DOI: 10.1002/ejic.201001002

Hydrothermal Synthesis of Pure-Phase Copper Silicate $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$ with Ammonia as Complexing Agent

Qizhou Jiang,[a] Qi Shi,[a] Hong Xu,*[a] Jinping Li,[a] and Jinxiang Dong*[a]

Keywords: Hydrothermal synthesis / Silicates / Copper / Pure phases / Competitive balance

Pure-phase copper silicate, $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$ (AV-23), was synthesized hydrothermally by starting with a molar ratio of $CuO:3.2SiO_2:3.02Na_2O:4.57NH_3:146H_2O$. To avoid the formation of polycrystalline CuO, aqueous ammonia was used as complexing agent. The inductively coupled plasma atomic emission spectroscopy ICP-AES, XRD, and SEM measurements of the precursors indicated that the sequence in which the starting materials are added can effectively adjust the competition between precipitation and complexation, and consequently the alkali balance in the solution, as copper is present in the form of both $Cu(OH)_2$ and $[Cu(NH_3)_4]^{2+}$. This adjustment optimizes the distribution of the precursor, which influences the morphology of $Cu(OH)_2$. The kinetics of the crystallization is thus affected in such a way that prevents the formation of impure phases.

Introduction

Microporous materials containing metal cations have been extensively studied recently due to their novel topologies, interesting chemical properties, and potential applications in optoelectronics, batteries, magnetic materials, and sensors. Such properties are introduced by metal centers not present in classical zeolites.[1,2] Representative examples of these porous transition-metal silicates include the titanium silicates ETS-4 and ETS-10, discovered in the late 1980s.[3–4] In the meanwhile, many microporous materials containing other metals such as Nb, V, Sn, Cu, and Ca, have been reported.[5–12]

Recently, some copper silicates with mixed octahedral/tetrahedral microporous siliceous frameworks have been studied for their novel framework topologies and interesting magnetic properties.[13–15] Using hydrothermal techniques under conditions comparable to those used in classical zeolite synthesis, a series of copper silicates were synthesized.[16] These were the first examples of this class of compounds containing the Cu^{2+} linking group and a novel framework structure; the copper silicate system has a general formula and a designated system: CuSH-1A $\{Na_4[Cu_2Si_{12}O_{27}(OH)_2][(AOH)_x(NaOH)_y(H_2O)_z]$ (A = Na, K, Rb, Cs, $x \approx 1$, $y \approx 1$, $z \approx 6$)$\}$.[17] Copper silicate $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$ (AV-23,[18] CuSH-2Na[16]), with a thermally stable three-dimensional microporous open framework and properties enabling reversible zeolitic water removal without destruction of the framework, was first prepared by treatment of a mixture of Na_2O, $CuSO_4$, SiO_2, and H_2O for 10 d at 230 °C, by Rocha et al. in 2004.[18] Soon after that, AV-23 and its dehydrated form were examined in detail as new magnetic chain compounds. These compounds are characterized by a strong alternation of the exchange interaction, which follows from the topology of the isolated chains of the edge-sharing octahedra (or square pyramids).[15] In later reports, Jacobson and co-workers did not gain pure-phase AV-23 by treating a mixture of NaOH, $Cu(OH)_2$, SiO_2, and H_2O for 2 d at 240 °C.[16] In our earlier investigation, using our previously reported procedures and molar ratio,[18] we always obtained AV-23 mixed with CuSH-1Na by treating a mixture of Na_2O, $Cu(NO_3)_2$, SiO_2, and H_2O for 4 d at 220 °C. Only by increasing the molar ratio of Na_2O/CuO could we avoid the formation of CuSH-1Na; however, the products were always mixed with some polycrystalline CuO and amorphous phases. Certainly, the copper source and the conditions of crystallization have influenced the experimental result.

