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Ex situ sulfidation by alkylpolysulfides: A route for the preparation of highly dispersed supported sulfides

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Abstract

A CoMo hydrotreating catalyst was presulfided ex situ by impregnation of the ditertio-nonylpentasulfide (TNPS) and subsequent hydrogen treatment up to 623 K at various pressures (1–21 bar). The genesis of the sulfide phase at each step of the activation procedure, impregnation, drying, hydrogen treatment was studied using several physicochemical techniques, UV–Vis Reflectance spectroscopy, XPS and HREM. By comparison with the conventional sulfiding procedure (H_2–H_2S), this ex situ sulfidation process brings about a significant increase in the dispersion of the active molybdenum sulfide phase. In agreement with these results, the hydrodesulfurization activity in the thiophene conversion is also increased. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The main purpose of the hydrotreating of petroleum feedstocks is the catalytic conversion of sulfur and nitrogen compounds into hydrocarbons, hydrogen sulfide and ammonia. The main benefit of the sulfided catalysts is their ability to catalyse hydrogenation and hydrogenolysis reactions in the presence of strong inhibitors such as H_2S and NH_3. This property explains why these materials are mostly utilized for oil hydroprocessing [1]. Besides this industrial application, several papers and patents have underlined that sulfide catalysts may present interesting properties in other reactions than those relevant of the hydrotreatment field. For instance, sulfides may catalyze the thiolation of ketones, alcohols and aldehydes [2] as well as the synthesis of amines by the direct amination of alcohols and selective hydrogenation of unsaturated nitro aromatics with acetylenic [3,4] or ethylenic groups [5]. However, these catalysts are commercially available only in their inactive oxide form and a sulfidation step is required prior to their utilization. The achievement of this sulfidation step needs a thermal treatment of the supported oxides in the presence of mixtures containing sulfur containing molecules i.e. H_2S, RSH and CS_2 CH_3SSCH_3. The use of such malodorous and volatile light compounds require specific equipments excluding the utilization

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of sulfides in fine chemical plants. Recently, a process which allows the transformation of an oxide into a stable and odorless sulfided intermediate has been patented by EURECAT [6,7]. This process, known as the SULFICAT process, consists in wetting ex situ the supported oxides with a hydrocarbon solution of a high molecular weight alkylpolysulfide (MW>400). After a thermal treatment step, the catalyst can be loaded into the refinery unit and efficiently activated without requiring any further sulfur addition. For hydrotreating application, the final sulfidation of the 'presulfided catalyst' is completed in situ during the start-up procedure performed under hydrogen pressure (1–10 MPa) and in the presence of the hydrocarbon liquid phase. These high hydrogen pressures may also rule out the use of such sulfiding process for applications other than those relevant to hydrotreating. The aim of this work was to characterize the presulfided solid and to study the influence of the hydrogen pressure on the decomposition of the organic polysulfide and on the degree of sulfiding of the catalyst. For this purpose, we have selected an alumina supported CoMo catalyst as a model solid while the ditertio-nonylpentasulfide was used as a model alkylpolysulfide.

2. Experimental

2.1. *Materials*

The solid studied in this work is an industrial CoMo/γAl_2O_3 containing 13 wt.% of Mo and 3.9.wt% of Co and having a BET area of 220 m^2/g. The oxidic phases were presulfided with a commercial ditertio-nonylpentasulfide (TNPS) containing about 37 wt.% of sulfur. The amount of polysulfide deposited onto the catalyst was calculated on the basis of the transformation of the oxidic Co and Mo phases into CoS and MoS_2. The activation was performed by heating the solid under hydrogen from room temperature up to 623 K (heating rate 4°/min.). This procedure was carried out in a stainless steel plug flow microreactor described elsewhere [8], under various hydrogen pressures. The heated part of the set up contains an inner quartz tube in which the catalyst was placed in order to prevent any consumption of the formed H_2S by reaction with the heated walls of the reactor. The gas phase composition was analyzed by means of a mass spectrometer (FISONS Instruments) equipped with a quadrupole analyzer (VG analyzer) working in a Faraday mode. A silica capillary tube heated at 453 K continuously bled off a small fraction of the gas phase into the spectrometer. In a typical TPR run, the more intense m/z signals were recorded: H_2S (34), C_3H_7 (43), C_4H_9 (57) and C_5H_{11} (71).

