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Alumina supported HDS catalysts prepared by impregnation with new heteropolycompounds. Comparison with catalysts prepared by conventional Co–Mo–P coimpregnation

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Abstract

Hydrodesulfurization (HDS) catalysts prepared by the incipient wetness impregnation method with Co–Mo–P based solutions were characterized with various physical techniques and their efficiencies in HDS of thiophene were evaluated. Depending on the Co–Mo–P precursors used to prepare the impregnating solution, different heteropolyanions (HPAs) were characterized. In conventional solutions, $P_2Mo_5O_{23}^{6-}$ or $P_2Mo_{18}O_{62}^{6-}$ type entities were evidenced. Preparations with Keggin type HPAs were also studied ($PMo_{12}O_{40}^{3-}$) and an original method of preparation which allows the deposition of alumina on reduced Keggin type HPAs ($PMo_{12}O_{40}^{7-}$) is described. If the non-reduced HPAs (whatever their structure) are decomposed on alumina, the reduced ones could be partially preserved even after calcination, leading to the synthesis of more efficient catalysts. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulphurization; Heteropolycompounds; Co–Mo–P catalysts

1. Introduction

Innovation in the development of Co–Mo–Al_2O_3 and Ni–Mo–Al_2O_3 catalysts has been driven by the need to produce clean fuels, based on the pressing requirement for environmental protection. Most of these commercial hydrodesulfurization (HDS) catalysts contain phosphorus as additive. They are obtained by sulfidation of an oxidic precursor which is prepared by impregnation of an alumina support with solutions containing the components to be deposited. A few number of procedures were reported in the literature for the preparation of Mo–P-based solutions. The most commonly used is based on the dissolution of ammonium heptamolybdate (AHM) in the presence of phosphoric acid [1]. The presence of the diphosphopentamolybdate anion ($P_2Mo_5O_{23}^{6-}$) in these conventional impregnating solutions has been proposed [2]. The use of Keggin ($Co_{3/2}PMo_{12}O_{40}$ or $Ni_{3/2}$-$PMo_{12}O_{40}$) [3] and Anderson salts ($H_6XY_6O_{24}^{x-}$ with X=Co or Ni and Y=Mo or W) [4,5] as starting material was also reported. Recently, we reported the synthesis of new reduced heteropolyanions having the Keggin type structure for the preparation of HDS catalysts [6]. The direct preparation by dissolution of the MoO_3 oxide in the presence of phosphoric acid was also reported in some patents [7]. Depending on the preparation method used, the nature of the species

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present in the impregnating solution should be different. It appears, therefore, very interesting to compare these different preparations. In the present paper, such comparisons were carried out through physical characterizations of the impregnating solutions as well as through the characterizations of the oxidic precursors at each step of their preparations, i.e. in their wet, dried and calcined states. These oxidic precursors were then sulfided and the activities of these catalysts were evaluated in HDS of thiophene. The efficiencies of the so-obtained catalysts were compared and discussed with reference to the nature of the oxomolybdate species present on the alumina surface of the oxidic precursor.

2. Experimental

All the products used in the preparations were certified pure reagent grade from Fluka and were used without further purification.

2.1. Preparation of the impregnating solutions

Impregnating solutions were prepared according to three different routes, i.e.:

1. Addition of phosphoric acid in an aqueous solution of ammonium heptamolybdate (AHM) followed by the addition of cobalt nitrate at room temperature.
2. Dissolution in water under reflux at 80°C of a mixture containing MoO_3, H_3PO_4 and $CoCO_3$.
3. Keggin-based solutions were prepared by dissolution in water with their corresponding cobalt salts, i.e. the unreduced $Co_{3/2}PMo_{12}O_{40}$ and the reduced $Co_{7/2}PMo_{12}O_{40}$ ones as previously described [6].

