Inorg. Chem. **2003**, *42*, 1764–1768

Inorganic Chemistry
Article

New Low-Temperature Preparations of Some Simple and Mixed Co and Ni Dispersed Sulfides and Their Chemical Behavior in Reducing Atmosphere

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Received September 11, 2002

A series of simple (CoS_2, Co_9S_8, NiS_2, NiS, Ni_3S_2) and mixed sulfides ($NiCo_2S_4$, $Ni_{0.33}Co_{0.67}S_2$, $Ni_3Co_6S_8$, $CuCo_2S_4$, $Cu_{0.33}Co_{0.67}S_2$) was prepared using low-temperature procedures. To obtain the mixed sulfides, the mixtures of the solutions of the corresponding salts were precipitated by Na_2S and then heated in a sulfiding atmosphere at 300 °C. It has been found that the product phase composition depends on the sulfiding atmosphere. Using a H_2S/Ar mixture leads to pyrite type sulfides, whereas treatment in H_2S/H_2 flow allowed the preparation of Ni–Co and Cu–Co thiospinels. The as prepared highly dispersed single-phase materials were characterized by X-ray powder diffraction, scanning electron microscopy, temperature-programmed reduction (TPR), elemental analysis, and BET surface area measurements.

Introduction

The sulfides of cobalt and nickel attract significant attention due to their importance for catalysis. Mixed Ni(Co)−Mo(W) sulfides are used as the hydrotreating catalysts; individual Ni and Co sulfides are active in the carbon liquefaction reaction.[1] High-temperature synthesis of Ni and Co sulfides from the metals and sulfur gives large crystals with low specific surface area, which are not suitable for catalytic applications. Therefore, many soft procedures were developed in order to increase the sulfides' dispersity, including "homogeneous precipitation",[2] solvothermal reaction between the corresponding salts and thiourea,[3] decomposition of dithiooxamate[4] or diethyldithiocarbamate complexes,[5] or sulfidation of the hexamine chlorides[6] or sulfates.[7] These methods allowed the preparation of the simple Co and Ni sulfides in a highly dispersed form. On the contrary, little attention was paid to the preparation of highly dispersed mixed sulfides. With exception of the work of Bouchard[8] reporting on the preparation of poorly crystalline $Co_xNi_{1-x}S_2$, $Fe_xCo_{1-x}S_2$ and $Cu_xNi_{1-x}S_2$ solid solutions, no information is available in the literature. As the most efficient catalysts are always mixed-metal sulfides,[1] development of methods allowing the preparation of highly dispersed ternary sulfides is of considerable interest.

Another important question related to the applications of the mixed sulfides as catalysts concerns their stability under different reaction conditions, in the presence of H_2S and H_2. If for the binary sulfides the data are available,[9,10] the behavior of mixed sulfides in these conditions was not studied.

In the present work we describe low-temperature preparation procedures which allow one to obtain dispersions of different mixed and simple Co- and Ni-containing sulfides.

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10.1021/ic026024j CCC: $25.00

Table 1. Preparation Conditions, Chemical Composition, and Some Properties of Sulfides Obtained in This Work

product	annealing atm[c]	crystallite size, Å	BET surface area, m^2/g[d]	% metal		
				metal	obsd	calcd
$NiCo_2S_4$	H_2S/H_2	243	26.6	Ni Co	19.2 39.5	19.3 38.7
$Ni_3Co_6S_8$[a]	$H_2S/H_2 \rightarrow H_2$	295	23.5	Ni Co	22.1 43.9	22.4 45.0
$Ni_{0.33}Co_{0.67}S_2$	H_2S/Ar	177	22.8	Ni Co	15.3 30.5	15.8 32.1
$CuCo_2S_4$	H_2S/H_2	346	21.8	Cu Co	21.4 38.6	20.5 38.1
$Cu_{0.33}Co_{0.67}S_2$	H_2S/Ar	152	25.7	Cu Co	16.3 31.4	16.9 31.7
Co_9S_8	H_2S/H_2	259	49.3		64.8	67.4
CoS_2	H_2S/Ar	144	48.6		45.0	47.9
NiS (millerite)	H_2S/H_2	489	5.6		63.3	64.7
NiS (NiAs type)[b]	H_2S/H_2	526	2.7		63.0	64.7
Ni_3S_2[a]	$H_2S/H_2 \rightarrow H_2$	520	7.1		72.8	73.3
NiS_2	H_2S/Ar	307	31.3		46.9	47.8

[a] 4 h in H_2S/H_2, then 4 h in H_2. [b] Prepared at 450 °C. [c] 300 °C, 4 h, 15 vol % of H_2S. [d] Measured after desorption at 300 °C during 15 h.