In this paper, an alternative synthesis method of AV-23 using aqueous ammonia as a complexing agent of Cu^{2+} is proposed. Here, copper is present in the forms of both $Cu(OH)_2$ and $[Cu(NH_3)_4]^{2+}$ in the precursors, which is good for the dispersion of precursors and influences the morphology of $Cu(OH)_2$, consequently avoiding the formation of impure phases during crystallization. Pure-phase copper silicate $Na_2Cu_2Si_4O_{11}\cdot 2H_2O$ (AV-23) was obtained successfully by using this procedure. This method may also be used to prepare other pure-phase porous transition metal silicates. Attention is focused on the $Na_2O–Cu(NO_3)_2–SiO_2–NH_3\cdot H_2O–H_2O$ system: the effect of different synthesis conditions and the competitive balance of chemical reactions in solution are discussed in detail. The samples were characterized by using X-ray diffraction (XRD), optical micro-

---

[a] Research Institute of Special Chemicals, Taiyuan University of Technology,
Taiyuan 030024, Shanxi, P.R. China
Fax: +86-351-6111178
E-mail: dongjinxiangwork@hotmail.com
xuhongwork@126.com

scopy, scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), and inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Results and Discussion

The powder XRD method was employed to identify the framework structures of the obtained samples. As shown in Figure 1, the positions and relative intensities of the diffraction peaks of the synthesized pure-phase samples AV-23 were found to be in agreement with those of a previously reported copper silicate (154123-ICSD).[19]

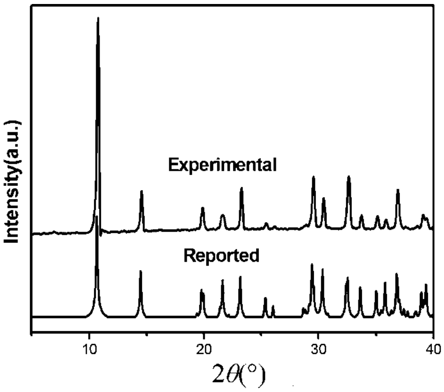

Figure 1. Reported and typical experimental powder XRD patterns of AV-23.

Synthesis

A systematic synthesis study of AV-23 in the Na_2O–$Cu(NO_3)_2$–SiO_2–$NH_3{\cdot}H_2O$–H_2O system was carried out. The different synthesis procedures and molar ratio of the reagents in the precursor were studied first and then crystallization time was investigated.

Effect of Ammonia

After fixing the starting molar ratio at CuO:3.2SiO_2:3.02Na_2O:4.57NH_3:146H_2O, which was aimed to insure the role of ammonia in the synthesis of pure-phase AV-23, two referential synthesis procedures were examined (Figure 2). As seen in the SEM (Figure 3) and optical microscopy (Figure 4) photographs, sample 1, obtained by procedure 1 with aqueous ammonia as the Cu^{2+} complexing agent, was pure-phase AV-23; it was isolated as large spherical aggregates of long green needles (Figures 3a and 4c) with no impurity. However, the samples obtained in different procedures, such as sample 2 (Figures 3b and 4a), obtained without using any aqueous ammonia, and sample 3 (Figure 3c and 4f), obtained by adding sodium hydroxide first, were always found to be mixed with some impure black phases. The EDS analysis results of elemental composition at certain positions and chemical analysis indicate that sample 2 (Figure 3e) is mixed with some polycrystalline CuO (Si/Cu = 2.142), and sample 3 (Figure 3f) is either mixed with polycrystalline CuO or amorphous phases (Si/Cu = 1.9229), whereas sample 1 is quite pure: the molar ratio of Si/Cu is 2.008, which is in agreement with the reported molecular formula (Si/Cu = 2).

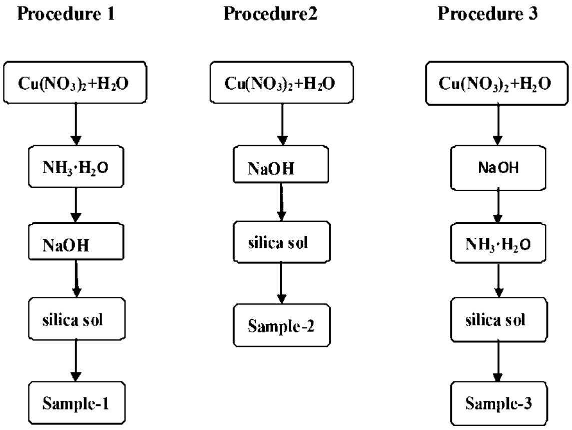

Figure 2. Effect of different synthesis procedures on copper silicate AV-23 synthesis.