2.2. *UV–VIS reflectance spectroscopy*

The UV–VIS diffuse reflectance spectra were recorded in the 200–1500 nm range using a Perkin Elmer Lambda 9 spectrometer. Barium sulfate was used as a reference compound for the study of solid materials while *n*-heptane was used as a reference and as a solvent for the study of TNPS solutions.

2.3. *XPS characterization*

XPS measurements were carried out with a ESCALAB 200R FISONS using an aluminum (Al K_α=1487 eV) X-Ray source. Binding energies are given by reference to C_{1s} at 284.5 eV as internal standard. Dispersions (D), defined as the ratio of the Mo and Al photopeaks, were calculated after subtracting both the non linear Shirley background and the contribution of the S_{2s} signal. Non linear least squares curve fitting method based on the Marquardt–Levenberg algorithm was used for calculating the distribution of the oxidation states of a given element. The same CoMo precursor was sulfided at 673 K by H_2–H_2S. This sample was utilized as reference for the XPS measurements.

2.4. *Electron microscopy characterization*

High resolution electron microscopy examinations were performed with a Jeol 100 CX instrument fitted with a UHP polar piece (resolving power=0.2 nm). After the hydrogen treatment, the solids were immediately immersed into the deoxygenated heptane at room temperature in order to prevent their oxidation. Then the samples were ultrasonically dispersed in this solvent and the suspension was collected on a carbon coated copper grid. Particle size distribution was determined by counting more than 800 particles. The average particle size was calculated according to the first moment of the distribution:

$$\frac{\sum_{i=1}^{n} n_i L_i}{\sum_{i=1}^{n} n_i}$$

2.5. Catalytic activity measurements

The catalytic properties of the different activated solids were determined at 573 K using the thiophene hydrodesulfurization as model reaction. The experiment was performed at atmospheric pressure using a 2.5 mol% of thiophene diluted in hydrogen. Conversions were kept lower than 15% in order to avoid mass transfer limitations.

3. Results and discussions

As shown in Fig. 1, the UV–Vis spectrum of a heptane solution of TNPS exhibits two absorption bands located at 260 and 320 nm. These bands characterize the $\sigma \rightarrow \pi^*$ charge transfer of the C–S_x bond present in aliphatic polysulfides. The impregnation of the alumina carrier by a solution of TNPS does not modify the relative intensity of these bands even when the solid is dried at 423 K suggesting that the C–S_5–C bonds of the initial TNPS are still present after deposition on the alumina support. The oxidic CoMo catalyst presents three absorption bands. According to the literature data, the band centered at 240 nm corresponds to Mo^{6+} while the two other bands at $\approx$575 and 1500 nm are related to the Co species in a tetrahedral and octahedral symmetry [9]. After impregnation of the oxide precursor and drying at room temperature (RT), the obtained spectrum contains the three previous bands as well as those of TNPS. After drying at 423 K, the spectrum is considerably enlarged since only a broad peak is observed in the 200–1500 nm range. According to Praliaud, this band enlargement could be ascribed to the reduction of Mo^{6+} into lower Mo oxidation states by the presence of a reducing atmosphere such as hydrocarbons [10].

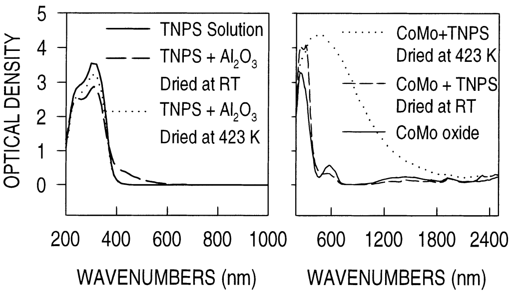

Fig. 1. UV–Vis spectra of TNPS solution and of TNPS deposited on the alumina support and on the CoMo oxide precursor.