The molybdenum concentration of the solutions (1.5 mol/l) corresponds to the one required for the preparation of catalysts containing a Mo loading of 14 wt% as MoO_3. To allow us the comparison between the different methods of preparation, two Co concentrations were used in each case, corresponding to Co/Mo atomic ratios of 1.5/12 and 3.5/12. Due to the method of preparation, different P/Mo atomic ratios were used. For preparations 1 and 2 these ratios were both 2/5 which correspond to the optimum value for a catalyst prepared by the simultaneous impregnation whereas this ratio is imposed by the stoichiometry of the starting material (i.e. 1/12) in preparation 3 method.

2.2. Preparation of the oxide precursor

The P–Co–Mo–based oxidic precursors were prepared by incipient wetness impregnation of extrudates of γ-Al_2O_3 (specific area of 250 m^2/g and porous volume of 0.8 cm^3/g) with the different impregnating solutions. The impregnated extrudates were dried at 383 K overnight and then calcined either in air or in nitrogen for 4 h at 673 K otherwise specified. The Mo, Co and P contents were determined by X-Ray fluorescence by the "Service Central d'Analyses du CNRS" (Vernaison, France). The following nomenclature will be used hereafter: the nomenclature of the solutions is Co_xYS, where x is the number of Co atoms for 12 Mo atoms, i.e. 3/2 or 7/2, Y is the method used, i.e. 1 (precursor=AHM), 2 (MoO_3) or 3 (Keggin). By extension the catalysts will be designed Co_xYC.

2.3. Physical characterizations

Laser Raman spectroscopy (LRS) was performed 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 at the sample of 1 mW.

The ^{31}P NMR measurements of the impregnating solutions were carried out on a Bruker AC300 spectrometer. Chemical shifts are negative towards higher field and are referenced to external 85% H_3PO_4 as a standard. The solvent used is H_2O and all the solutions were prepared at 1.5 mol Mo per litre, i.e. the concentration of the impregnating solutions. The ^{31}P NMR measurements of the supported catalysts were carried out on a Brucker ASX100, operating at 40.53 MHz in MAS experiments. The pulse length and the relaxation time were, respectively, equal to 1.8 μs and 20 s.

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 analyzed by gas chromatography.

3. Results and discussion

3.1. Impregnating solutions

Molybdenum and phosphorus in aqueous solution may create, depending on the preparation conditions, many heteropolyanions (HPAs). The most known are the Keggin, Dawson and diphosphopentamolybdate ones, the structures of which are presented in Fig. 1.

It has been previously shown by ^{31}P NMR, that upon solubilization in water of the unreduced $Co_{3/2}$-$PMo_{12}O_{40}$ and the reduced $Co_{7/2}PMo_{12}O_{40}$, the Keggin structure is maintained. This is also confirmed by LRS. The Raman spectra of this solution (Fig. 2(e)) exhibit the features of the Keggin unit with reference to the literature data [8]. Moreover, ^{31}P NMR studies evidenced a stronger interaction of the Co ions with the HPA entities than the one observed with solutions prepared with molybdophosphoric acid and Co nitrate [6].

The ^{31}P NMR spectrum (not presented here) of the H_3PO_4-AHM-based solution (without cobalt) shows two lines at about 2 and 0.6 ppm which characterize, respectively, the protonated $P_2Mo_5O_{23}^{6-}$ and phosphate entities [10,9]. Such a formation has already been proposed by van Veen et al. [2] and by Kraus and Prins [10]. Although the final pH of these unbuffered solutions is about 3, no more condensed HPAs are present due to the very high P/Mo ratio. This result is observed with Co containing solutions. Indeed, the Raman spectra of the Co_x1S (Fig. 2(a) and (b)) present two main lines at 892 and 940 cm^{-1} which characterize $P_2Mo_5O_{23}^{6-}$ anion in agreement with literature data [8,11]. The line at 1046 cm^{-1} is due to the presence of nitrate anions in the solutions.