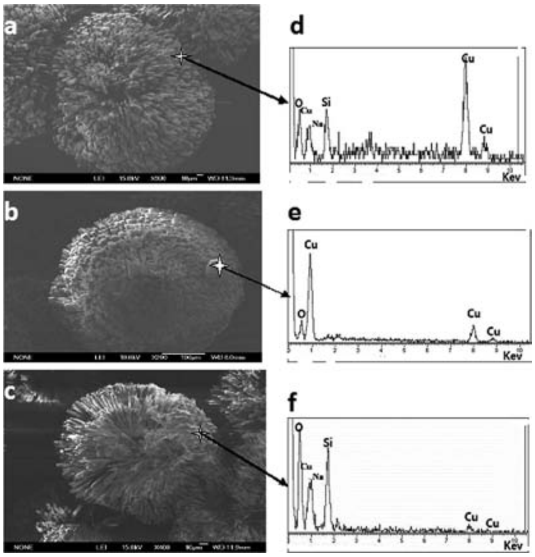

Figure 3. Crystal morphology and EDS results of elemental composition at certain positions of the samples obtained with different synthesis procedures: (a) sample 1, (b) sample 2, and (c) sample 3.

Different amounts of ammonia were added into the system as the Cu^{2+} complexing agent when using procedure 1 (Figure 2). XRD analysis revealed no different phase peaks when the molar ratio of NH_3/CuO was changed from 0 to 9.14. However, when the ratio was increased to 22.85, an impure-phase peak was found mixed with AV-23 (Figure 5), and we consider this as an unknown phase after XRD analysis. The optical microscopy photographs show that when the molar ratio of NH_3/CuO was 4.57, only the green AV-23 phase was obtained (Figure 4c); with a decrease in the NH_3/CuO ratio, some black phases attributed to polycrystalline CuO and amorphous phases appeared (Figures 4a,b). With an increase in the NH_3/CuO ratio, the previously mentioned unknown phase, which was described as small deep-blue spheres, appeared (Figures 4d,e).

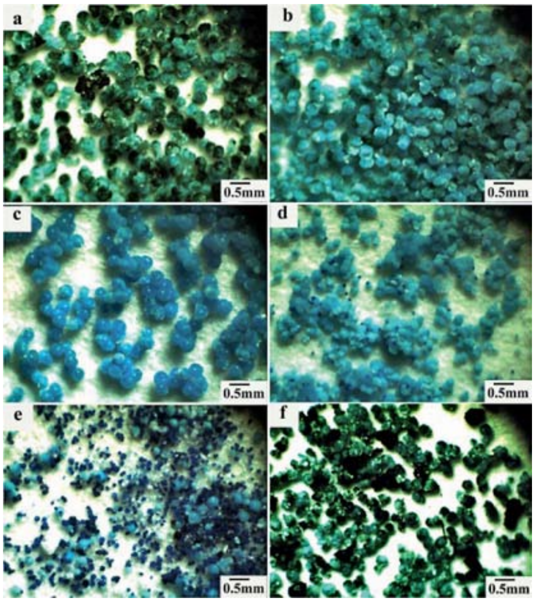

Figure 4. Optical microscopy photographs of typical samples at different synthesis conditions: (a) $NH_3/CuO = 0$ (sample 2); (b) $NH_3/CuO = 2.28$; (c) $NH_3/CuO = 4.57$ (sample 1); (d) $NH_3/CuO = 9.14$; (e) $NH_3/CuO = 22.85$; and (f) sample 3.

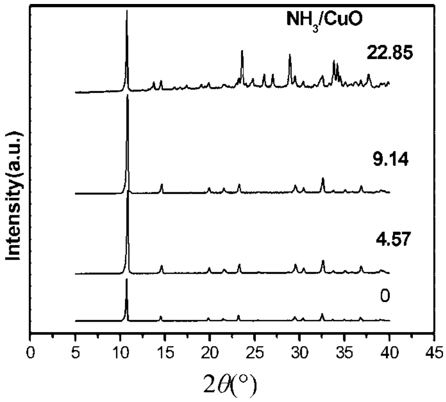

Figure 5. Effect of the starting NH_3/CuO molar ratio on copper silicate AV-23 synthesis.