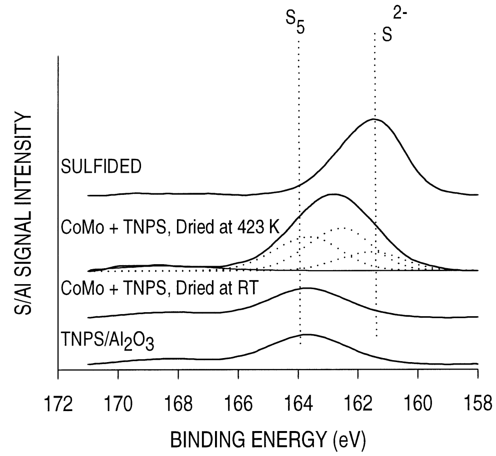

Fig. 2. S2p XPS characterization of the TNPS impregnated solids. Comparison with the H_2–H_2S sulfided CoMo catalyst.

Figs. 2 and 3 report the S2p and the Mo3d XPS spectra of various samples including those obtained on a completely sulfided CoMo oxide. The latter denoted as ‘sulfided’, was prepared by heating the oxide pre-

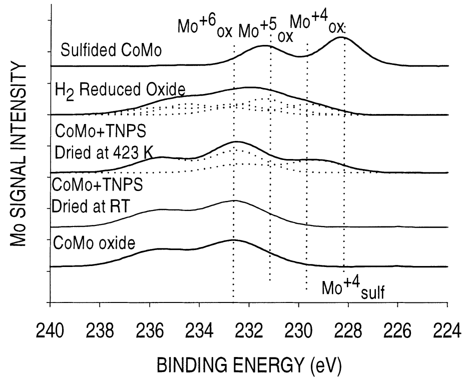

Fig. 3. Mo3d XPS characterization of the TNPS impregnated solids. Comparison with the H_2–H_2S sulfided CoMo catalyst and with the hydrogen reduced CoMo oxide precursor.

cursor at 673 K using an H_2 (85%)–H_2S (15%) as a sulfiding mixture. For this catalyst, the S2p binding energy (BE) was detected at 161.4 eV and the corresponding Mo3d5/2 and Mo3d3/2 doublet appeared, respectively, at 228.4 and 231.5 eV. These values agree fairly well with those characterizing the S^{2-} and Mo^{4+} in a sulfur environment (denoted hereafter by Mo^{4+}_{sulf}) currently observed on MoS_2 [11]. As evidenced in Fig. 2, the S2p BE of TNPS adsorbed on the alumina support was found at 163.6 eV in accordance with the data reported by Lindberg et al. for organic compounds containing –C–S–C– and –C–S–S–C bonds [12]. A similar spectrum was observed for the CoMo+TNPS system dried at RT indicating that the sulfur species are the same on both systems. By contrast if the solvent is eliminated at 423 K, the sulfur BE shifted towards lower values (maximum at 162.9 eV) suggesting a reduction of the overall S oxidation state. Curve fitting indicated that the S2p envelope can be decomposed into three individual components one corresponding to the initial S_5 species (163.6 eV), another one at 161.4 (S^{2-}) and an intermediate moiety at 162.9S eV. This strongly suggests that during drying at 423 K a fraction of the S_5 chain is broken leading to S^{2-} and S_x species with x<5. Fig. 3 evidences that this drying step also modifies the molybdenum oxidation state. As a matter of fact, the Mo3d envelope of the initial oxide CoMo catalyst or of the solid dried at RT can be curve fitted as a single doublet with BE values characteristic of Mo^{6+} ($Mo3d_{3/2}$: 235.3 eV, $Mo3d_{5/2}$: 232.2 eV) while for the solid dried at 423 K, fitting required an additional doublet with $Mo3d_{5/2}$ BE value at 229.1 eV which cannot be assigned to the presence of sulfided Mo^{4+}_{sulf} species (BE at 228.4 eV). In order to get an insight into the nature of this species, the CoMo oxide precursor was reduced at 673 K for 1 h in the presence of a hydrogen flow. According to Hercules et al., this procedure should give a mixture of Mo^{6+}, Mo^{5+} and Mo^{4+} in an oxygen environment [12,13]. Results showed that the three Mo species are effectively obtained in these conditions, each of them having a Mo3d5/2 centered at 232.6, 231.4 and 229.7 eV. Accordingly, the BE of the intermediate species found at 229.1 eV lies between Mo^{4+}_{ox} and Mo^{4+}_{sulf} suggesting probably the existence of a Mo^{4+} species having both oxygen and sulfur in its coordination shell, because the replacement of some oxygen atoms by a less electronegative sulfur ions should decrease the BE of a given species.

