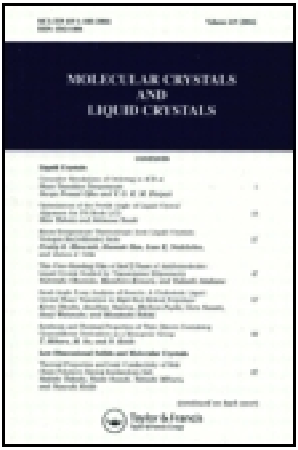

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Catalytic Sulfide Ion Oxidation over substituted $NiPS_3$ layered compounds and their sodium intercalates: A kinetic and XPS study

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Catalytic Sulfide Ion Oxidation over substituted $NiPS_3$ layered compounds and their sodium intercalates: A kinetic and XPS study

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The bimetallic $Ni_{0.6}Fe_{0.4}PS_3$ and and $Ni_{0.83}Cu_{0.34}PS_3$ layered compounds are shown to be more efficient than $NiPS_3$ at catalysing the oxydation of sulfide ions into sulfur at room temperature. The related sodium intercalates exhibit an even larger efficiency. An XPS study of these compounds is presented and discussed in relation to the catalytic activity.

Keywords: Intercalation; $NiPS_3$; XPS; Catalysis; Sulfide Oxidation; Environmental Protection

INTRODUCTION

Sulfide ions are one of the most powerful pollutants in industrial waste water and sewage water. Their oxidation by oxygen from the air according to the reaction: $S^{2-} + 1/2\ O_2 + H_2O$ ----> $S^0 + 2OH^-$ leads to the formation of non-poisonous elemental sulfur which can be removed by filtration or biological treatment. This process is of great importance for environmental protection and determines the necessity of design of novel effective industrial catalysts.

Previous studies[1] have shown that $NiPS_3$ catalyzes sulfide ions oxidation and an attempt has been made to explain the catalytic activity of $NiPS_3$ on the basis of a mechanism involving sequences of intercalation / deintercalation processes of sodium ions associated to redox modifications of the host lattice.We have shown previouly that $NiPS_3$ actually reacted with sodium sulfide aqueous solutions to give a sodium intercalate[2] that has turned out to be a more efficent catalyst than pristine $NiPS_3$ itself[3]. Subsequent exchange of the sodium ions by pyridinium ions has yielded an even more efficient intercalate. The catalytic efficiency of these compounds seems to be related to their ability to be deeply reduced by sulfide ions[3].

This communication shows that the bimetallic $Ni_{0.83}Cu_{0.34}PS_3$ and $Ni_{0.6}Fe_{0.4}PS_3$ compounds and their sodium intercalates are more efficient catalysts than $NiPS_3$ and its sodium intercalate. An XPS study of the electronic structure of these compounds provides evidence that the Ni ions in the bimetallic phases are more deeply reduced by sulfide ions than they are in pure $NiPS_3$.

EXPERIMENTAL

Subsituted $NiPS_3$ layered compounds $Ni_{0.83}Cu_{0.34}PS_3$ (denoted [NiCu]) and $Ni_{0.6}Fe_{0.4}PS_3$ (denoted [NiFe]) have been synthesized by reaction over one week of stoichiometric amounts of the elements at 700°C[4]. The material obtained was ground and refired for another week. Sodium intercalates were prepared by reacting the bimetallic phases with aqueous Na_2S under inert atmosphere, as they are very sensitive to oxidation[3]. XPS measurements were made by using a Leybold LHS 10 spectrometer. Details of the procedure, calibration method and data treament have already been described[3].

The catalytic activity of the samples (typically 0.01 g) for sulfide ion oxidation was measured under static conditions through the amount of oxygen consumed by an aqueous solution of Na_2S (20 ml). Measurements were carried out at different temperatures. The catalytic activity is expressed in moles of S^{2-} ions oxidized per gram -atom of Ni.

RESULTS

The [NiFe] and [NiCu] compounds and their sodium intercalates have been characterized by elemental analysis (obtained from the CNRS analytical service, see Table 1). The infrared spectra of both pristine [NiFe] and [NiCu] compounds display the usual $\nu(PS_3)$ mode at 570 cm^{-1}. This band is also present in the spectra of the intercalates, which in addition display a weak band at 520 cm^{-1} previously attributed to $(PS_4)^{3-}$ species formed during the insertion process[3], as well as broad bands characteristic of water. The X-ray diffraction patterns of both intercalates display sharp 001 reflections. Complete intercalation was ensured by the disappearance of the 001 reflection of the pristine compounds.