Effect of the Na_2O/CuO Molar Ratio

The Na_2O/CuO molar ratio plays a very important role in the synthesis of copper silicate AV-23. Experiments were carried out at 220 °C for 96 h. After fixing the starting molar ratio at $CuO:3.2SiO_2:4.57NH_3:146H_2O$, the starting Na_2O/CuO molar ratio was varied from 2.0 to 4.0. This variation in the Na_2O/CuO ratio in the precursor led to the formation of different types of products as shown in Figure 6. Pure-phase AV-23 samples were obtained when the Na_2O/CuO ratio was 3.02. As the concentration of sodium hydroxide decreased, the crystallinity of the AV-23 phase became poor, and a CuSH-1Na impurity phase crystallized with AV-23; pure CuSH-1Na was obtained when the ratio was 2.2. In contrast, an increase in the Na_2O/CuO ratio produced dark polycrystalline CuO and some unidentified amorphous phases mixed with AV-23. With an increase in the Na_2O/CuO ratio to 4.0, an unknown phase mixed with some dark polycrystalline CuO and amorphous phases was produced, which had the same XRD pattern as the previously mentioned unknown phase found during the study of the molar ratio of NH_3/CuO, so we consider this as the unknown phase, too. We did not obtain the CuSH-3Na phase, as previously reported.[16]

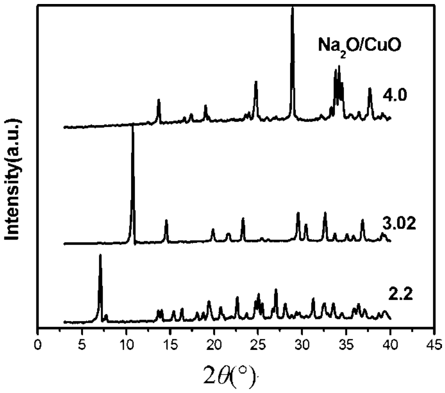

Figure 6. Effect of the starting Na_2O/CuO molar ratio on copper silicate AV-23 synthesis.

Effect of the Molar Ratios of SiO_2/CuO and H_2O/CuO

The effects of the molar ratios SiO_2/CuO and H_2O/CuO on the synthesis of AV-23 products is shown in Table 1. Experiments were carried out at 220 °C for 96 h. After fixing the starting molar ratio at $CuO:3.02Na_2O:4.57NH_3:146H_2O$, the SiO_2/CuO molar ratios were varied from 1.6 to 9.6 in the synthesis mixture for AV-23. A pure AV-23 product was obtained when the SiO_2/CuO molar ratio was 3.2. In agreement with the previous reports,[16] the products contained a mixture of AV-23, polycrystalline CuO, and an amorphous phase when the SiO_2/CuO molar ratio was decreased. With an increase in the SiO_2/CuO molar ratio, CuSH-1Na was found mixed in the products; pure-phase CuSH-1Na was obtained when the SiO_2/CuO molar ratio reached 4.8. A further increase in the SiO_2/CuO molar ratio afforded quartz phases.

Table 1. Effect of the starting SiO_2/CuO and H_2O/CuO molar ratio on copper silicate AV-23 synthesis.[a]

Run	SiO_2/CuO	H_2O/CuO	Products
1	1.6	146	AV-23+polycrystalline CuO+ amorphous
2	3.2	146	AV-23
3	4.8	146	AV-23 + CuSH-1Na
4	6.4	146	CuSH-1Na
5	9.6	146	CuSH-1Na + quartz
6	3.2	85	AV-23 + polycrystalline CuO + amorphous
7	3.2	146	AV-23
8	3.2	195	AV-23 + CuSH-1Na
9	3.2	243	CuSH-1Na
10	3.2	316	CuSH-1Na + amorphous

[a] $CuO:3.02Na_2O:4.57NH_3$, 96 h, 220 °C.

