Catalyst made of NiMo sulfide supported on hydroxyapatite: influence of Al addition on support properties and on the catalytic conversion of dimethyldisulfide.

NADIA EL AZARIFI¹, ABDELHAK EL OUASSOULI¹, MAHJOUB LAKHDAR¹, ABDELAZIZ EZZAMARTY¹, JACOBUS van GESTEL², and JACQUES LEGLISE^{2,*}

¹ Laboratoire de Catalyse Hétérogène, Université Hassan II, Faculté des sciences Aïn Chock, BP. 5366, MAARIF, Casablanca, Morocco.

² Laboratoire Catalyse et Spectrochimie, UMR.CNRS.6506, ISMRA, 6 Bd du Maréchal Juin, 14050 Caen Cedex, France. * author correspondence

Abstract A hydroxyapatite and two AlPO_4 -enriched apatites have been synthesized to support NiMo sulfide. The NiMo/apatite catalysts convert selectively dimethyldisulfide into methanethiol, contrarily to their analogues NiMo/ Al_2O_3 . We established that the activity is improved when using a calcium-deficient apatite. It is showed that superficial HPO_4^{2-} groups favor the NiMo sulfide dispersion. A small amount of AlPO_4 increases the surface area, and thus the catalyst activity. The activity is compared to that of a commercial NiMoP/ Al_2O_3 catalyst.

INTRODUCTION

Phosphorus is often found in the formulation of commercial hydrotreating catalysts such as NiMo/ Al_2O_3 . The presence of phosphate groups improves the dispersion of the sulfided NiMo phase on the alumina support, resulting in higher activity for hydrogenation and C-heteroatom breakage¹. On the other hand, calcium phosphate ores are easily available and constitute a cheap source of material². In spite of this, phosphate materials are not much utilized in catalysis³. Hence, the combination of a calcium phosphate solid with the NiMo couple may provide a catalyst that can find use in hydrotreatment or sulfur chemical synthesis.

We investigate here a hydroxyapatite as a support of NiMo sulfide catalyst. Calcium phosphates prepared in presence of Al ions with the objective of improving the textural properties will be also tested. The sulfided NiMo/phosphate catalysts will be compared to a series of NiMo/ Al_2O_3 and commercial NiMoP/ Al_2O_3 catalysts.

EXPERIMENTAL

Supports and catalysts The phosphate supports were prepared by precipitation. A volume of 300 cm³ of calcium or aluminum nitrate solution (0.26 M) was poured dropwise

in 1000 cm³ of an ammonium hydrogenophosphate boiling solution (0.09 M). Two supports were prepared from a mixed Al-Ca solution at the same global molarity; Al ions amounted to 10 or 20% of the cations. Every solution was adjusted to pH 10 with ammonia before the precipitation. The solids were filtered, washed, and dried in air during 12 h at 80°C. The calcium phosphate is denoted later as CP, the Al-enriched solids as ACP-x, with x the Al weight content (Table 1), and the aluminum phosphate as AP.

The NiMo oxidic precursors were prepared by successive pore filling impregnation with an ammonium heptamolybdate solution at pH 7, then, after intermediate calcination at 400°C, with a nickel nitrate solution at the same pH. The Mo content ranged from 0 to 13 wt %, and the Ni content up to 3.5 wt %; the Ni/(Ni+Mo) atomic ratio was fixed at 0.38. The same procedure was applied to an γ -alumina from Ketjen 000.1.5E (220 m² g⁻¹, 0.6 cm³ g⁻¹), but with a Ni/(Ni+Mo) ratio of 0.30. The NiMo catalysts were confronted to a commercial NiMoP/Al₂O₃, HR348 from Procatalyse.

Structures were assessed from X-rays diffraction and infrared spectroscopy. The morphology was examined using scanning electron microscopy, and the textural properties were determined by means of nitrogen adsorption at -196°C.