The ^{31}P NMR spectrum of the H_3PO_4–MoO_3-based solution (without cobalt) presents two main lines at −2.45 and 0.5 ppm which characterize, respectively, the heteropolymolybdate of Dawson structure $P_2Mo_{18}O_{62}^{6-}$ [9,11], and free phosphates as the atomic ratio P/Mo is higher than the corresponding stoichiometric one. A small line is observed at −0.9 ppm and is ascribed to the presence of a small amount of $PMo_9O_{34}^{9-}$ type entities [11]. Such a formation of a Dawson type structure is in agreement with the procedure of preparation of well-defined Dawson salts as defined in the literature [12]. A Raman study of the $Co_{3/2}$2S solution confirms, with reference to literature data [8], the presence of Dawson entities (Fig. 2(d) – main line at 974 and 713 cm^{-1}). Nevertheless, upon increasing the Co content, if the Co is introduced as a carbonate salt, the Raman spectra also show two lines at 892 and 944 cm^{-1} characteristic of the presence of a $P_2Mo_5O_{23}^{6-}$ type entity. This shows that a partial decomposition of the Dawson structure occurs due to an increase of the pH upon introduction of cobalt carbonate in the solution (Fig. 2(e)).

So it clearly appears that each type of preparation reported here induces mainly the formation of only one type of HPA whereas van Veen et al. [11] showed that a mixture of HPA was obtained by acidification with HCl of an aqueous solution containing sodium molybdate and sodium phosphate.

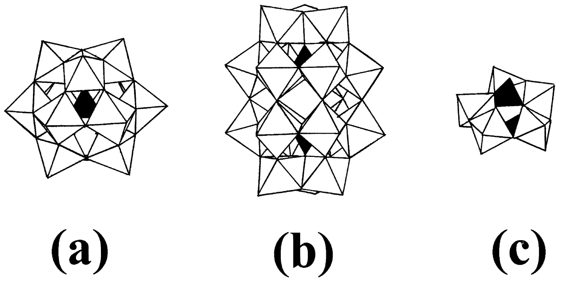

Fig. 1. Structure of: (a) $PMo_{12}O_{40}^{3-}$, (b) $P_2Mo_{18}O_{62}^{6-}$, and (c) $P_2Mo_5O_{23}^{6-}$ (clear octahedra and dashed tetrahedra represent, respectively, MoO_6 and PO_4 groups).

3.2. Dried oxide solids

Fig. 3 shows the Raman spectra of some dried catalysts. A careful monitoring of the power of the laser beam is necessary in order to avoid a degradation as evidenced in Fig. 3(b) and (c).

As the Raman microprobe allows the analysis of selected particles, some heterogeneities were evidenced for the dried Co_x1C solid. The Raman spectra of some particles exhibit well-defined lines at 946, 873, 370 and 219 cm^{-1} which characterize as a main component the ammonium diphosphopentamolybdate salt which should have precipitated (Fig. 3(b)) in the