After fixing the starting molar ratio at CuO:3.2SiO_2:4.57NH_3:146H_2O, and when the H_2O/CuO ratio is 146, pure AV-23 product can be formed. A lower H_2O content in the gel usually results in the formation of impure phases of polycrystalline CuO and amorphous phases. At a higher H_2O content in the reaction mixture, CuSH-1Na was found in the products, and pure-phase CuSH-Na was obtained when the H_2O/CuO molar ratio reached 243. However, a further increase in the H_2O content leads to the formation of amorphous phases.

Effect of Crystallization Time

To study the effect of crystallization time, after fixing the starting molar ratio of the components at CuO:3.2SiO_2:3.02Na_2O:4.57NH_3:146H_2O, experiments were carried out at 220 °C (Figure 7). The XRD patterns of the products that crystallized after 6 h were attributed to CuSH-1Na (Figure 7). However, highly crystallized CuSH-1Na was not obtained with any change in the crystallization time at the current molar ratio of the components. Figure 8 shows that the AV-23 phase appeared upon crystallization after 12 h. Well-crystallized, pure-phase AV-23 was obtained after a crystallization time of 96 h (Figure 8). In the framework of CuSH-1Na, the molar ratio of Cu/Si is 1:4, and copper is present in the form of $[(CuO_4)\cdot 2H_2O]$ single chains, which are sandwiched by silicate double layers containing one-dimensional 12-ring channels. However, in the framework of AV-23, the Cu/Si molar ratio is 1:2, and copper is present in $[(Cu_2Si_4O_{11})\cdot 2H_2O]$ chains that are interconnected along the *b* direction to form layers. The adjacent layers are connected via corner-sharing tetrahedral SiO_4, which leads to a three-dimensional microporous framework with major channels running along the *a* direction. This indicates that the long crystallization times preferably lead to a higher ratio of Cu/Si and a three-dimensional framework in this system, and the formation of AV-23 may be due to the recrystallization of CuSH-1Na.

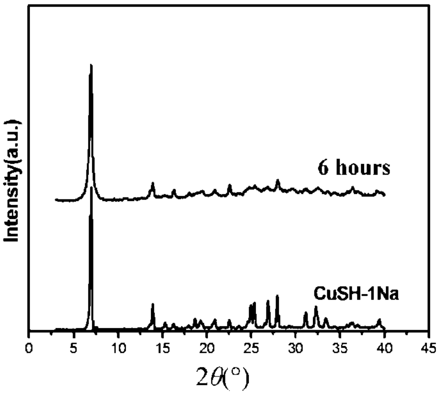

Figure 7. X-ray powder diffraction patterns of the sample with fixed starting molar ratio crystallized for 6 h and typical CuSH-1Na.

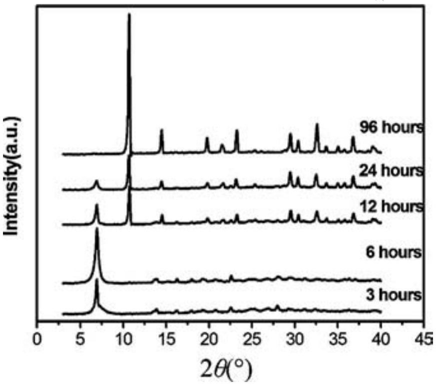

Figure 8. Effect of crystallization time on copper silicate AV-23 synthesis.

Competitive Balance between Precipitation and Complexation in Solution

In order to investigate the reasons for the formation of impurity phases, we characterized the copper species in the precursors of different procedures by ICP-AES, XRD, and SEM analyses. As the adding sequence of silica sol is not so critical to the synthesis of pure-phase AV-23, the following experiments were carried out with the samples obtained from the precursors to which we had not added silica sol.