TABLE I: Analytical data (mass %) and spacing of the bimetallic compounds

	Ni	Fe	Cu	P	S	Na	H	d(Å)
$Ni_{0,6}Fe_{0,4}PS_3$ [NiFe]	19.05	12.42		16.28	52.54			6,38
[NiFe] $Na_{0.95}(H_2O)_{1.6}$	13.55	8.75		10.45	36.67	8.37	1.2	12.42
$Ni_{0,83}Cu_{0,34}PS_3$[NiCu]	25.24		10.88	15.42	48.72			6.32
[NiCu] $Na_{0.70}(H_2O)_{1.7}$	20.80		7.54	12.70	38.15	6.61	1.45	12.37

The catalytic properties of pristine [NiFe] and [NiCu] have been compared to those of pristine $NiPS_3$ and $FePS_3$ at room temperature for a concentration of 15 g/l of the sulfide ions in aqueous solution. Results are shown in Figure 1. Although $FePS_3$ displays only a weak activity, the bimetallic, iron containing [NiFe] is two times more efficient than $NiPS_3$.

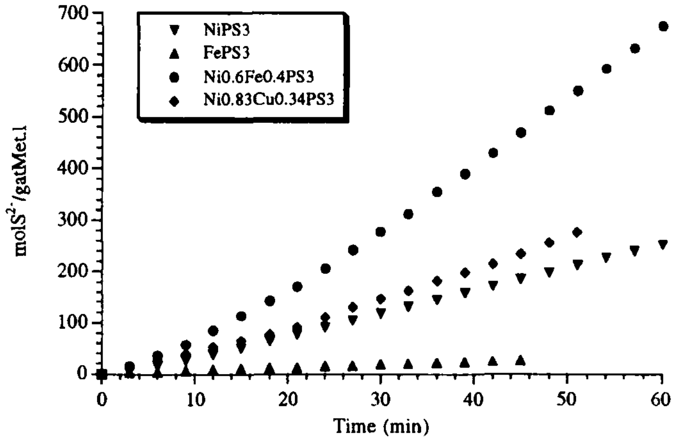

FIGURE 1 Kinetic curves of the sulfide ion catalytic oxydation at 20°C.

A comparative study of the catalytic properties of [NiFe], [NiCu] and their sodium intercalates has been carried out at different temperatures (T = 20, 30, 40, 50°C) using a sulfide ion concentration of 15 g/l in aqueous solution. Results are reported in Figure 2. In both cases, the efficency of the intercalates is larger than that of the pristine materials. However, in contrast to $NiPS_3$[3], the activation energies for the [NiFe] and [NiCu] sodium intercalates are found larger (32 and 38 kJ mol^{-1}, respectively) than those for the pristine [NiFe] and [NiCu] compounds (20 and 23 kJ mol^{-1}, respectively) .

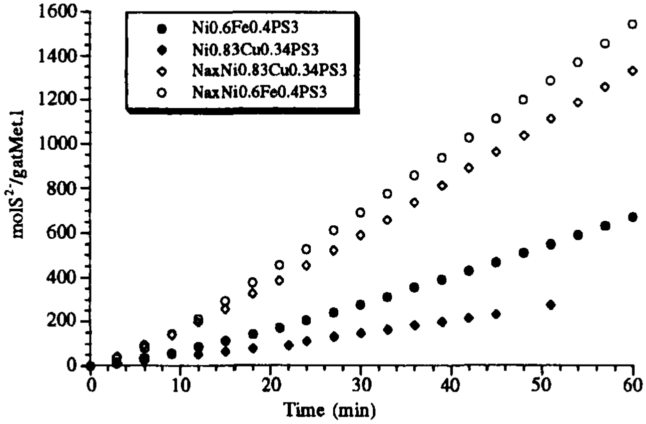

FIGURE 2 Kinetic curves of the sulfide ion catalytic oxydation at 20°C.

