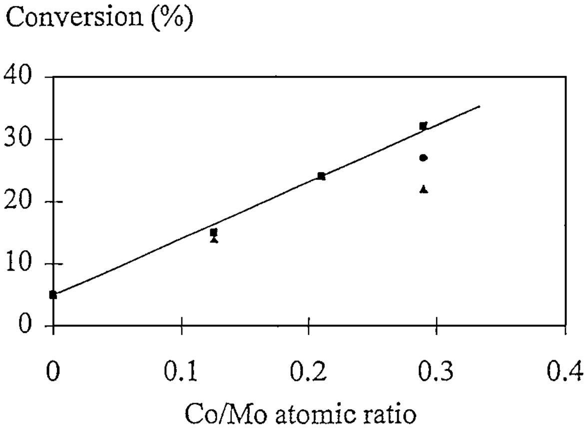

FIG. 9. Conversion (%) of thiophene as a function of the atomic ratio Co/Mo: ■, HPC-based catalysts; ▲, AHM reference catalysts; ●, Co7/2Cn(H7).

For unreduced heteropolycompounds the cobalt content is limited by the stoichiometry of the well-defined entities. After partial reduction, it is possible to increase the amount of cobalt and therefore to increase the HDS conversion as evidenced in Fig. 9. A linear relationship is observed that shows that all the Co atoms added are use to promote the disulfide crystallites. The activity of the reduced HPC-based catalyst is higher than that of the reference one. This improvement cannot be ascribed to the morphology of the disulfide crystallites because no variation of their size is observed by comparison with the reference catalysts and because the stacking has no effect on the thiophene conversion (38). It should therefore be correlated to the stability of the reduced Keggin unit at a high pH value near the isoelectric point of the alumina support. This allows its preservation upon impregnation and drying and avoids the formation of the classical polymolybdate phase that generally occurs during the maturation step. Thus, the good interaction between Co and Mo atoms existing in the impregnating solution should therefore be maintained on the dried catalyst.

But a decomposition occurs upon calcination, regardless of the nature of the gas. When the calcination is performed under nitrogen, the transformation leads to the formation of reduced and of nonreduced polymolybdate entities. The better activity of the catalysts prepared with reduced HPC should also be correlated to the different natures of the surface oxomolybdate phase that originates from the decomposition of the starting reduced HPC upon calcination under nitrogen. Indeed, if the oxidic precursor has been calcined under air, a decrease of the activity is seen. However, its activity remains higher than the one of the reference Co7/2(AHM) catalyst. This improvement should be ascribed to the absence of foreign counterions in the impregnating solution that allows a direct interaction of the promoter atom with the HPC structure, as previously observed by ^{31}P NMR spectroscopy. Indeed, a decrease of the activity is observed (cf. Table 1) when cobalt nitrate [Co7/2Ca(H7)] instead of cobalt carbonate is used in the synthesis of reduced HPC cobalt salt.

Due to the higher stability of the reduced HPC, the good interaction between the Co and the Mo existing in the impregnating solution is maintained on the dried solids. These results also suggest that the metals should remain in close contact during all the steps of preparation of the oxidic precursor, as have previously been stated by van Veen *et al.* (37). This interaction which can be achieved by the use of reduced HPC cobalt salts allows one to limit the fraction of cobalt atoms involved in the formation of the well-known surface "$CoAl_2O_4$" species that is not available for the formation of the CoMoS active phase.

5. CONCLUSION

This study has shown that HPCs are convenient starting materials for the preparation of HDS oxidic precursors. It appears that the use of nonreduced HPC cobalt salt always gives the well-dispersed surface polymolybdate phase observed with conventional preparation with AHM. This is due to the buffer effect of the support that induces a decomposition of the Keggin unit. Conversely, the nature of the surface species obtained with reduced HPC as starting material is quite different. The salient beneficial effects of the use of reduced HPC salts as the starting materials for the preparation of HDS oxidic precursors are as follows:

(i) They allow one to avoid the presence of foreign counterions in the impregnating solution and therefore to have a strong interaction between the promotor atom and the oxomolybdate in the impregnating solution.

(ii) Their stability allows their preservation upon impregnation and drying.

(iii) Upon calcination in nitrogen these entities are transformed, but the use of reduced HPCs allows one to avoid the formation of the classical surface polymolybdate phase.

All these features are at the origin of the improvement in thiophene conversion that should be assigned to a better decoration of the disulfide crystallites formed upon sulfidation.

ACKNOWLEDGMENTS

The authors would like to thank the FEDER, the CNRS, the "Région Nord Pas de Calais," and the "Ministère de l'Enseignement Supérieur et de la Recherche Scientifique" for their financial support for acquisition of the XPS spectrometer.

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