Catalytic measurement The NiMo solids, calcined at 500°C, were sulfided in the catalytic reactor at 360°C (5°C min⁻¹) and 1 atm during 3 hours by a flow (0.08 mol h⁻¹) of dimethyldisulfide (DMDS, 2.9 kPa) diluted in hydrogen.

The DMDS reaction was studied at 150°C or 200°C. The products were CH₃SH and CH₃SCH₃ only, identified by GC (OV1, FID detector). The steady-state fractional conversion x was obtained after 30 min with the phosphate catalysts. The catalyst activity was evaluated at conversion lower than 10% after changing if necessary the catalyst mass or DMDS flow rate. The catalyst activity is thus given by the first-order rate constant,

$$k = -\frac{F^\circ}{WC^\circ} \ln(1-x), \text{ in L h}^{-1} \text{ g}^{-1}$$

With F[°] the DMDS flow rate (1.8-5.6 mmol h⁻¹), C[°] the concentration (0.83 mmol L⁻¹) in the reactor at 150°C, and W the weight of catalyst (0.02-0.5 g).

The selectivity was measured at 200°C at conversions higher than 50%.

RESULTS AND INTERPRETATION

Characterization of the supports The Ca/P atomic ratio of the calcium phosphate CP is equal to 1.58 that agrees with a calcium deficient apatite². The X-rays diagram showed one structure only with space group P_{6₃m}; the parameters of the hexagonal unit-cell (Table 1) are conformed to the apatite structure⁴. This is supported by the infrared study; one found the band at 875 cm⁻¹ assigned to the HPO₄²⁻ groups substituting for PO₄³⁻ ions in the lattice of the calcium-deficient apatite²⁴. Furthermore, the intense band at 3570 cm⁻¹ shows OH stretch in hydroxyapatite (Fig. 1B).

From X-rays peak broadening, the crystalline domains were about 40 nm in size, whilst, from SEM, the solid CP appeared to be made of spherical grains of 0.1 to 5 μm in diameter. Outside the grains, numerous irregular cracks with a foam-like shape are evidenced. They account for the specific area S_{BET} and the porous volume V_p (Table 1). The porosity is essentially intercrystalline since there is no microporous volume. Hence, the pore radius R_p is large enough (Table 1) to provide an easy access for the reactants.

FIGURE 1. Infrared spectra of calcium phosphate CP and mixed aluminum-calcium phosphates ACP-1.5 and ACP-3.4 calcined at 500°C: A- band structure region, outgassed at 150°C; B- hydroxyl stretching regions, outgassed at 350°C. self-supported disk 20 mg cm^{-2} .

TABLE 1. Elemental analyses, textural properties, and unit-cell parameters of the phosphate supports.

Support	Chemical analyses			Adsorptiometry ^a			X-rays diffraction ^b	
	Ca wt. %	Al wt. %	P wt. %	S_{BET} m^2g^{-1}	V_p cm^3g^{-1}	R_p nm	a nm	c nm
CP	38.3	0	18.8	83	0.32	7.7	0.942	0.689
ACP-1.5	36.0	1.5	19.4	140	0.54	7.7	0.942	0.689
ACP-3.4	33.8	3.4	18.0	194	0.60	6.2	0.943	0.688
AP	0	25.1	24.5	155	0.91	11.7	-	-

^a solids treated under vacuum at 400°C – ^b calcined at 500°C

The X-rays diagrams of the aluminum-containing supports ACP resemble that of the hydroxyapatite CP. The cell parameters did not change because of Al addition (Table 1). This indicates that the aluminum ions do not substitute for calcium in the apatite lattice. Indeed, both Al samples show two new bands at 3679 and 3791 cm^{-1} (Fig. 1B), of which intensities increase with the Al content. The bands resist upon calcination at 500°C, and

hence reveal stable hydroxyl species. These bands are observed in high surface area AlPO_4 ⁵. Therefore, the occurrence of such extra AlPO_4 phase in both mixed Al-Ca phosphates is very likely. In the SEM images, the apatitic grains appeared effectively glued by some other material. As further evidence, the composition of the aluminum phosphate AP agrees with AlPO_4 . Moreover, AP was found amorphous and exhibits high surface area and porous volume as the ACP samples (Table 1). This shows the benefit of adding Al ions at the preparation stage on the textural properties of apatitic supports.

