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Research Article

Study of Gel Growth Cobalt (II) Oxalate Crystals as Precursor of Co_3O_4 Nano Particles

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Abstract

Crystal growth of cobalt (II) oxalate in silica gel at room temperature as precursor of Co_3O_4 nano particles has been studied. Specifically, this project is focusing on the use of two different reaction tube types toward crystallization of cobalt (II) oxalate in gel. The gel was prepared at pH 5 by reacting sodium metasilicate solution with dilute nitric acid (for U-tube) and oxalic acid (for straight tube), with gelling time of 4 days and crystal growth time of 8 (for straight tube) and 12 (for U-tube) weeks. Result shows that pink crystalline powder was directly formed using straight tube method. The use of different solvents in straight tube method affects crystallization and could delay direct precipitation of the product. In contrast, bigger and better shape of red block crystal was yielded from U-tube method; however, longer growth time was needed. FTIR studies suggest that both growth method produces identical compound of hydrated cobalt (II) oxalate.

Keywords: cobalt (II) oxalate; silica gel; reaction tube type; nano particles

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1. Introduction

The use of cobalt (II) oxalate crystals as magnetic materials [1], and as precursor of other materials, such as superconductive oxide [2], or $CoTiO_3$ [3] has been reported. In the last decade, cobalt(II) oxalate is also been extensively used as main precursor of Co_3O_4 nano particles in the development of supercapasitors [4] and for other uses [5-9], instead of other low soluble cobalt (II) salts such as cobalt (II) acetate [10] and cobalt (II) hydroxide [11].

Several method of synthesizing cobalt (II) oxalate has been published and mostly based on solution method due to its simplicity, *i.e.* directly precipitated from solution [12], using many kind of additives [13], differet cobalt salts precursors [14] or precipitated from alkaline system [15]. Mean while, gel as crystal growth media for simple or complex salts has been explored by many scientists. In 1976, Khan reported the growth of some transition metal oxalate in gels [16], after that, information on the optimation of cobalt (II) oxalate crystals growth in silica gel is limited.

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Synthesis of low solubility transition metal salts crystals, in this case is oxalate, using gel as growth medium posses fascinating results, i.e. Lead (II) oxalate hydrate [17] and cadmium (II) oxalate [18] due to its ability on controlling crystals nucleation by lowering the diffusion rate of ions. The stability of Si–O–Si networks in gel also provide space for crystal nucleii to grow into bigger and good quality single crystals [19].

Due to high demand of cobalt (II) oxalate as precursor of multi-function materials of Co_3O_4, research on this issue is predicted to be rising in the next years. In this paper, we are reporting the growth of cobalt (II) oxalate crystals in silica gel using two different reaction tube types, namely straight tube and U-tube.

Straight tube method is the simplest way to grow crystals in gels. In this method, one of the reactant is mixed in gel, while another reactant is added later on top of the gel and named as supernatant. In several cases, reactant that mixed in gel could also act as pH conditioner, for example in calcium tartrate; in which tartaric acid is used in gel both as reactant and pH conditioner [19, 20].

Meanwhile, U-tube method is commonly used to grow very low soluble salts or metal complexes which difficult to grow in straight tube method, for example lead (II) oxalate [21]. In this method, gel consists of an acid which is only act as pH conditioner. The reactants (supernatants) are added in two side of the tube in equal volume and later will reacts in gel. The products usually formed in between both supernatants pathways (middle part of the gel).

2. Materials and Method

2.1. Materials and Instrumentations

Laboratory reagents, which are $Na_2SiO_4.9H_2O$, HNO_3, $Co(NO_3)_2.6H_2O$, $H_2C_2O_4$, $Na_2C_2O_4$, KBr, and aquabidest as solvents, were used without further purification and obtained from standard commercial suppliers (Merck). Meanwhile, instrumentations used in this research were IKAMAG® RH hot plate, HERAEUS KR170E Oven, Orion 420A pH-meter, and Jasco FTIR-5300.