XPS Study

The Ni XPS spectra of the samples investigated consist of spin-orbit doublets $2p_{3/2}$ and $2p_{1/2}$, each component of the doublet showing a satellite feature. The $2p_{3/2}$ experimental spectra of [NiFe], [NiCu] and their sodium intercalates are shown in Figure 3(B and C). The spectra of $NiPS_3$ and its sodium intercalate are recalled in Figure 3A for comparison. The parameter values derived from the best fit are listed in Table 2. Insertion of the sodium ions results in a significant shift towards lower binding energy by 2 eV for [NiCu], 1 eV for [NiFe], whereas almost no shift is oberved in the case of $NiPS_3$. The insertion process also considerably weakens the intensity of the satellites. These results clearly demonstrate that the insertion process increases the electron density on the nickel ions, in agreement ith results previously published.[5]

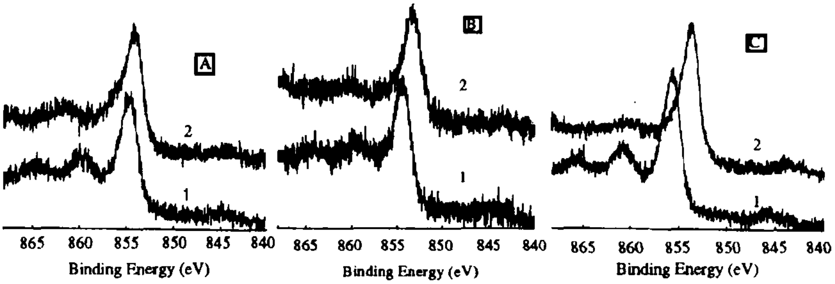

FIGURE 3 Ni $2p_{3/2}$ XPS spectra of (A1) $NiPS_3$; (B1) [NiFe]; (C1) [NiCu]. The related sodium intercalates are labelled A2,B2,C2, respectively.

Additional data have been obtained for [NiCu]: upon sodium insertion, the Cu, P and S XPS doublets all shift towards lower energy: from 933.4 to 932.3 eV for Cu, from 132.8 to 132.3 eV for P, from 163.1 to 162.0 eV for S.

TABLE 2. Parameter values obtained from the best fit of Ni $2p_{3/2}$; E: position in binding energy, I: intensity calculated as the total area under each line, relative to the principal line, D: separation of the satellite structure from the main line.

Compound	E_b (eV) main peak	I	E_b (eV) S_1	I_1	E_b (eV) S_2	I_2	E_b (eV) S_3	I_3
$NiPS_3$	854.60	1	856.30	0.14	859.60	0.35	864.30	0.12
Na_xNiPS_3	854.45	1	856.20	0.66	861.35	0.36	864.26	0.12
[NiCu]	855.61	1	856.62	0.31	860.74	0.44	865.60	0.21
Na_x[NiCu]	853.83	1	856.37	0.19	860.70	0.19		
[NiFe]	854.40	1	856.20	0.15	859.50	0.35	864.20	0.15
Na_x[NiFe]	853.40	1	855.20	0.45	860.40	0.20	863.2	0.13

The Fe and P XPS spectra have been recorded for [NiFe] and its intercalate, but the peaks are somewhat broad due to the presence of surface impurities (presence of Fe(III) and of phosphates). The ^{57}Fe Mossbauer spectrum of the [NiFe] intercalate shows a spectrum very similar to that of the Li_xFePS_3 intercalates[6], which is an indication that the Fe ions are also reduced.

DISCUSSION

The kinetic study shows in the first place that the bimetallic [NiCu] and [NiFe] compounds are more efficient catalyst than $NiPS_3$. Comparison of the XPS spectra of the bimetallic compounds with those of $NiPS_3$ clearly demonstrates that intercalation of the sodium ions causes a larger increase of the electron density on the nickel ions in [NiCu] and [NiFe] than in $NiPS_3$. In other words, the sulfide ions cause a deeper reduction of the bimetallic compounds, which means that the latter can more easily take up electrons from the sulfide ions and help them to be oxidized.

The question then arises as why do the bimetallic phases more readily react with sulfide solution than $NiPS_3$ does. We have shown previously that the reaction of $NiPS_3$ with sodium sulfide led to side reactions, such as loss of phosphorus, appearance of PS_4^{3-} ions[3]. Such side reactions seem to be more limited in the case of the bimetallic compounds. One possible reason is that the latter contains more lattice defects, which facilitate intercalation.

As the intercalates of the bimetallic compounds are already deeply reduced, it is not obvious why they should be more efficient than the pristine phases at catalyzing sulfide oxidation. We note that the activation energy is actually higher for the intercalates. It is obvious from the synthesis that the intercalates are in a more divided state than the pristine phases, and hence a possible reason for the higher activity of the intercalates may be a higher specific surface.

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