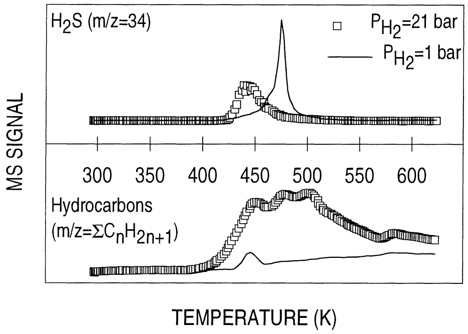

Fig. 4. MS analysis of the effluent gases evolved during a hydrogen treatment of the TNPS impregnated CoMo oxide catalyst.

In order to achieve the sulfidation of the solid, the impregnated CoMo catalyst was heat treated in the presence of a hydrogen flow. During this activation procedure, Fig. 4 shows that the solid releases mainly H_2S and hydrocarbons which are formed at the same temperature which corresponds to the decomposition of the adsorbed TNPS species. Thus, it is proposed that upon hydrogen the organic species are first decomposed leading to the concomitant formation of hydrocarbons and H_2S which is further used for the sulfidation of the metal ions. An increase of the hydrogen pressure provokes an increase of the decomposition rate of the adsorbed organic species since the temperature which corresponds to the peak maxima is shifted downwards by about 50°. Moreover the amount of H_2S evolved from the solid surface under 21 bar is lower than at atmospheric pressure which indicates that the sulfur species present on the surface of the catalyst have been utilized for the sulfidation of the CoMo phase and that this interaction is pressure favored. This assumption is consistent with the Mo XPS data represented in Fig. 5. Results related to the Co promotor were not reported because the observed signals were not intense enough whatever the activation procedure. As previously mentioned the Mo3d XPS signal of the initial solid contains both oxidic Mo^{6+} and Mo^{4+} species. For the solid treated at atmospheric pressure, the Mo3d signal can be decomposed into three different species with maxima $Mo3d_{5/2}$ BE at 228.4, 230.6 and 232 eV. The photopeak at 228.4 eV represents the fraction of the sulfided molyb-

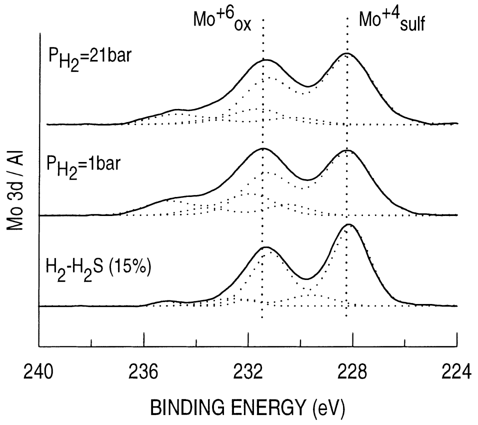

Fig. 5. Mo3d XPS characterization of the hydrogen activated solids.