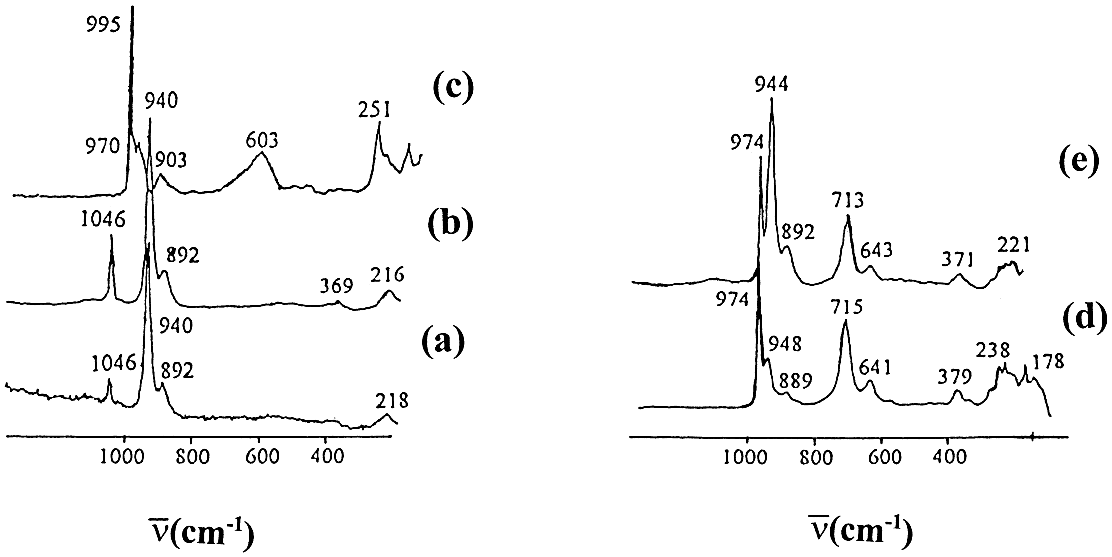

Fig. 2. Raman spectra of impregnating solutions: (a) Co$_{3/2}$1S, (b) Co$_{7/2}$1S, (c) Co$_{3/2}$3S, (d) Co$_{3/2}$2S, and (e) Co$_{7/2}$2S.

pore of the alumina. Most of the analyzed particles show a spectrum with an intense line at 880 cm^{-1} (Fig. 3(a)) but further investigations are necessary for a better identification of the species present which should correspond to a partial degradation of the $P_2Mo_5O_{23}^{6-}$ entity as the main line at 943 cm^{-1} characteristic of this HPA is still observed. Such a partial preservation is possible as the pH at the zero point charge (ZPC) of a Mo based solid [13] is inside the pH range of stability (i.e. 4–6) of this HPA. Moreover the temperature of drying is below the temperature of thermal decomposition of this HPA (determined by TGA analysis not reported here). The dried Co$_{3/2}$-2-C presents also some heterogeneities. The classical reported oxomolybdate phase is evidenced (line at 950 cm^{-1} – Fig. 3(d)) on some particles. However, the Raman spectrum of other ones exhibits a sharp line at 974 cm^{-1} which could be assigned to the decomposition of the Dawson anion into a $PMo_9O_{34}^{9-}$ type specy as the line at 715 cm^{-1} is not observed (Fig. 3(e) and (f)) [8]. Finally, the Raman spectrum of the dried Co$_{3/2}$-3C shows only the features of the classical oxomolybdate phase (Fig. 3(g)). These results are not in agreement with other studies [2,10,14]. In particular Cheng and Luthra [14] studied the impregnation of $P_2Mo_{18}O_{62}^{6-}$ and $PMo_{12}O_{40}^{3-}$ on alumina and considered that these two entities adsorb intact.

No Raman spectrum has been observed for the Co$_{7/2}$3C. After drying in air or in nitrogen, the ^{31}P NMR spectrum of the Co$_{7/2}$3C sample (Fig. 4) exhibits a broad line at −8.2 ppm which corresponds to the one observed for the corresponding bulk reduced HPA. This indicates the preservation of the heteropolyanionic structure and that the Co ions remain in close contact with the Mo entities [6]. This observation is in agreement with the stability of reduced Keggin anions at high pH [15]. These results are in agreement with the different pH ranges of stability of these HPA. If non-reduced Keggin and Dawson anions are stable only in acidic medium, the reduced Keggin as well as the diphosphorepentamolybdate anions are stable at higher pH values. These results also show that the decomposition of these different HPA leads to the formation of different isopolymolybdate species some of them being not yet identified.

