

The Preparation and Phase Transformation of Nanocrystalline Cobalt Sulfides via a Toluene Thermal Process

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Nanocrystalline cobalt sulfides were prepared by the reactions between cobalt chlorides and sodium polysulfide via a toluene thermal process in the temperature range 120–170 °C. Two single phases of Co_9S_8 and CoS_2 were obtained. TEM microphotos showed that the Co_9S_8 and CoS_2 particles were both spherical in shape with sizes of about 20 nm. Chemical analysis gave the formulas $\text{Co}_9\text{S}_{7.93}$ and $\text{CoS}_{1.97}$, respectively. The transformations among cobalt sulfides (Co_9S_8 , Co_3S_4 , and CoS_2) with changing reaction conditions and precursors were studied.

Introduction

There are many phases of cobalt sulfides such as CoS , Co_3S_4 , CoS_2 , and Co_9S_8 .¹ Among them, Co_9S_8 and CoS_2 have attracted attention for their properties for a long time.² Co_9S_8 is of importance in hydrosulfurization catalysts and magnetic devices.³ Pyrite CoS_2 is a metallic ferromagnet with a Curie temperature of about 120 K.⁴

Crystalline transition-metal sulfides were synthesized using solid state reactions between stoichiometric amounts of the constituent elements in evacuated silica tubes in the temperature range 500–1200 °C,^{4,5} but intermittent grinding and reheating were often necessary to obtain single phases of these sulfides. Hydrogen sulfide is another sulfur source to prepare transition-metal sulfides. For instance, Co_9S_8 was prepared with anhydrous cobalt sulfate salt in a flowing gas of hydrogen sulfide and hydrogen at 525 °C.⁶ CoS_2 was prepared by the reaction between anhydrous hexammine cobalt(II) with hydrogen sulfide⁷ at low temperature, and further treatment was necessary for crystallization at 800 °C. Recently, pyrolysis of metal complexes^{8,9} having Co–S bonds inside has been carried out to prepare CoS_2 . Overall, with those technologies, the products were highly crystalline.

To obtain single phases of transition-metal sulfides, it is important to investigate phase transformation during the preparation process. Hiromichi et al.¹⁰ reported the transformation between Co_9S_8 and CoS in a H_2S atmosphere above 600 °C. Yamaguchi et al.¹¹ investigated the phase transformations of iron sulfides during hydrothermal processes at temperatures

lower than 200 °C; however, only mixed phases of Fe_3S_4 and FeS_2 were obtained.

In this paper, nanocrystalline Co_9S_8 and CoS_2 have been successfully prepared via a toluene thermal process using sodium polysulfide and cobalt chlorides as the starting materials. The phase transformations among cobalt sulfides with changing reaction conditions and redox atmosphere are discussed.

Experimental Section

Analytical grade solvent and reagents were purchased from Shanghai Chemistry Co. Ltd. Na_2S_3 was prepared according to the literature.¹²

Preparation of Nanocrystalline Co_9S_8 . Appropriate amounts of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and Na_2S_3 (50% excess over $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$) were added to a Teflon-lined autoclave of 120 mL capacity. The autoclave was filled with toluene up to 75% of the total volume, maintained at 120 °C for 24 h, and then cooled to room temperature naturally. A black precipitate was collected after being washed with carbon disulfide, absolute ethanol, and distilled water. The final product was dried in a vacuum box at 80 °C for 4 h.

Preparation of Nanocrystalline CoS_2 . Appropriate amounts of anhydrous CoCl_2 and Na_2S_3 (50% excess over CoCl_2) were added to a Teflon-lined autoclave. The autoclave was filled with toluene up to 75% of the total volume, maintained in the temperature range 140–170 °C for 12 h, and then cooled to room temperature naturally. The washing procedures were the same to those for Co_9S_8 .

Phase transformations were investigated by adding Zn or I_2 to adjust the redox atmosphere. The washing procedures were similar to those for Co_9S_8 with the exception of adding dilute HCl (0.1 mol/L) in some cases to remove impurities. The detailed processes and the as-prepared samples are listed in Table 1.

