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Hydrazine-Assisted Low-Temperature Hydrothermal Preparation of Nanocrystalline Jaipurite

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Nanocrystalline Jaipurite has been successfully prepared from amorphous cobalt sulfide in hydrazine solution at 120°C for 24 h using a hydrothermal process. The additive hydrazine is a critical factor for mineralization of amorphous CoS to Jaipurite. X-ray powder diffraction analysis indicated that the product was single-phase Jaipurite. Transmission electron microscopy images showed that as-formed Jaipurite particles were of laminar morphology. The composition of the product with the atomic ratio of 1.009 for Co/S is approximately stoichiometric, determined by chemical analysis. IR analysis suggested that the product was not contaminated in the hydrothermal process. © 1999 Academic Press

Key Words: **Jaipurite; sulfide; hydrazine; chemical synthesis.**

1. INTRODUCTION

Cobalt monosulfide (Jaipurite) is an important kind of catalyst for hydrodesulfurization and hydrodearomatization (1, 2). Conventionally, cobalt sulfide powders were prepared by traditional solid state methods. For example, cobalt sulfide could be formed by the reaction of cobalt with sulfur (3) or hydrogen sulfide (4) or by the reaction of cobalt monoxide (CoO) with hydrogen sulfide (5). There have also been reports regarding the synthesis of cobalt sulfide by the reaction of Co_3O_4 with SO_2 in the presence of carbon (6). With these methods, high-temperature quenching (600–800°C) was needed to form crystalline cobalt monosulfide (6, 7). As we know, the low-temperature chemical solution route has seldom been reported to be used to prepare crystalline cobalt monosulfide. Moreover, various material preparation methods have considerable effects on material microstructure and physical properties. Recently, important synthetic techniques of chemical solution routes have been applied to the preparation of various materials (8, 9). The hydrothermal method is one of the most promising chemical solution routes, by which the particle size, morphology, and phase homogeneity can be well controlled (9, 10).

In this work, we report a low-temperature hydrothermal synthesis route to nanocrystalline cobalt monosulfide in hydrazine (N_2H_4) solution from the natural precipitation of the reaction of $Co(Ac_2)$ and Na_2S. This precipitation method has been applied to the preparation of a wide range of sulfides such as CdS and ZnS (11–13). In this process, N_2H_4 aqueous solution did not react with CoS but rather acted as a medium for crystallization of cobalt monosulfide. The composition of as-formed cobalt sulfide was also well controlled by this process.

2. EXPERIMENTAL

One hundred milliliters of a 0.1 M solution of analytical grade sodium sulfide was mixed with the equivalent solution of cobalt acetate, resulting in a fluffy black slurry that was filtered and washed with deionized water several times to remove contaminated ions. The as-collected slurry was then put into a Teflon-lined hydrothermal autoclave of 100-ml capacity. Six milliliters of analytical hydrazine monohydrate ($N_2H_4 \cdot H_2O$) was added and deionized water was added to the autoclave up to 85% of the total volume. The autoclave was maintained at 120°C for 24 h and then cooled to room temperature naturally. A black precipitate was filtered, washed with deionized water several times, and finally dried in a vacuum box at 80°C for 4 h. The final product with metallic luster was obtained.

The samples were characterized using the X-ray powder diffraction (XRD) method. The XRD analysis was carried out with a Japan Rigaku D/max-γA X-ray diffractometer using Ni-filtered Cu$K\alpha$ radiation. A scanning rate of 0.05°/s was applied to record the patterns in the range 10–80°. The morphology and particle size of CoS were determined by transmission electron microscopy (TEM). The TEM images were taken with a Hitachi H-800 transmission electron microscope, using an accelerating voltage of 200 kV. The samples were also investigated by infrared analysis, which was conducted on a Magna IR-750FT spectrometer at room temperature using KBr pellets as self-supporting wafers.