The copper content in the solutions from which all the precipitate had been filtered out was measured by ICP-AES. In the designed experiment (procedure 1), when ammonia solution is added first and then sodium hydroxide, the copper content is 670.6 mg/L; however, in procedure 2, without ammonia solution, and procedure 3, in which sodium hydroxide is added first and then ammonia solution, the copper contents are 1.9 and 153.6 mg/L, respectively. This indicates that the copper in the precursor of procedure 1 shows a greater tendency to dissolve in the solution than the copper in the precursors of the other two procedures. As we know, if more copper dissolves in the solution, the conditions will be more suitable for the dispersion of the precursors than for the precipitation of $Cu(OH)_2$. This indicates that the precursor of procedure 1 will be obviously better distributed than the other two precursors and will thus be better at the synthesis of pure-phase AV-23.

The difference in the precursors can be explained by the balance of competing chemical reactions in the solutions (Table 2).[19–23] For the precursor of procedure 1, if Cu^{2+} reacts with aqueous ammonia firstly, then a lot of NH_4^+ will be contained in the solution. When sodium hydroxide is added, precipitation and complexation reactions compete with each other, which leads to an acid/alkali balance in the solution.[23] The equilibrium constant, *K*, of this reaction [Equation (3)] is relatively large; copper is present in the forms of both precipitated $Cu(OH)_2$ and soluble $[Cu(NH_3)_4]^{2+}$. However, in procedure 2, the equilibrium constant is even larger [Equation (1)]; the precipitation of $Cu(OH)_2$ occurs completely. There will even be an equilibrium between $Cu(OH)_2$ and $[Cu(OH)_4]^{2+}$, as the pH is not high enough to make $Cu(OH)_2$ dissolve [Equation (2)]. And in procedure

Table 2. Values of *K* under different reaction conditions.[19–23]

Run	Equation	*K*
Equation (1)	$Cu^{2+}+2OH^- = Cu(OH)_2$ (s)	3.85×10^{18}
Equation (2)	$Cu(OH)_2$ (s) + $2OH^- = Cu(OH)_4^{2-}$	3.38×10^{-3}
Equation (3)	$Cu(OH)_2$ (s) + $4NH_3 + 2NH_4^+ = [Cu(NH_3)_4]^{2+}+2NH_3\cdot H_2O$	3.21×10^{3}
Equation (4)	$Cu(OH)_2$ (s) + $4NH_3 = [Cu(NH_3)_4]^{2+}+2OH^-$	1.04×10^{-6}

3, where sodium hydroxide was added first instead of aqueous ammonia, Cu^{2+} first reacts with sodium hydroxide, and $Cu(OH)_2$ precipitates completely. After the addition of aqueous ammonia, even the $Cu(OH)_2$ precipitate can react with free NH_3 in the solution; however, the equilibrium constant of Equation (4) is relatively small, and the effect of Equation (3) is also very small as there is not much NH_4^+, so the precipitates are difficult to dissolve in ammonia solution.

The XRD and SEM analysis indicate that the competition balance can also influence the morphology and the purity of precipitated $Cu(OH)_2$. The SEM photograph of the $Cu(OH)_2$ samples prepared by procedure 1 (Figure 9) shows very uniform aggregates of long needles. However, the SEM photograph of the $Cu(OH)_2$ samples obtained by the procedures 2 and 3 do not have a uniform morphology. The XRD patterns indicate that the samples are always mixed with some CuO (Figure 10). This may influence the kinetics of the crystallization of the products, and consequently the formation of polycrystalline CuO and amorphous phases during crystallization.

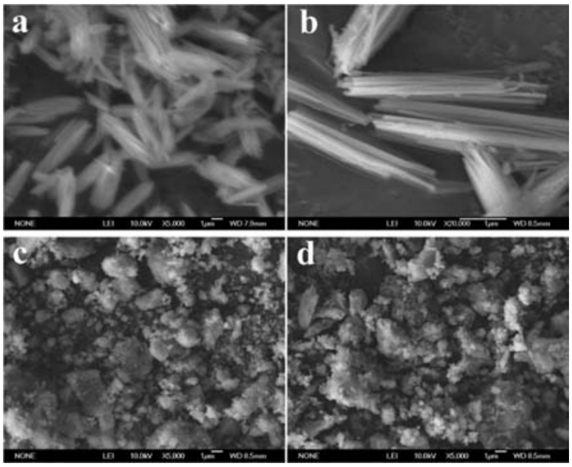

Figure 9. Crystal morphology of the $Cu(OH)_2$ samples obtained by different synthesis procedures. (a) procedure 1 (×5000), (b) procedure 1 (×20000), (c) procedure 2 (×5000), (d) procedure 3 (×5000).