The X-ray powder diffraction (XRD) patterns were recorded on a Japan Rigaku Dmax γA X-ray diffractometer with $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). Transmission electron microscopy (TEM) images were taken with a Hitachi H-800 transmission electron microscope. The contents of the single-phase cobalt sulfides were determined by chemical analysis.⁶

Results and Discussion

Figure 1a shows the XRD pattern of sample 1 (in Table 1). All of the peaks can be indexed to the single phase of Co_9S_8 . After refinement, the cell constant $a = 9.92 \text{ \AA}$ is close to that reported in the JCPDS cards (19-364). The size of Co_9S_8

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- (1) Wold, A.; Dwight, K. *Solid State Chemistry*; Chapman & Hall, Inc.: New York, 1993.
- (2) Wold, A.; Dwight, K. *J. Solid State Chem.* **1992**, 96, 53.
- (3) Pecoraro, T. A.; Chianelli, R. R. *J. Catal.* **1981**, 67, 430.
- (4) Morris, B.; Johnson, V.; Wold, A. *J. Phys. Chem. Solids* **1967**, 28, 1565.
- (5) Schneemeyer, L. F.; Sienko, M. J. *Inorg. Chem.* **1980**, 19, 789.
- (6) Pasquariello, D. M.; Kershaw, R.; Passaretti, J. D.; Dwight, K.; Wold, A. *Inorg. Chem.* **1984**, 23, 872.
- (7) Passaretti, J. D.; Dwight, K.; Wold, A.; Croft, W. J.; Chianelli, R. R. *Inorg. Chem.* **1981**, 20, 2631.
- (8) Singhal, G. H.; Botto, L. D.; Colle, K. S. *J. Solid State Chem.* **1994**, 109, 166.
- (9) Abboudi, M.; Mosset, A. *J. Solid State Chem.* **1994**, 109, 70.
- (10) Kiuchi, H.; Nakamura, I. *Nippon Kosyo Kaishi* **1983**, 99, 401.
- (11) Yamaguchi, S. *Colloid Interface Sci.* **1969**, 31 (4), 578.

- (12) Draves, C. Z.; Tarter, H. V. *J. Am. Chem. Soc.* **1926**, 48, 1527.

Table 1. Reaction Conditions for the Preparation of Cobalt Sulfides

no.	precursors	additive	solvent	temp (°C)	time (h)	products
1	Na ₂ S ₃ + CoCl ₂ ·6H ₂ O		toluene	120	24	Co ₉ S ₈
2	Na ₂ S ₃ + CoCl ₂ ·6H ₂ O		toluene	150–170	12	Co ₉ S ₈ + Co ₃ S ₄ + CoS ₂
3	Na ₂ S ₃ + CoCl ₂ ·6H ₂ O	Zn	toluene	170	12	Co ₉ S ₈ ^a
4	Co ₉ S ₈ ^b	I ₂	toluene	120	4–12	Co ₉ S ₈ + Co ₃ S ₄ ^c
5	Co ₉ S ₈ ^b	I ₂	toluene	170	4	CoS ₂ + Co ₃ S ₄
6	Co ₉ S ₈ ^b	I ₂	toluene	170	12	CoS ₂
7	Na ₂ S ₃ + CoCl ₂		toluene	120	12	CoS ₂

^a The sample prepared was washed with HCl additionally to remove Zn and Zn(OH)₂. ^b Co₉S₈ is first formed by a toluene thermal process at 120 °C for 24 h. Without any posttreatment, I₂ is added. ^c The amount of Co₃S₄ in the mixture is about 80%.

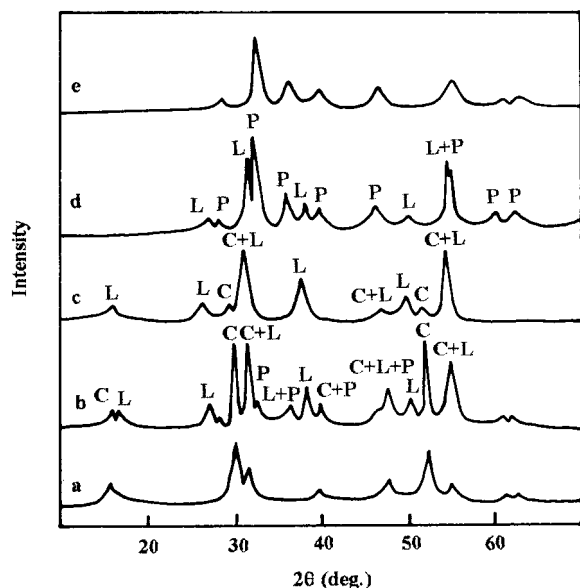


Figure 1. XRD patterns of nanocrystalline cobalt sulfide powders (C = Co₉S₈, L = Co₃S₄, P = CoS₂): (a) the single phase of Co₉S₈ prepared by the reaction between CoCl₂·6H₂O and Na₂S₃ for 24 h at 120 °C; (b) a mixed phase of Co₉S₈, CoS₂, and Co₃S₄ prepared by the reaction between CoCl₂·6H₂O and Na₂S₃ in the range 150–170 °C for 12 h; (c) a mixed phase of Co₃S₄ and Co₉S₈ prepared through the reaction of Co₉S₈ and I₂ for 4–12 h at 120 °C; (d) a mixed phase of Co₃S₄ and CoS₂ prepared through the reaction of Co₉S₈ and I₂ for 4 h at 170 °C; (e) the single phase of CoS₂ prepared by the reaction between Co₉S₈ and I₂ for 12 h at 170 °C.