Chemical behavior of the obtained highly dispersed solids in H_2S/H_2 and H_2S/Ar atmospheres was also studied.

Experimental Section

High purity grade $Co(NO_3)_2{\cdot}6H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$, and $Na_2S{\cdot}9H_2O$ from Aldrich were used as starting materials in the syntheses of pure and mixed Co and Ni sulfides. To prepare the Cu−Co sulfides the $Cu(NO_3)_2{\cdot}3H_2O$ and $[Co(NH_3)_6]Cl_3$ were employed. In a typical preparation, 0.01 mol of the salt or of the mixture of the corresponding salts was dissolved in 50 mL of water. Fifty milliliters of the solution containing the stoichiometric amount of $Na_2S{\cdot}9H_2O$ was then added dropwise at room temperature with vigorous stirring. The precipitate obtained was thoroughly washed with water and dried under vacuum at room temperature during 12 h. The as prepared fresh precursors were treated in a flow of 15 vol % H_2S/Ar or 15 vol % H_2S/H_2. The samples were then cooled to room temperature in the same atmosphere, flushed with Ar, and stored in sealed tubes under Ar atmosphere to prevent their oxidation. The treatment conditions and some properties of the prepared sulfides are given in Table 1.

X-ray powder diffraction patterns were recorded on a SIEMENS D5000 diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å) with a 0.03° 2Θ scan step. BET surface areas were calculated from N_2 adsorption isotherm at 78 K measured on a MICROMERITICS ASAP 2010 instrument. Scanning electron microscopy (SEM) images were taken on a JEOL 6400 scanning electron microscope. Temperature-programmed reduction (TPR) was carried out in a quartz reactor. The sulfide samples (ca. 0.01 g) were linearly heated under hydrogen flow up to 1000 °C (5 °C/min). Hydrogen sulfide evolved during reduction was detected by an HNU photoionization detector equipped with a 10.2 eV UV light source. The amount of H_2S evolved was quantified after the detector was calibrated with a gas mixture of known H_2S concentration. The chemical analysis of the sulfides were performed in the Central Analysis Service of National Center for Scientific Research (Vernaison, France).

Results and Discussion

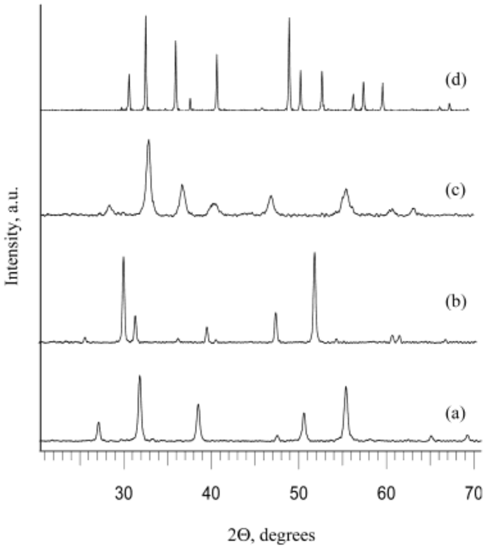

Figure 1. XRD patterns of some sulfides prepared in this work: (a) $NiCo_2S_4$, (b) $Ni_3Co_6S_8$, (c) CoS_2, and NiS (millerite).

Composition, Structural and Textural Properties. The precipitates obtained after addition of Na_2S to the transition metal containing solutions are X-ray amorphous. The exact nature of these materials was not studied here, but it was previously supposed that the composition of the Co and Ni sulfides freshly precipitated from the aqueous solution is close to $M(OH,SH)_2$, which during further aging transforms into a complex mixture of sulfides and basic salts.[11] We have found that such amorphous precursors can be easily transformed into different sulfides using low-temperature treatments in H_2S-containing gaseous mixtures.

In the case of a Cu−Co−S system the situation is less simple. We have found that utilization of $Cu(NO_3)_2{\cdot}3H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$ does not allow one to obtain a single phase of mixed sulfides and that mixtures of phases form after treatment of the precipitate both in H_2S/H_2 and in H_2S/Ar atmospheres. Probably, a significant difference in the solubility products of CoS and CuS (10^{-20} and 10^{-35} correspondingly[11]) provokes the phase separation already during the precipitation. Utilization of $[Co(NH_3)_6]Cl_3$ as the cobalt source may have allowed the production of a homogeneous precipitate.