Obviously, the key to the preparation of pure-phase copper silicate AV-23 is controlling the precipitation of $Cu(OH)_2$ in the precursor. The order in which the reagents are mixed obviously influences the dispersion of the precursors and the morphology and purity of $Cu(OH)_2$, consequently the kinetics of crystallization and the purity of products.

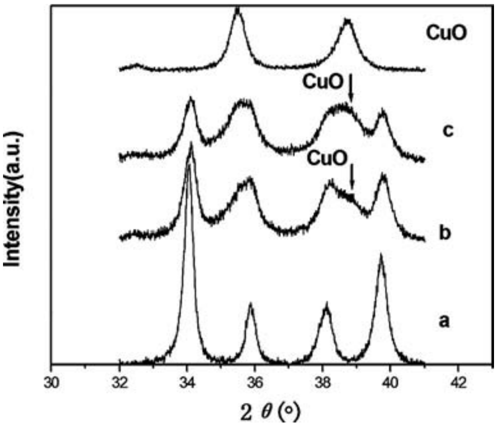

Figure 10. The XRD analysis of $Cu(OH)_2$ samples obtained by different procedures. (a) procedure 1, (b) procedure 2, (c) procedure 3.

Conclusions

It has been shown that the adding sequence of reagents in the synthesis of AV-23 using ammonia as complexing agent can obviously influence the dispersion of the precursors, the morphology and the purity of $Cu(OH)_2$, which can consequently influence the kinetics of crystallization and the purity of the products. The best adding sequence is distilled water, copper nitrate trihydrate, ammonia solution, sodium hydroxide, and silica sol. The molar ratio is $CuO:(2.8–3.4)SiO_2:(2.9–3.1)Na_2O:(4.57–6.86)NH_3:146H_2O$. The competition between precipitation and complexation and alkali balance in the precursor mixture obviously imply that the synthesis procedure is a key factor in producing pure-phase AV-23. In the crystallization time study, there was a phase transition process, and an intermediate phase CuSH-1Na was produced.

Experimental Section

The reagents used in the experiments were copper nitrate trihydrate [$Cu(NO_3)_2\cdot 3H_2O$, Sinopharm Chemical Reagent, China, 99.5%], sodium hydroxide (NaOH, Sinopharm Chemical Reagent, China, 96%), and ammonia solution (NH_3, Sinopharm Chemical Reagent, China, 25%), which were all analytical-grade reagents. Silica sol (Qingdao Haiyang Chemical, China, SiO_2, 30 wt.-%) is an industrial chemical. All chemicals were purchased from commercial sources and used without further purification. Distilled water was prepared in the laboratory. A typical synthesis for the crystallization of pure-phase AV-23 was prepared from a gel as follows. Copper nitrate trihydrate, ammonia solution, and distilled water were thoroughly mixed in a beaker by stirring at room temperature for 5 min. Sodium hydroxide and silica sol were then added. After further stirring for about 10 min, the mixture with a molar ratio of $CuO:3.2SiO_2:3.02Na_2O:4.57NH_3:146H_2O$ was transferred into a 30 mL Teflon-lined steel autoclave and kept without stirring at 220 °C in an oven for 96 h. The solid product was collected by cooling the mixture to room temperature, filtered, washed with distilled water, and dried at 100 °C overnight. The crystallinity and phase purity of the product was characterized by XRD patterns collected with a Rigaku Mini Flex II diffractometer with Cu-K_α radiation operated at 30 kV and 15 mA. The scanning range was from 5 to 40° (2θ) at 4°/min. SEM images were observed with JEOL JSM-6700F equipment at 10 kV. The samples were coated with gold to increase their conductivity before scanning. EDS (Oxford 7421) was used to detect the constituent elements in the samples using the characteristic X-rays generated from a sample bombarded with electrons. An optical microscope camera (DCM300 MICROSCOPE CAMERA #5880) was used for purity and microscopic analysis. The precursors of the three different procedures that were conducted without adding silica sol were filtered, and the precipitates were dried at room temperature overnight. They were characterized by XRD from 32 to 41°(2θ) at 0.25°/min and by SEM with JEOL JSM-6700F equipment at 10 kV. The copper content in the filtered solutions was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES) with a Plasam-Spec-I spectrometer.