3.3. *Calcined oxidic catalysts*

Fig. 5 shows the Raman spectra of the calcined catalysts transferred in air. Whatever the solid neither bulk MoO_3 nor $CoMoO_4$ formation is evidenced with reference to the literature data [16]. A good dispersion is thus obtained which is confirmed by XPS measurements (not reported here). The Raman features of all

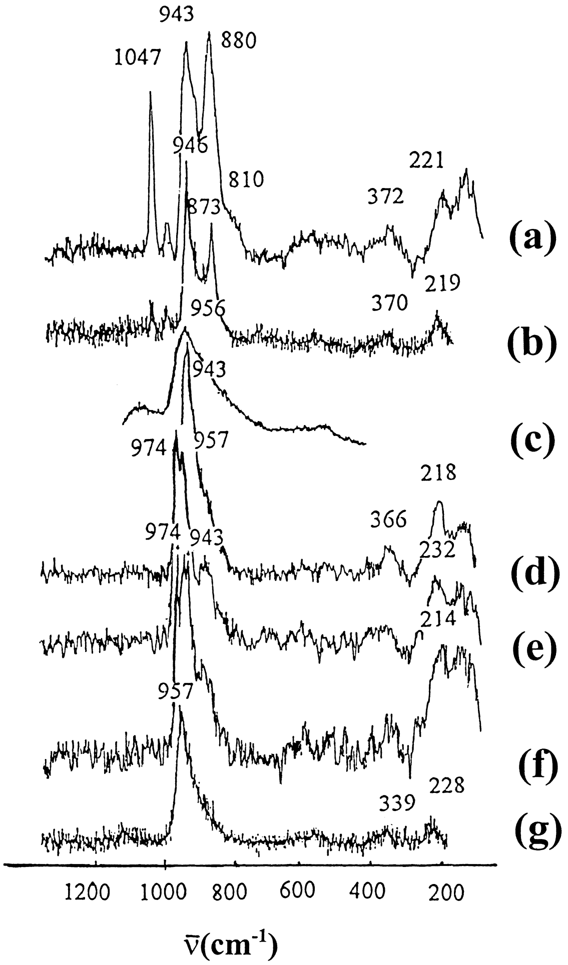

Fig. 3. Raman spectra of dried catalysts (P_{laser}=1 mW otherwise specified): (a, b) $Co_{7/2}1C$, (c) $Co_{7/2}1C$, P_{laser}=10 mW, (d–f) $Co_{3/2}2C$, and (g) $Co_{3/2}3C$.

the non-reduced samples characterize the surface polymolybdate phase with the main line at 952 cm^{-1}, the exact nature of which is not clearly established. Some authors [17,18] recently reported that it consists of 6-molybdoaluminate anions well-dispersed at the surface of the support, the formation of which is due to the solubilization of some surface aluminium atoms. So after calcination at 400°C, the non-reduced HPAs are not preserved.

As for the dried solid, no Raman spectrum is observed for the calcined $Co_{7/2}$-3C sample (under air or nitrogen) and the ^{31}P NMR spectrum remains similar to the one of the bulk HPA salt (Fig. 4(e)). A

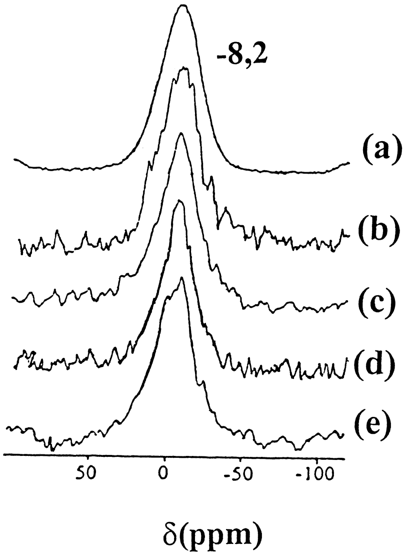

Fig. 4. ^{31}P MAS-NMR spectra of: (a) bulk $Co_{7/2}PMo_{12}O_{40}$, (b) $Co_{7/2}3C$ dried in air, (c) $Co_{7/2}3C$ dried and calcined in air, (d) $Co_{7/2}3C$ dried in N_2, and (e) $Co_{7/2}3C$ dried and calcined in N_2.