On the other hand, assuming that all Al ions belong to an AlPO_4 phase, the Ca/P ratio of the apatite component in ACP-3.4 is calculated at 1.66, whereas the Ca/P ratio of the ACP-1.5 sample was similar to that of the calcium phosphate CP. Hence, the apatite is certainly stoichiometric in the Al richer ACP-3.4 sample. The disappearance of the band at 875 cm^{-1} characterizing calcium-deficient apatite corroborates such hypothesis (Fig. 1A).

In conclusion, the calcium phosphate CP is a calcium deficient hydroxyapatite with formula $(\text{Ca})_{9.5}(\text{HPO}_4)_{0.5}(\text{PO}_4)_{5.5}(\text{OH})_{1.5}$. The Al-enriched ACP-1.5 and ACP-3.4 samples associate a crystalline apatite respectively with 7 wt.% and 15 % of amorphous AlPO_4 . The supports are thus different, which may effect the localization of the NiMo phases and consequently the catalyst activity.

Catalytic activity DMDS is totally converted into H_2S and CH_4 at 360°C . Therefore, the sulfided NiMo/apatite catalysts exhibit hydrodesulfurization properties as the classical NiMo/ Al_2O_3 hydrotreating catalysts¹.

FIGURE 2. Influence of the Mo coverage (atom nm^{-2} of support) on the activity of sulfided NiMo catalyst supported on: CP (●), ACP-1.5 (▲), ACP-3.4 (▼), and Al_2O_3 (■) calcined at 500°C .

At 150°C , DMDS is selectively reduced to CH_3SH . With all catalysts, the activity increases proportionally to the NiMo content up to a limiting coverage, then stays constant beyond (Fig. 2). Strikingly, a similar limit, about 3.5 Mo atoms per nm^2 , is found with the

calcium-deficient apatitic supports CP or ACP-1.5 and with alumina. At the same coverage, the NiMo/ACP-1.5 catalysts are more active than their homologue NiMo/CP (Fig. 2) because the NiMo phases are better sulfided (Table 2). Moreover, the NiMo/ACP-1.5 catalysts accommodate more NiMo due to their higher surface area, and in any case are more active than the NiMo/CP catalysts. The two above features show again the importance of adding Al at the stage of the precipitation.

On the other hand, the Al-rich NiMo/ACP-3.4 samples differed from the other apatitic catalysts. They are much less active although they have the highest surface area (Table 1). Furthermore, the activity appears to be limited at a lower metal coverage (Fig. 2). This is related to the apatite support since the activity measured with the NiMo/AP sample is about the same as that of the NiMo/ACP-3.4 catalyst (Table 2). Indeed, in the ACP-3.4 sample, the stoichiometric apatite component bears a smaller amount of superficial HPO_4^{2-} groups. This should be detrimental to an optimal anchoring of metal ions. Consequently, the sulfidation of NiMo is more incomplete (Table 2), pointing to lower sulfide dispersion⁶.

To elucidate this behavior, we vary the calcination temperature of the support. At higher temperature, the concentration of superficial HPO_4^{2-} groups should decrease. Accordingly, the activity was much higher when the apatitic supports were calcined at 400°C instead of 500°C, while the calcination little effects the activity of the AP and alumina samples (Table 2). We therefore conclude that the presence of apatitic HPO_4^{2-} groups or related surface defects is required to improve the dispersion of the Mo ions in the oxidic precursor, resulting in a better sulfide dispersion.