The XRD data show that the prepared sulfides are single-phase solids having diagrams corresponding to the known JCPDS patterns (Figure 1). In the case of $NiCo_2S_4$ and $CuCo_2S_4$ the positions of the XRD peaks give direct evidence for the formation of the mixed sulfides. In the case of the pyrite-type solid solutions the conclusion is not straightforward, because low crystallinity of these compounds makes impossible precise determination of their cell parameters. Thus, taking into account the closeness of the cell parameters of the individual components (NiS_2, CuS_2, and CoS_2), the formation of mixed sulfides cannot be directly proven. However, in this case formation of the solid solutions might be inferred from the chemical behavior of the solids. Indeed, both solids $Ni_{0.33}Co_{0.67}S_2$ and $Cu_{0.33}Co_{0.67}S_2$ can be easily transformed into the corresponding thiospinels after treatment

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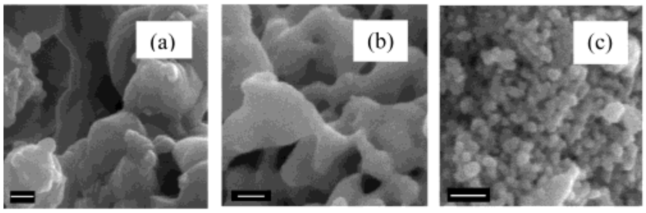

Figure 2. Scanning electron microscopy photographs of (a) NiS (NiAs type), (b) NiS (millerite), and (c) Co_9S_8 (scale bar is 100 nm).

at 300 °C under H_2S/H_2 atmosphere during 4 h (see below). Such mild conditions of phase transformation suggest homogeneous distribution of the elements in the precursor.

The crystallite sizes calculated from the peak widths according to the Sherrer equation[12] show that the degree of crystallinity depends on the nature of the sulfide (Table 1). Poorly crystalline materials are obtained for the simple and mixed sulfides having the pyrite structures. Nearly the same crystallite size was reported previously for CoS_2 prepared in a different way (150 Å after heating at 300 °C[6]). The binary nickel sulfides have the largest crystallites, showing nearly the same crystallite size regardless of the preparation temperatures (300 °C for millerite and 450 °C for the hexagonal NiS). The ability of nickel sulfides to form well-crystallized materials under mild conditions was observed previously. For example, it has been found that the reaction between $NiCl_2$ and $Na_2S_2O_4$ in aqueous solution at pH = 6 leads to well-defined Ni_3S_2 particles already at room temperature.[13]

The developed low-temperature procedures allowed the preparation of well-dispersed solids having high surface areas (Table 1), whereas traditional preparations from elements in sealed evacuated silica tubes do not allow one to attain surface areas exceeding 3−5 m^2/g. Comparison between the SEM images of Co_9S_8 and nickel sulfides reveals clearly the difference in the texture of these materials (Figure 2). Regardless of the difference in the preparation temperature, both Ni sulfides consist of large particles (about 100−200 nm) forming compact agglomerates (Figure 2a,b). The crystallites of Co_9S_8 are much smaller (ca. 10−20 nm) and packed less tightly, thus providing the material a high intercrystalline surface area.

The chemical compositions of the sulfides correspond well to the simple stoichiometry, with the exception of Co_9S_8 and CoS_2. By contrast, all the Ni-containing sulfides show lower metal to sulfur atomic ratios (Table 1). For Co_9S_8, deviation from the stoichiometry was previously reported. For example, after annealing at 600 °C, the composition of the Co sulfide was found to be $Co_9S_{8.3}$.[5] Such a deviation can be explained by the presence of weakly bound surface sulfur species. Their amount might be considerable due to the high specific surface area of the simple cobalt sulfides and therefore high share of superficial atoms in the total amount of matter. Such species are often observed on the surface of highly dispersed sulfide catalysts prepared in H_2S-containing atmosphere.[14] Thus, the excess sulfur observed in our case is due to the surface rather than a bulk overstoichiometry. In the case of Co_9S_8 these surface species can be easily eliminated by means of reaction with hydrogen without any change in the structure. The reaction is clearly seen in the Co_9S_8 TPR pattern in which the peak at ca. 270 °C corresponds to the elimination of such species (Figure 3a).

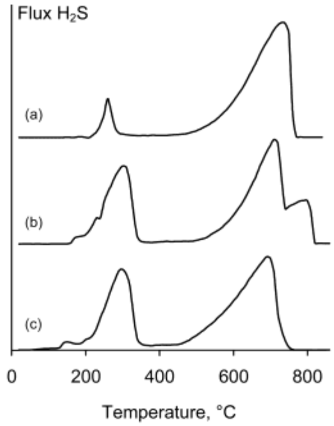

Figure 3. Temperature-programmed reduction (TPR) patterns of (a) Co_9S_8, (b) $CuCo_2S_4$, and (c) $NiCo_2S_4$.