denum species (Mo^{4+}) while the higher energy peak corresponds to Mo^{6+} in an oxygen environment. The third species (230.6 eV) is indicative of the presence of an intermediate oxidation state whose identification is still not completely elucidated. By comparison with the data reported in Fig. 3, this species does not seem to correspond to a Mo^{5+} in an oxygen environment (detected at 231.4 eV) but it may be related to the presence of a Mo^{5+} oxysulfide type species. However the presence of oxysulfide –S–Mo^{6+}–O- species or $MoO_2S_2^{2-}$ like complexes cannot be excluded since Arnoldy et al. found that the low temperature sulfidation proceeds via an O–S exchange reaction [14] and the replacement of some oxygen atoms by a less electronegative sulfur ions should again decrease the BE of Mo^{6+} species. According to these data, the augmentation of the hydrogen pressure increases the concentration of sulfided Mo species at the expense of the Mo–O species.

Quantitative XPS data reported in Table 1, show that TNPS sulfidation leads to a lower fraction of sulfided Mo^{4+} than the conventional H_2–H_2S activation procedure, probably because a fraction of sulfur is released as H_2S during the hydrogen activation (see Fig. 4) and therefore cannot participate in the sulfidation of the catalyst. In order to compensate this H_2S released, a small concentration of H_2S was added into the feed from 433 K up to 623 K. The amount of sulfur introduced into the system was adjusted in order to counterbalance the amount lost during the activation procedure under pure hydrogen (hydrogen pressure 21 bar). Data shows that this procedure effectively increased the S/Mo ratio which becomes identical to the one obtained using an H_2–H_2S mixture. However, it should be pointed out that the smaller fraction of Mo^{4+}_{sulf} detected with the alkylpolysulfides sulfiding method is largely compensated by a higher dispersion of the Mo phase defined by the ratio Mo_{total}/Al, so that the dispersion of the active phase ($\frac{Mo^{4+}_{sulf}}{Al}$) is identical or even higher than the one observed with conventional sulfiding. In order to confirm this higher dispersion, the solids treated either under 21 bar hydrogen pressure or under an H_2–H_2S atmosphere were characterized by high resolution electron microscopy (HREM). In order to get reliable results, several micrographs were taken and the statistics were done on more than 800 crystallites. Fig. 6 reports the distribution of the particle length and of the number of layers. For the TNPS activated solid the mean particle size and the average number of layers are respectively 25 Å and 1.6. This values are significantly lower than those determined on the H_2–H_2S sulfided catalyst (31 Å

Table 1
Quantitative XPS data and catalytic properties as a function of the activation procedure (Mo_t: total Mo3d XPS signal, Mo_{sulf}: sulfided Mo^{4+} species)

Catalyst	$D=\left(\frac{Mo_{total}}{Al}\right)\times(10)^2$	$\frac{Mo^{4+}_{sulf}}{Mo_{total}}$	$\frac{Mo^{4+}_{sulf}}{Al}\times(10)^2$	Specific activity (μmol/s.g.)
Initial catalyst	10	0	0	–
Activ. at 1 bar	8.3	68%	5.56	1.3
Activ. at 21 bar	8.4	76%	6.38	2
Activ. at 21 bar+with H_2S	7.9	81%	6.39	2.1
Sulfided by H_2/H_2S	6.8	82%	5.64	1.2

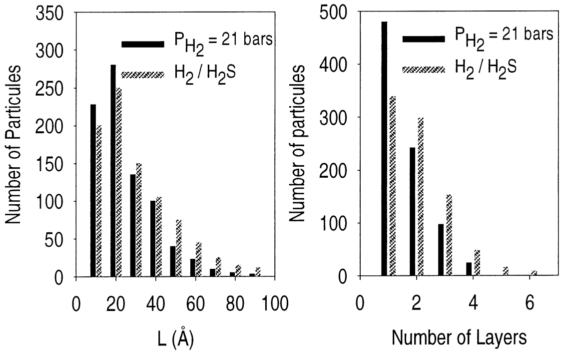

Fig. 6. HREM characterization.