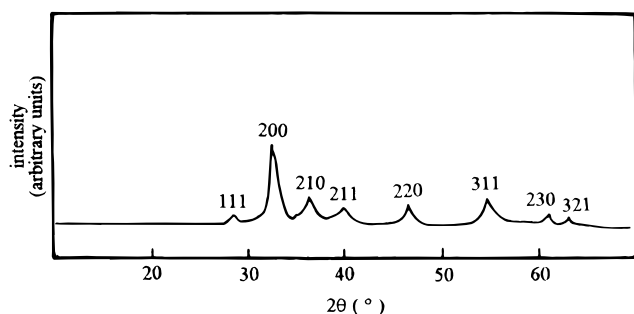


Figure 2. XRD patterns of nanocrystalline CoS₂ prepared by the reaction between anhydrous CoCl₂ and Na₂S₃ at 120 °C for 12 h.

particles is about 18 nm calculated by half-width of peaks using the Scherrer equation.¹³ The TEM microphotograph (Figure 3a) of the sample shows that the Co₉S₈ particles are in a uniform spherical shape with an average size of about 20 nm.

The XRD pattern of sample 7 is shown in Figure 2. All of the peaks can be indexed as the single phase of CoS₂ (JCPDS

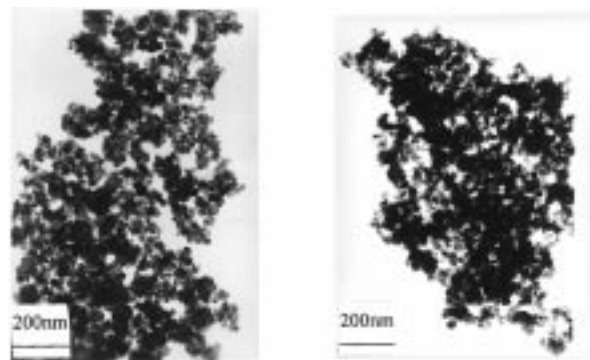


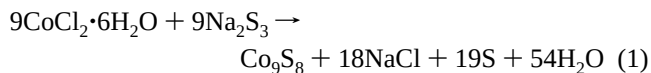
Figure 3. TEM microphoto of nanocrystalline cobalt sulfide powders: (a) TEM microphoto of nanocrystalline Co₉S₈ powder prepared by the reaction between CoCl₂·6H₂O and Na₂S₃ for 24 h at 120 °C; (b) TEM microphoto of nanocrystalline CoS₂ powder prepared by the reaction between anhydrous CoCl₂ and Na₂S₃ in the range of 120 °C for 12 h.

cards No. 41-1471). The average size is about 20 nm estimated by half-width of peaks using the Scherrer equation. This result also can be confirmed by the TEM image (Figure 3b) in which the as-prepared CoS₂ particles are in a uniform spherical shape with an average size of about 20 nm.

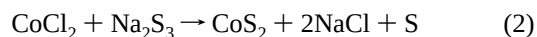
Figure 1c is the XRD pattern of sample 4, the reflections at *d* spacings of 2.85, 1.67, and 2.36 Å corresponding to the 311, 440, and 400 planes of Co₃S₄. The reflections at *d* spacings of 1.76, 2.98, and 1.91 Å correspond to the 440, 311, and 311 planes of Co₉S₈. The amount of Co₃S₄ is about 80% estimated by the relative intensity of peaks in the XRD pattern.

Chemical analysis was used to detect the sulfur contents of the as-prepared single phases Co₉S₈ and CoS₂. These samples were heated to constant weight in a stream of oxygen. According to ref 6, to prevent overoxidation of CoO, the heating temperature should not exceed to 900 °C. Samples prepared by the above procedure corresponded to the formulas Co₉S_{7.93} and CoS_{1.97}, respectively.