Table 2. The Products Obtained from the Precipitates vs the Gaseous Mixtures Used

	product obtained at 300 °C		
precursor	15% H_2S/Ar	15% H_2S/H_2	H_2[b]
Co−S	CoS_2	Co_9S_8	Co_9S_8
Ni−S	NiS_2	NiS (millerite) NiS (NiAs type)[a]	Ni_3S_2
Ni−Co−S	$Ni_{0.33}Co_{0.67}S_2$	$NiCo_2S_4$	$Ni_3Co_6S_8$
Cu−Co−S	$Cu_{0.33}Co_{0.67}S_2$	$CuCo_2S_4$	$Cu_2S+Co_9S_8$

[a] At 450 °C. [b] After a sulfiding treatment (H_2S/Ar or H_2S/H_2).

Chemical Behavior. The chemical behavior of the dispersed sulfide precipitates in different atmospheres is summarized in Table 2. The general feature of all the systems studied is that the treatment of the amorphous precursors in H_2S/Ar (15 vol %) atmosphere leads to formation of pyrite-type structures. The $Co_xNi_{1-x}S_2$ pyrite solid solutions were also prepared previously in $H_2S/N_2 \approx 1$ flow from the mixed-metal hydrated sulfates,[8] and CoS_2 was shown to form from $Co(NH_3)_6Cl_2$ under pure H_2S at 250 °C.[6] These similarities indicate that in pure H_2S or in H_2S/Ar mixture independently of the nature of the precursor the most stable structure for simple and mixed Co and Ni sulfides is pyrite.

However, in hydrogen atmosphere (with or without H_2S) all the pyrite-type sulfides are unstable and easily transform into sulfides containing S^{2-} anions, the particular structure depending on the metals involved.

Simple Co and Ni Sulfides. In the case of nickel, single phases of all the known sulfides can be obtained from the same amorphous sulfide precursor, depending on the conditions (Table 2). The millerite phase can be prepared at 300 °C in H_2S/H_2 flow. The same treatment at higher temperatures leads to the formation of NiS with the hexagonal (NiAs-

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type) structure. Thus, after the heating at 400 °C during 4 h ca. 70% of millerite is transformed into NiAs-type NiS, which is obtained pure after treatment at 450 °C. Alternatively, the Ni_3S_2 compound (hazelwoodite) can be prepared from millerite through a post-treatment in pure H_2. This transformation is reversible: heating of Ni_3S_2 in H_2S/H_2 flow at 300 °C allows the restoration of the NiS composition and the millerite structure. Finally, above 500 °C, reduction to metallic Ni occurs under H_2 as shown by the TPR experiment.

The experimentally observed chemical behavior of the nickel sulfides agrees well with the corresponding thermodynamical data (see Supporting Information). Whereas reduction of both NiS_2 and NiS is favorable, the presence of H_2S in the gaseous atmosphere allows stabilization of the intermediate composition: NiS.

The treatment of the Co−S precipitate in H_2S/H_2 atmosphere at 300 °C results in the formation of Co_9S_8, which also remains intact in pure H_2. Contrary to the mixed Ni−Co and Cu−Co sulfides (see below), the thiospinel Co_3S_4 did not form in our experiments. In order to clarify the stability of this compound it was prepared from the cobalt and sulfur in a silica sealed tube at 600 °C. It was then found that Co_3S_4 is stable in H_2S/H_2 atmosphere at 300 °C. However, in pure hydrogen, it transforms readily into Co_9S_8.

According to the thermodynamical data (see Supporting Information), under hydrogen CoS_2 can be reduced to Co_3S_4 or to Co_9S_8. On the contrary, the reduction of Co_3S_4 to Co_9S_8 observed under hydrogen flow at 300 °C should not proceed taking into account the very small value of the corresponding equilibrium constant ($K_a = 2.23 \times 10^{-45}$ at 600 K). This discrepancy is likely due to the fact that under hydrogen flow the conditions cannot be considered to correspond strictly to equilibrium.