TABLE 2. Rate constants determined at 150°C over various NiMo catalysts (3.5 Mo atoms nm⁻²) on support calcined at 400°C or 500°C. Degree of sulfidation of NiMo on support calcined at 500°C. Comparison with the commercial NiMoP/Al₂O₃.

Catalyst	Rate constant (L h ⁻¹ g ⁻¹)		S/(Ni+Mo) at/at.
	400°C	500°C	
NiMo/CP	25.4	10.2	0.99
NiMo/ACP-1.5	35.7	14.9	1.20
NiMo/ACP-3.4	6.3	4.7	0.73
NiMo/AP	4.2	5.2	-
NiMo/Al ₂ O ₃	14.5	15.5	1.50
NiMoP/Al ₂ O ₃ ^a	15.5	16.3	-

^a the commercial NiMoP catalyst was calcined at 400°C or 500°C

Finally, the apatitic catalysts appeared to be more active than the alumina-based catalysts including the commercial NiMoP catalyst (Table 2). The superiority of the apatite catalysts is further evident when one focuses on selectivity. The apatite-based catalysts

are found very selective into CH_3SH formation while their alumina counterparts produce high amounts of CH_3SCH_3 ⁷ (Table 3), which is explained by a lower Lewis acidity in the case of the apatitic catalysts⁸. This is an attractive feature of NiMo/apatite catalysts because CH_3SH is an important intermediate in organic synthesis⁹.

TABLE 3. Selectivity into CH_3SH at different conversions measured at 200°C.

Catalyst	NiMo/ACP-1.5		NiMo/ Al_2O_3	
DMDS conversion (%)	65.8	94.2	60.4	89.3
CH_3SH selectivity (mol%)	99.5	99.0	89.9	25.4

CONCLUSION

Hydroxyapatites are efficient support of NiMo sulfide catalyst for desulfurization and selective reduction of dimethyldisulfide. Addition of Al ions during the preparation results in an intimate mixture of crystalline apatite and amorphous AlPO_4 . This leads to an important increase in surface area and porous volume that is beneficial to the catalytic activity. The highest activity is obtained with calcium-deficient apatite because superficial HPO_4^{2-} species facilitate the dispersion of the NiMo phases. The activity is maximal for the same coverage regardless of calcium-deficient apatite and alumina supports. When the support is calcined at 400°C, the apatitic catalysts are superior to NiMo/ Al_2O_3 and a commercial NiMoP/ Al_2O_3 catalysts.

ACKNOWLEDGEMENT

The authors thank the Comité Mixte Franco-Marocain for financial support in the frame of Action Intégrée through grant 97/018/SM.

REFERENCES

- 1 H. Topsøe, B.S. Clausen, and F.E. Massoth, in "Hydrotreating Catalysis, Science and Technology", Springer-Verlag, Berlin (1996).
- 2 J.C. Elliot, in "Structure and Chemistry of the Apatites and Other Calcium Orthophosphates", Elsevier, Amsterdam, (1994).
- 3 M.V. Twigg, in "Catalyst Handbook", Manson Publishing, London (1996).
- 4 A. El Ouassouli, A. Ezzemouri, A. Ezzamarty, M. Lakhdar, and J. Leglise, *J. Chim. Phys.*, 1999 (in press).
- 5 J.B. Peri, *Discuss Farad. Soc.*, 52, 55 (1971).
- 6 A. Cherif, A. El Ouassouli, A. Ezzamarty A., M. Lakhdar, and J. Leglise, in "Actes 4^{ème} Coll. Franco-Maghrébin de Catalyse", Presse université, Lille, 1, 83 (1996).
- 7 E. Cadot, M. Lacroix, M. Breyse, and E. Arretz, *J. Catal.*, 164, 490 (1996).
- 8 M. Ziolek, J. Kujawa, O. Saur, and J.C. Lavalley, *J. Phys. Chem.*, 97, 9761 (1993).
- 9 C. Forquy, and E. Arretz, *Stud. Surf. Sci. Catal.*, 41, 91 (1988).