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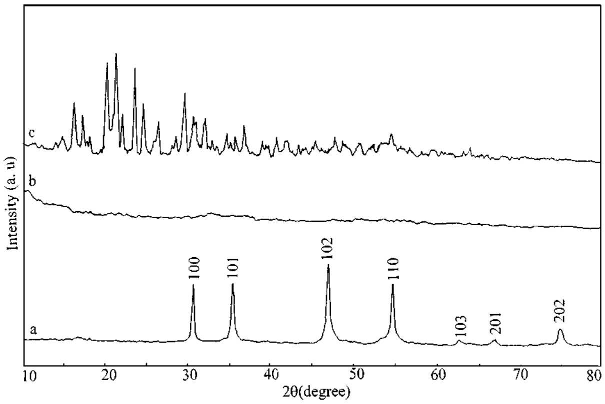

FIG. 1. XRD patterns of the samples: (a) prepared by hydrothermal treatment of amorphous CoS in 1.4 kmol/m^3 N_2H_4 solution at 120°C; (b) prepared by simple hydrothermal treatment of amorphous CoS; (c) prepared by hydrothermal treatment in 1.4 kmol/m^3 NH_3 solution at 120°C.

The composition of the as-obtained Jaipurite was determined by chemical analysis. The sample was oxidatively decomposed in HNO_3 dilute solution in a hydrothermal autoclave at 100°C for 10 h and a clear solution was obtained. Then, the cobalt content was determined by chelatometric titration (14) and the sulfur content by using a gravimetric method as for $BaSO_4$.

3. RESULTS AND DISCUSSION

A typical XRD pattern of the as-formed sample was shown in Fig. 1a. The X-ray diffraction data of which are shown in Table 1. All the peaks could be indexed as hexagonal β-CoS phase (Jaipurite) with the cell constants $a = 3.352$ Å and $c = 5.138$ Å ($c/a = 1.532$), which are close to those reported in the literature (JCPDS No. 251081). No other impurities in the XRD pattern such as CoO or other cobalt sulfide were detected. The average particle size of as-prepared cobalt sulfide is about 20 nm estimated from XRD pattern using the Scherrer equation.

The Jaipurite particle size and morphology were directly investigated by transmission electron microscopy. The TEM image (Fig. 2) shows that the as-formed Jaipurite particles are mainly of laminar shape. Some of them stack on each other to form a big particle. The laminar morphology of these nonspherical particles also points out the different between TEM observation and XRD estimation. The precursor ion concentration was considered as a factor influencing the particle size. Ranging from 00.1 to 1 M, the concentration had no considerable effects on the final particle size, because the amorphous cobalt sulfide formed from the instant precipitation of the precursors of cobalt acetate and sodium sulfide.

TABLE 1
X-Ray Diffraction Data of the As-Prepared CoS
($\lambda = 1.54178$ Å)

d (Å)	I/I_0	*hkl*
2.9087	71.4	100
2.5346	84.7	101
2.9344	100	102
1.6807	81.6	110
1.4839	12.2	103
1.3967	23.4	201
1.2686	43.1	202

Results of chemical analysis suggest that the as-formed Jaipurite with Co/S atomic ratio of 1.009 seems to be sulfur-deficient, which is different from that prepared by traditional solid state reaction methods (6, 7). Moreover, differences occur in the relative reflection intensities (I/I_0) and the cell constants are a little smaller than the reported values (15).

All the above differences may be related to the NiAs structure of Jaipurite. The sulfur ions adopt a hexagonal close-packing arrangement and cobalt ions occupy all the octahedral interstices (O sites) with T_+ and T_- sites empty. Therefore S has 6 Co neighbors arranged as a trigonal prism, but Co has 6 S neighbors arranged octahedrally. A characteristic feature for compounds with the NiAs structure is their variable compositions. Usually, Jaipurite prepared by annealing at high temperature crystallizes with a defective NiAs structure, attributed to $Co_{1-x}S$ (6) with vacant metal sites. As mentioned above, the as-formed Jaipurite ($Co_{1.009}S$) is close to stoichiometric composition, that is to say, a little sulfur-deficient. This composition may lead to differences in the relative reflection intensities and a small variation (about 1%) in cell constants with the approximate c/a value contrasted with the reported value.