Mixed Ni−Co and Cu−Co Sulfides. Heating of mixed Ni−Co and Cu−Co amorphous precursors as well as of the pyrite solid solutions under H_2S/H_2 flow at 300 °C leads to the formation of $NiCo_2S_4$ and $CuCo_2S_4$ (Table 2). It was established previously that these thiospinels are direct,[15,16] i.e., the cobalt atoms occupy octahedral sites and Ni or Cu tetrahedral ones in the hexagonal close packing of the sulfur atoms. Taking into account that these compounds formally contain Co(III), their formation under the highly reducing H_2S/H_2 atmosphere could not be predicted a priori. The stability of the mixed cobalt thiospinels means therefore that the d^6 electronic configuration could provide a high stability to octahedrally surrounded Co(III) not only in the low-spin complexes with strong donor ligands but also in sulfide environment within an extended solid phase.

However, this stability is not sufficient to prevent the transformation of Cu−Co and Ni−Co thiospinels in pure H_2 at 300 °C. $CuCo_2S_4$ decomposes into Co_9S_8 and Cu_2S; $NiCo_2S_4$ also loses sulfur, but it transforms into a new phase $Ni_3Co_6S_8$ having a pentlandite-type structure.[17] This compound was not previously described, but its stability can be anticipated since in $Ni_3Co_6S_8$ the average atomic number of the cations (27.33) is in the range 26.5−27.5 for which the pentlandite structure was found to be stable.[18]

The consecutive steps of reduction of the mixed sulfides can be easily followed by the TPR method (Figure 3b,c). In the TPR patterns, which describe the complete reduction of the sulfides to the metals, the first peaks correspond to the low-temperature transformations. The areas of these peaks (related to the amount of H_2S evolved during the reaction) represent 34% ($NiCo_2S_4$) and 45% ($CuCo_2S_4$) of the whole surface under the curves, which corresponds well to the part of the sulfur eliminated according to the equations (33% for $NiCo_2S_4$ and 43% for $CuCo_2S_4$):

$$3NiCo_2S_4 + 4H_2 \rightarrow Ni_3Co_6S_8 + 4H_2S \qquad (1)$$

$$18CuCo_2S_4 + 31H_2 \rightarrow 4Co_9S_8 + 9Cu_2S + 31H_2S \qquad (2)$$

We have also found that the transformation of the Ni−Co thiospinel into the pentlandite-like phase is reversible: heating of $Ni_3Co_6S_8$ in H_2S/H_2 flow leads to the initial thiospinel:

$$Ni_3Co_6S_8 + 4H_2S \rightarrow 3NiCo_2S_4 + 4H_2 \qquad (3)$$

Though the catalytic properties of the thiospinels in the hydrodesulfurization cannot be studied due to their low stability under reduced H_2S pressure, the data on the chemical behavior of the mixed sulfides can be correlated with some assumptions made about the properties of Co sulfide species present in the hydrotreatment catalysts. One of them concerns the oxidation state of the Co cations in the Co−Mo−S phase which was supposed to be higher than II.[19] The stability of the thiospinels Co_3S_4, $CuCo_2S_4$, and $NiCo_2S_4$, containing formally Co(III), in H_2S/H_2 atmosphere shows that in principle the Co atoms could really preserve in CoMoS catalysts an oxidation degree greater than II despite the highly reducing character of the gaseous medium involved in the hydrodesulfurization reaction.

It also was suggested that the ability of the Co and Ni atoms to change reversibly their coordination sphere and electronic configuration can play a key role in the catalytic desulfurization of sulfur-containing molecules.[20] The easy transformation of the spinel $NiCo_2S_4$ into the pentlandite $Ni_3Co_6S_8$ and vice versa in a reducing atmosphere is an example of such a phenomenon. The rearrangement of the anionic environment of the Co cations coupled to the change of their electronic state observed in this bulk phase transformation should naturally be much easier when the same atoms are located on the surface of the sulfide catalysts.

Conclusions

It is shown that a simple coprecipitation reaction in aqueous solution can be used as an efficient synthetic method

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for the preparation of highly dispersed mixed metal sulfides. The proper choice of the sulfiding atmosphere allows a control over the structure and composition of the solids. In H_2S/Ar atmosphere the pyrite structure is the most stable for the mixed Ni−Co and Cu−Co systems as well as for simple Co and Ni sulfides. The thiospinels $NiCo_2S_4$ and $CuCo_2S_4$ have been synthesized for the first time in poorly crystalline state in reducing atmosphere (H_2S/H_2, 300 °C). The treatment of $NiCo_2S_4$ in H_2 leads to its transformation into a new pentlandite-type phase $Ni_3Co_6S_8$.

Supporting Information Available: Table containing equilibrium constants for the reactions of simple Co and Ni sulfides with hydrogen at 600 K. This material is available free of charge via the Internet at http://pubs.acs.org.

IC026024J