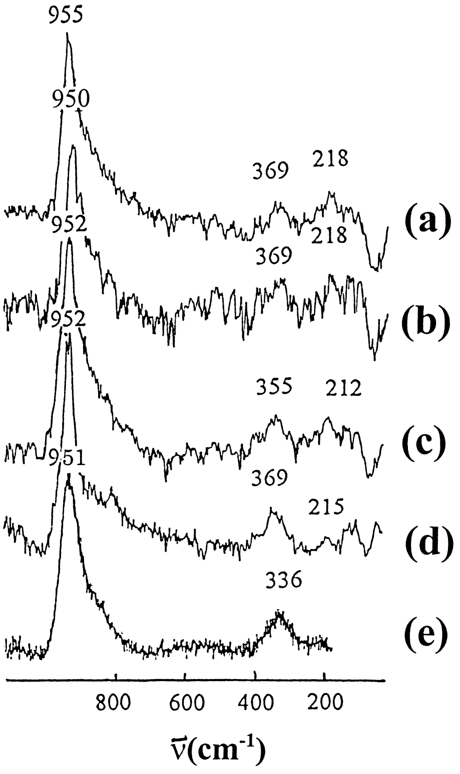

Fig. 5. Raman spectra of calcined catalysts: (a) $Co_{3/2}1C$, (b) $Co_{7/2}1C$, (c) $Co_{3/2}2C$, (d) $Co_{7/2}2C$, and (e) $Co_{3/2}3C$.

Table 1
Thiophene HDS activity of the catalysts for different calcination procedures of the oxidic precursors

Catalysts	Calcination procedure	Thiophene HDS (% conversion)
$Co_{3/2}1C$	500°C/air	14
$Co_{7/2}1C$	400°C/air	24
$Co_{7/2}1C$	500°C/air	26
$Co_{3/2}2C$	500°C/air	14
$Co_{7/2}2C$	400°C/air	25
$Co_{7/2}2C$	500°C/air	27
$Co_{3/2}3C$	400°C/air	15
$Co_{7/2}3C$	400°C/N_2	32
$Co_{7/2}3C$	500°C/N_2	27
$Co_{7/2}3C$	550°C/N_2	25.5

recent study of classical hydrotreating catalysts reports a strong decrease of the intensity of the ^{31}P NMR lines due to the paramagnetic effect of the Co in direct interaction with the phosphate groups [19]. So, in our samples, the observation of a NMR signal could be an evidence of the partial preservation of some Keggin units in interaction with Co ions, preventing a direct interaction of Co ions with the P atoms. Indeed, the temperature of degradation is higher than the temperature of calcination of the solids [20]. Further experiments are now under progress to check this hypothesis.

3.4. Activity

Table 1 shows the catalytic performances of the so-obtained solids expressed as a conversion percentage of thiophene. Whatever the method of preparation of the oxidic precursor, the activities of the low Co loading catalysts are similar. At higher Co loadings, the highest promoting effect is observed with the $Co_{7/2}3C$ calcined at 400°C. This result could be correlated to the aforementioned preservation of the HPA in the pore and to the strong interaction between the promoter and the HPA as well as to the different nature of the surface oxomolybdate species present on the oxidic precursor. This should induce a decrease of the fraction of Co atoms involved in the formation of the well-known surface "$CoAl_2O_4$" species [21]. Thus more Co atoms would participate in the formation of the CoMoS active phase obtained by sulfidation, the existence of which was evidenced by XPS measurements (not presented here). The decrease of the activity of this catalyst upon calcination at 500°C is in agreement with this hypothesis. Indeed upon calcination at 500°C, its activity decreases and becomes similar to those obtained for the $Co_{7/2}1C$ and $Co_{7/2}2C$ calcined at 500°C. This means that the reduced HPA is completely decomposed when the oxidic precursor is calcined at 500°C, a temperature higher than the temperature of decomposition of the bulk HPA.