In the case of the formation of Co₉S₈, the reaction could be described as follows:



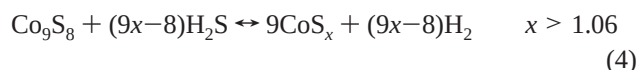
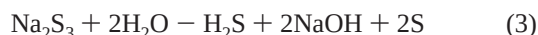
The optimum condition for preparing Co₉S₈ was about 120 °C for 24 h. The water of crystallization in the precursor CoCl₂·6H₂O is critical in the process. As anhydrous CoCl₂ was used as the precursor, only CoS₂ was obtained. The reaction could be described as follows:



With the presence of the water of crystallization in the CoCl₂·6H₂O, the temperature and duration of the reaction and the redox

(13) Klug, H. P.; Alexander, L. E. *X-ray Diffraction Procedures*; Wiley: New York, 1974.

atmosphere would also have effects on the formation of cobalt sulfides and the transformations among them. If the reaction temperature was higher than 150 °C, besides the phase of Co₉S₈, the phases of CoS₂ and Co₃S₄ were also present (Figure 1b), which might be due to the high reactive activation of nanocrystalline Co₉S₈ and an enriched sulfur environment in the autoclave. The reactions could be as follows (CoS_x represents the phases of CoS₂ and Co₃S₄ according to the literature¹⁴:



Through adjusting the redox atmosphere, the phase transformations among cobalt sulfides (Co₉S₈, Co₃S₄, and CoS₂) could be controlled.

A reductive atmosphere can be created by introducing Zn powder to the reaction system. Within the temperature range 120–170 °C, the appearance of other cobalt sulfides such as Co₃S₄ and CoS₂ mentioned above vanished and only the single phase of Co₉S₈ was obtained. This process could be explained by the effect of a reductive atmosphere on the equilibrium in eq 4. The reaction between zinc powder and crystalline water of CoCl₂·6H₂O can generate hydrogen as shown in eq 5, which would prevent the equilibrium in eq 4 toward the right. Although zinc powder itself can act as a reductive agent in many chemical reactions directly, hydrogen was believed to be the main reductive agent since it can disperse homogeneously in this system, which is beneficial for the formation of the single phase of Co₉S₈. At the same time Zn(OH)₂ could react with H₂S generated in eq 3 to form ZnS, which could be removed easily by dilute HCl solution.



If I₂ was added to Co₉S₈ prepared according to reaction 1 and then reacted at 120 °C for 4–12 h, mixed phases of Co₉S₈ and Co₃S₄ (sample 4) were obtained, in which the amount of Co₃S₄ is about 80% determined by the intensity of XRD (Figure

1c). If the reaction temperature reached up to 170 °C for 4 h, only the mixed phases of Co₃S₄ and CoS₂ (sample 5, Figure 1d) was obtained and no Co₉S₈ phase occurred. With prolonging the reaction time up to 12 h at 170 °C, a single phase of CoS₂ (sample 6, Figure 1e) was formed. The transformation may be due to the presence of I₂ which reacts with H₂ to form HI and decrease the amount of H₂, thus making eq 4 transfer toward the right and form CoS_x ($x > 1.06$).¹⁴



The byproducts such as S, NaCl, and the excess Na₂S₃, Zn, and I₂ can be removed by washing with carbon disulfide, absolute ethanol, hydrogen chloride (0.1 M), and distilled water.

In the preparation process, toluene is chosen due to its appropriate boiling point (110.6 °C) and the pressure. The pressure of the toluene¹⁵ is about 5 atm at 178 °C, which is lower than that of water (about 10 atm) at the same temperature. This low pressure makes the toluene thermal process safer than the hydrothermal process. Furthermore, toluene is a poorly polar organic solvent, and it can avoid the immediate reaction of Na₂S₃ and CoCl₂·6H₂O at room temperature, which is beneficial to control the rate of the reaction and the phase transformation.

Conclusion

Nanocrystalline cobalt sulfides were prepared by the reactions between cobalt chlorides and sodium polysulfide via a toluene thermal process in the temperature range 120–170 °C. Two single phases of Co₉S₈ and CoS₂ were obtained. TEM microphotos show that the Co₉S₈ and CoS₂ particles are both spherical in shape with sizes of about 20 nm. The ratios of Co to S for Co₉S₈ and CoS₂ are about 9:7.93 and 1:1.97, respectively, determined by chemical analysis. The phase transformations among cobalt sulfides (Co₉S₈, Co₃S₄, and CoS₂) with changing reaction conditions and redox atmosphere by adding Zn and I₂ were studied. The interconversion reactions between the various cobalt sulfides depending on the reaction conditions may be of importance for other systems.

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(14) Krabbes, G.; Oppermann, H.; Henke, J. Z. *Anorg. Allg. Chem.* **1978**, *442*, 79–85.

(15) Robert, C. W. *CRC Handbook of Chemistry and Physics*, 63rd. ed.; CRC Press, Inc.: Boca Raton, FL; p D-219.