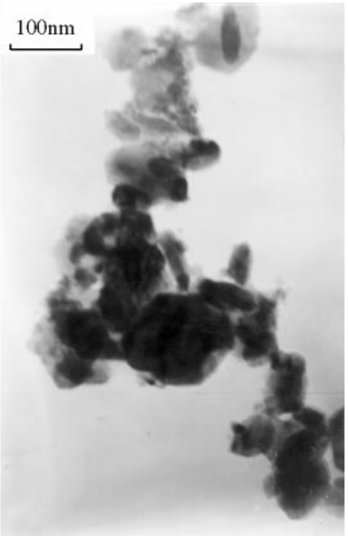

FIG. 2. TEM image of as-formed Jaipurite.

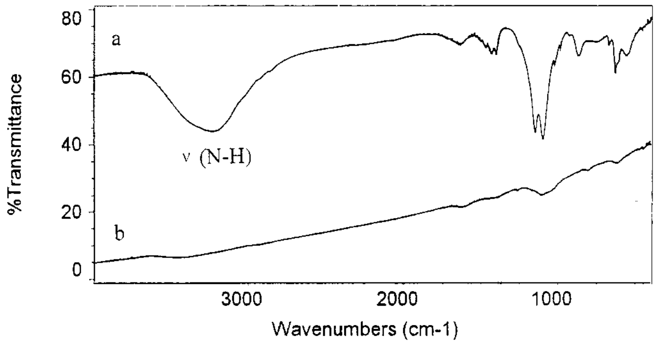

FIG. 3. IR spectra of the samples: (a) prepared by hydrothermal treatment in 1.4 kmol/m^3 NH_3 solution at 120°C; (b) prepared by hydrothermal treatment of amorphous CoS in 1.4 kmol/m^3 N_2H_4 solution at 120°C.

During this hydrothermal process, several factors, such as temperature and the concentration of the additive $N_2H_4 \cdot H_2O$, have much effect on the formation of Jaipurite. Moreover the additive plays a critical role in the formation of Jaipurite. If the hydrothermal system was free of hydrazine with no change in the other conditions, regardless of pH value from 1.0 to 14.0, the product was amorphous as indicated by the XRD pattern (Fig. 1b). When hydrazine (N_2H_4) was substituted with ammonium (NH_3), an unidentified compound formed and no Jaipurite phase can be detected from the XRD pattern (Fig. 1c). This compound could be a stable complex coordinated by NH_3 and the existence of ammonium has been confirmed by IR analysis (Fig. 3a). In the case of ethylenediamine, no phase was detected from the XRD patterns. The additive concentration of hydrazine is also an unignorable factor for the formation of nanocrystalline cobalt sulfide. When the concentration is below 1.1 kmol/m^3, no crystalline Jaipurite can be formed. The experiment indicated that hydrothermal treatment at 120°C for 24 h with the additive concentration of hydrazine 1.4 kmol/m^3 was the optimum condition for crystallization of amorphous CoS to nanocrystalline Jaipurite.

Although Jaipurite nanoparticles were formed in a solution of hydrazine, they were not contaminated by the hydrazine. The IR spectrum indicates no absorption from N_2H_4, as shown in Fig. 3b. It also suggests that Jaipurite nanoparticles are not only pure phase but also free from contaminants. On the other hand, after the mineralization was completed, the solution maintained reductivity with no change, which could be confirmed by the potassium permanganate method.

4. CONCLUSIONS

Hydrothermal treatment at low temperature with the additive hydrazine as mineralizer has been successfully used to prepare pure nanocrystalline Jaipurite from amorphous cobalt sulfide, which is the natural precipitate of reaction between $CoAc_2$ and Na_2S. The hydrazine solution functions as a medium for crystallization of amorphous cobalt sulfide. With this method, an effective reversible route between the solution phase and the solid state phase is established that allows the rearrangement of atoms in the solid state phase. The XRD results show that the product is pure phase hexagonal CoS with NiAs structure and the average particle size is about 20 nm. TEM observations show that as-formed Jaipurite nanoparticles are of lamellar shape. The composition is approximately stoichiometric, as determined by chemical analysis, which is different from that prepared by annealing at a high temperature. Moreover, IR analysis suggests that samples prepared with this low-temperature hydrothermal method are pure and not contaminated with hydrazine.

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