2.2. Preparation of Gel

Silica gel for U–tube method was made by mixing 100 ml HNO_3 1 M with Na_2SiO_3 0.5 M until pH 5. A 30 ml of the solution was then transferred in a U-tube glass (inner diameter = ±2.5 cm) and stand at room temperature for 4 days. Meanwhile, silica gel for straight tube method was prepared from a mixture of 0.5 g $H_2C_2O_4$ (3.97 mmol) in a 25 mL of water with Na_2SiO_3 0.5 M 1 M until pH 5. Next, a 30 ml of the solution was transferred in a straight tube glass (inner diameter = ±2.5 cm) and stand at room temperature for 4 days.

Both method were using gel at pH 5, not only because pKa_2 value of oxalate is 4.19, but also in order to avoid cobalt (II) hydroxide precipitation which formed at pH above 7 [21].

2.3. Preparation of Supernatant Solutions

For straight tube method, the supernatant was prepared by dissolving 578 mg $Co(NO_3)_2.6H_2O$ (1.985 mmol) in 10 ml of solvents (water, methanol, ethanol, and acetonitrile). Meanwhile, for U-tube method, there were two supernatant solutions, named as supernatant A and B. Supernatant A was prepared by diluting 200 mg of $Co(NO_3)_2.6H_2O$ (0.687 mmol) with 20 ml of water, while supernatant B was prepared by diluting 92.1 mg of $Na_2C_2O_4$ (0.687 mmol) with 20 ml of water.

Only water as solvents was used in U-tube method, in contrast to those mentioned in straight tube method. The use of several solvents for straight tube method was conducted in order to minimize the diffusion rate of cobalt (II) ions into gel, as well as to study the effect of different solvents toward cobalt (II) ions solubility which might affect diffusion rate. This is necessary because direct precipitation of products at gel's surface is commonly obtained using straight tube method, especially for cobalt (II) oxalate which has low Ksp value of $2.9x10^{-9}$ [21]. Precipitation at gel's surface often affects negatively during crystal nucleation of targeted compound.

2.4. Synthesis and Characterization of Cobalt (II) Oxalate in Gel

After the gel was ready (4 days), all supernatant solutions were added on top of gel slowly through inner wall of glass tube. For U-tube method, supernatant A was added in one side of the tube, while supernatant B was added on the other side of the tube, as shown in Figure 1. Next, all tubes were closed and saved at room temperature for 8 weeks (single tube) and 12 weeks (U-tube). During the reaction, all tubes were placed in a rack and must be avoided from physical disturbances, *i.e.* shake or motion.

After 8 weeks, the crystals were isolated by firstly remove the supernatant solutions and then dissolve the gel with hot water several times. The solutions were then filtered off with filter paper and the products were then dried in an oven at 105 °C until reaches constant mass and then saved in desiccators. All products were then analyzed by FTIR using KBr disc and recorded at wave number of 4000 – 500 cm^{-1}.

3. Results and Discussion

3.1. Synthesis using straight tube method

In this experiment, cobalt (II) nitrat was used as supernatant solution, while oxalic acid was used both as reactant and pH conditioner (Figure 1), hence the mol ratio of oxalate:Co (II) used was 2:1. Based on visual examination, pink powders formed at gel's surface after one day for water as solvents and after two days for other solvents. This precipitation was continuing yielded deeper into gel (until for about 2 cm below gel's surface for all solvents) and has bigger size until the end of week 8. This direct precipitation was unexpected because four different solvents were used to avoid this. This is probably due to the concentration of cobalt (II) ions in supernatant solution, which was nearly 0.2 M, was considered too high. Hence, the diffusion rate of cobalt (II) ions into gel is still high, although using different solvents. In order to decrease the diffusion rate, the use of smaller cobalt (II) concentration is likely could minimize direct precipitation on the gel's surface.