and 2). Accordingly smaller and less stacked crystallites are obtained when the catalyst is activated by the polysulfide method corroborating the calculated XPS data. From the literature data it is now well established that the CoMoS phase is the active component presents on such kind of materials [1]. This phase could be depicted as an homogeneous distribution of the promotor Ni or Co at the edges of the lamellar structure of MoS_2. As the number of edge Mo sites is inversely proportional to the crystal length, lower the particle size higher is the catalytic activity in agreement with the HDS results reported in Table 1.

4. Conclusions

The deposition of ditertio-nonylpentasulfide at the surface of an oxidic CoMo followed by a mild drying step does not modify either the structure of the organic molecule or the nature of the Mo^{6+} species present at the surface of the alumina support. By contrast, both the solid and the organic substrate are partly transformed when the impregnated solid is dried at 423 K i.e. molybdenum is partly reduced and the initial $-S_5$-chain is broken. XPS data have shown that this temperature is high enough to create some oxisulfide species which are probably the intermediates of the transformation of molybdenum oxide into the active sulfide phase. Treated under hydrogen, the remaining organic species decompose at temperatures as low as 433–623 K converting the initial Mo^{6+} species into sulfided Mo^{4+}. At atmospheric pressure, the dispersion and the sulfidation state of the active Mo phase are similar to those obtained using the usual H_2–H_2S mixture. The sulfidation state of the active phase increases with the hydrogen pressure. By comparison with conventional sulfiding (H_2–H_2S), the SULFICAT procedure brings about a significant increase in catalytic activity as well as in the dispersion of the active MoS_2 phase. As this method does not require any addition of sulfur containing molecule, the SULFICAT process could be considered as an off site sulfiding procedure. Accordingly, this clean and safe method actually used in the refineries may be also applied to factories without handling malodorous and corrosive chemicals.

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References

[1] H. Topsoe, B.S. Clausen, F. Massoth, Hydrotreating Catalysis, Catalysis Science and Technology, in: J.R. Anderson, M. Boudard (Eds.), Spinger, Berlin/Heidelberg, New York, vol. 11, 1996.
[2] O. Weisser, S. Landa, Sulphides Catalysts: Their Properties and Applications, Pergamon Press, Oxford, UK, 1973.
[3] A. Onopchenko, E.T. Sabourin, C.M.J. Selwitz, J. Org. Chem. 44(21) (1979) 3671.
[4] A. Onopchenko, E.T. Sabourin, C.M.J. Selwitz (to Gulf R&D) US 4 219 679 (1978).
[5] R. Braden, H. Kaupfe, S. Hartung, (to Bayer Aktiengesellschaft) US 4 002 673 (1977).
[6] G. Berebi, European Patent No. 0 130 650 (1984).
[7] S.R. Murff, E.A. Carliste, P. Dufresne, H. Rabehasaina, Preprints of the American Chemical Society, Div. Petrol. Chem. 38(1) (1993) 81.
[8] F. Labruyère, M. Lacroix, D. Schweich, M. Breysse, J. Catal. 167 (1997) 464.
[9] P. Gajardo, P. Grange, B. Delmon, J. Catal. 63 (1980) 201.
[10] H. Praliaud, J. Less Com. Metals 55 (1977) 387.
[11] G.B. Mc Garvey, S. Kasztelan, J. Catal. 148 (1994) 149.
[12] B.J. Lindberg, K. Hamrin, G. Johasson, U. Gelius, A. Fahlman, C. Nordling, K. Siegbahn, Physica Scripta 1 (1970) 286.
[13] M. Mulcahy, M.M. Houalla, D.M. Hercules, J. Catal. 139 (1993) 72.
[14] P. Arnoldy, J.A.M. van den Heijkant, G.D. de Bok, J.A. Moulijn, J. Catal. 92 (1985) 35.