4. Conclusion

A comparison between three methods of preparation of Co–Mo–P–based HDS catalysts has been undertaken through impregnation with solutions containing well-defined heteropolyanions, i.e. $PMo_{12}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$, $P_2Mo_5O_{23}^{6-}$ and $PMo_{12}O_{40}^{7-}$. The main findings of this work can be summarized as follows:

1. The nature of the supported oxomolybdate phase of the oxidic precursor prepared with non-reduced HPA is similar to the one obtained for solids prepared without phosphorus in the impregnating solution and could be described as consisting of well-dispersed 6-molybdoaluminate entities.
2. The structure of the reduced Keggin anion is preserved upon impregnation and a strong interaction of the promoter atoms with the HPA entities is evidenced. The nature of the oxomolybdate phase after calcination is different from those obtained by impregnation with non-reduced entities.
3. The catalysts prepared with reduced Keggin are the most active. This could be attributed to the stabilization of this Co-HPA structure which induces after sulfidation a better decoration of the MoS_2 platelets by the promoter atoms. Such a preparation could also affect the size of these crystallites. A study by high resolution electron microscopy is therefore underway to characterize their morphology.

References

[1] C. Wivel, B.S. Clausen, R. Candia, S. Morup, H. Tøpsøe, J. Catal. 87 (1984) 497.

[2] J.A.R. van Veen, P.A.J.M. Hendriks, R.R. Andrea, E.J.G.M. Romers, A.E. Wilson, J. Phys. Chem. 94 (1990) 5282.

[3] A. Spozhakina, S. Damyanova, V. Sharkova, D. Shopov, T. Yrieva, Proceedings of the Sixth International Symposium on Heterogeneous Catalysis, part 1, Sofia, 1987, p. 503.
[4] S. Damyanova, A. Spozhakina, D. Shopov, Appl. Catal. 48 (1989) 177.
[5] A.M. Maitra, N.W. Cant, D.L. Trimm, Appl. Catal. 48 (1989) 187.
[6] A. Griboval, P. Blanchard, E. Payen, M. Fournier, J.L. Dubois, Stud. Surf. Sci. Catal. 106 (1997) 181.
[7] J.J. Heinerman, A.J. van-Hengstum, M. de-Wind, EP Patent 0469675 A1, 1992.
[8] L. Lyhamn, L. Pettersson, Chem. Script. 12 (1977) 142.
[9] L. Pettersson, I. Andersson, L-O. Öhman, Inorg. Chem. 25 (1986) 4726.
[10] H. Kraus, R. Prins, J. Catal. 164 (1996) 251.
[11] J.A.R. van Veen, O. Sudmeijer, C.A. Emeis, H. De Wit, J. Chem. Soc. Dalton Trans. (1986) 1825.
[12] M.T. Pope, in: Heteropoly and Isopoly Oxometalates, Springer, Berlin, 1983, and references therein.
[13] D.S. Kim, K. Segawa, T. Soeya, I.E. Wachs, J. Catal. 136 (1992) 539.
[14] W.-C. Cheng, N.P. Luthra, J. Catal. 109 (1988) 163.
[15] R. Massart, G. Hervé, Revue de Chimie Minérale 5 (1968) 501.
[16] E. Payen, J. Barbillat, J. Grimblot, J.P. Bonnelle, Spect. Lett. 11(12) (1978) 997.
[17] X. Carrier, J.F. Lambert, M. Che, J. Am. Chem. Soc. 119 (1997) 10137.
[18] L. Le Bihan, P. Blanchard, M. Fournier, J. Grimblot, E. Payen, J. Chem. Soc. Far. Trans. in press.
[19] H. Kraus, R. Prins, J. Catal. 170 (1997) 20.
[20] P. Rabette, D. Olivier, in: P.C.H. Mitchell (Ed.), First International Conference on the Chemistry and Uses of Molybdenum, Climax Molybdenum Company, Reading, MA, 1973, p. 159.
[21] H. Tøpsøe, B.S. Clausen, Appl. Catal. 25 (1986) 273.