Acknowledgments

The authors thank the China National Funds for Distinguished Young Scientists (20825623), the Chinese National Natural Science Foundation (50972098), the Program for the Top Young and Middle-Aged Innovative Talents of Higher Learning Institutions of Shanxi, and the Program for the Top Science and Technology Innovation Teams of Higher Learning Institutions of Shanxi for financial support.

---

[1] J. Rocha, M. W. Anderson, *Eur. J. Inorg. Chem.* **2000**, 801–818.
[2] S. C. Colin, A. C. Paul, *Chem. Rev.* **2003**, *103*, 663–702.
[3] S. M. Kuznicki (Engelhard Corp.), US Patent 4 853 202, **1989**.
[4] S. M. Kuznicki (Engelhard Corp.), US Patent 4 938 939, **1990**.
[5] J. Rocha, Z. Lin, *Rev. Mineral. Geochem.* **2005**, *57*, 173–201.
[6] R. F. Howe, Y. K. Krisnandi, *Chem. Commun.* **2001**, 1588–1589.
[7] P. Calza, C. Paze, E. Pelizzetti, A. Zecchina, *Chem. Commun.* **2001**, 2130–2131.
[8] L. Al-Attar, A. Dyer, R. Harjula, *J. Mater. Chem.* **2003**, *13*, 2963–2968.
[9] C.-Y. Li, C.-Y. Hsieh, H.-M. Lin, H.-M. Kao, K.-H. Lii, *Inorg. Chem.* **2002**, *41*, 4206–4210.
[10] Z. Lin, J. Rocha, A. Valente, *Chem. Commun.* **1999**, 2489–2490.
[11] J. Huang, X. Q. Wang, A. J. Jacobson, *J. Mater. Chem.* **2003**, *13*, 191–196.
[12] J. Huang, X. Q. Wang, L. M. Liu, A. J. Jacobson, *Inorg. Chem.* **2003**, *42*, 4057–4061.
[13] A. M. dos Santos, P. Brandao, A. Fitch, M. S. Reis, V. S. Amaral, J. Rocha, *J. Solid State Chem.* **2007**, *180*,16–21.
[14] P. Brandao, J. Rocha, M. S. Reis, A. M. dos Santos, R. Jin, *J. Solid State Chem.* **2009**, *182*, 253–258.
[15] A. M. dos Santos, V. S. Amaral, P. Brandao, F. A. A. Paz, J. Rocha, L. P. Ferreira, M. Godinho, O. Volkova, A. Vasiliev, *Phys. Rev. B* **2005**, *72*, 0924031–0924034.
[16] X. Q. Wang, L. M. Liu, A. J. Jacobson, *Solid State Sci.* **2005**, *7*, 1415–1422.
[17] X. Q. Wang, L. M. Liu, A. J. Jacobson, *Angew. Chem. Int. Ed.* **2003**, *42*, 2044–2047.
[18] P. Brandao, F. A. A. Paz, J. Rocha, *Chem. Commun.* **2005**, 171–173.
[19] *Das Kupferoxyd-Ammoniak, ein Auflösungsmittel für die Pflanzenfaser*: E. Schweizer, *J. Prakt. Chem.* **1857**, *72*, 109–111.
[20] J. A. Dean, *Lange's Handbook of Chemistry*, McGraw-Hill, New York, **1973**, vol. 1, pp. 357–360.
[21] J. Inczedy, P. H Andrea, T. Julian, *Analytical Applications of Complex Equilibria*, Wiley, New York, **1976**, pp. 22–31.
[22] Q. Wang, *Chemical Reaction Competitive Balance in Solution*, Beijing Agriculture Univ. Press, Beijing, **1988**, pp. 8–18.
[23] X. Deng, Z. Chen, *Mater. Lett.* **2004**, *58*, 276–280.

Received: September 20, 2010