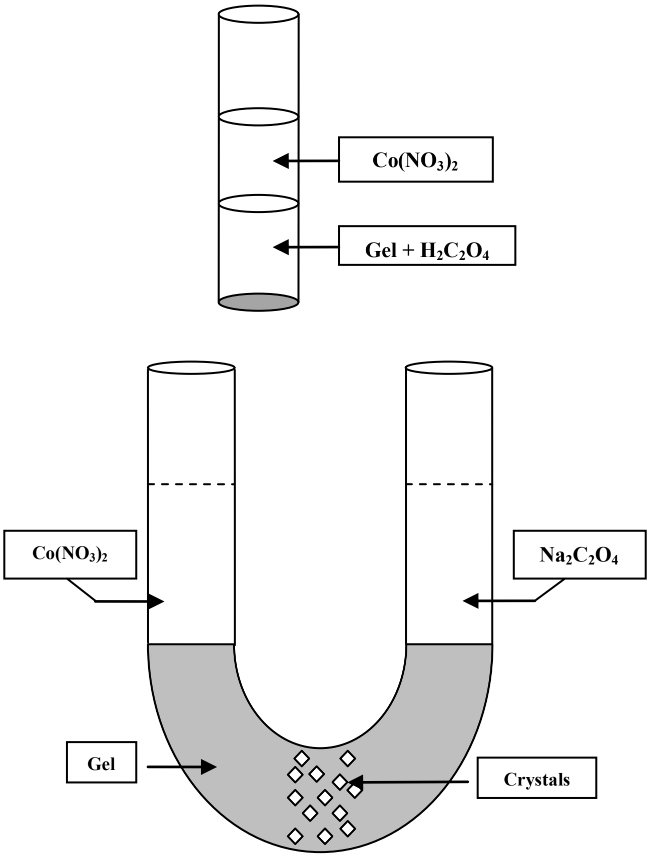

Figure 1. Reaction scheme of straight tube (top) and U-tube (bottom) method

Furthermore, the fact that the use of methanol, ethanol, and acetonitrile as solvents could delay direct precipitation compare to water is also interesting. This result is likely due to molecule radius of solvated cobalt (II) of $[Co(H_2O)_6]^{2+}$ is much smaller than molecule radius of $[Co(CH_3OH)_6]^{2+}$, $[Co(CH_3CH_2OH)_6]^{2+}$, and $[Co(CH_3CN)_6]^{2+}$. Consequently, diffusion rate of $[Co(H_2O)_6]^{2+} >> [Co(CH_3OH)_6]^{2+} \approx [Co(CH_3CN)_6]^{2+} \approx [Co(CH_3CH_2OH)_6]^{2+}$. This diffusion rates were also affected by polarity where "like dissolved like" principle involved. Because water is major components in silica gel, then $[Co(H_2O)_6]^{2+}$, which has similar polarity level, diffuse faster into gel and formed precipitate much quicker compare to $[Co(CH_3OH)_6]^{2+}$, $[Co(CH_3CH_2OH)_6]^{2+}$, and $[Co(CH_3CN)_6]^{2+}$. However, this principle cannot be applied independently because the ability of creating hydrogen bonds between methanol and ethanol might also lead to similar polarity level with water in silica gel.

Infrared spectra of products from all solvents are presented in Figure 2. The line color represents each solvent, which are purple (acetonitrile), green (water), red (methanol) and blue (ethanol). Details of selected bands are given in Table 1. Analysis of products from all solvents by FTIR shows that all products give identical band adsorption pattern, in which the highest absorbance was exhibited by spectra from acetonitrile. This is reasonable because acetonitrile has the highest dipole moment (3.92 D) compare to water, methanol or ethanol. However, due to no sharp peak observed at 2100 – 2200 cm^{-1} which corresponds to C≡N, the absence of acetonitrile as either ligand or free molecule in the crystal lattice is confirmed. Similarly, the inexistence of methanol and ethanol as either ligand or free molecule in the crystal lattice is confirmed from the absence of peak at 2800 – 2900 cm^{-1} which corresponds to terminal C – H (sp^3) alkyl.

Based on the FTIR observation and discussion, it is suggested that products from all solvents using straight tube method has identical composition of hydrated cobalt (II) oxalate. Overall proposed reactions that occur during the synthesis:

$$Co^{2+}{}_{(aq)} + C_2O_4{}^{2-}{}_{(aq)} \rightarrow CoC_2O_{4(s)}$$

3.2. Synthesis using U-tube method

In this experiment, nitric acid was used as pH conditioner, cobalt (II) nitrat was used as supernatant A and disodium oxalate was used as supernatant B with a mol ratio of oxalate:Co (II) of

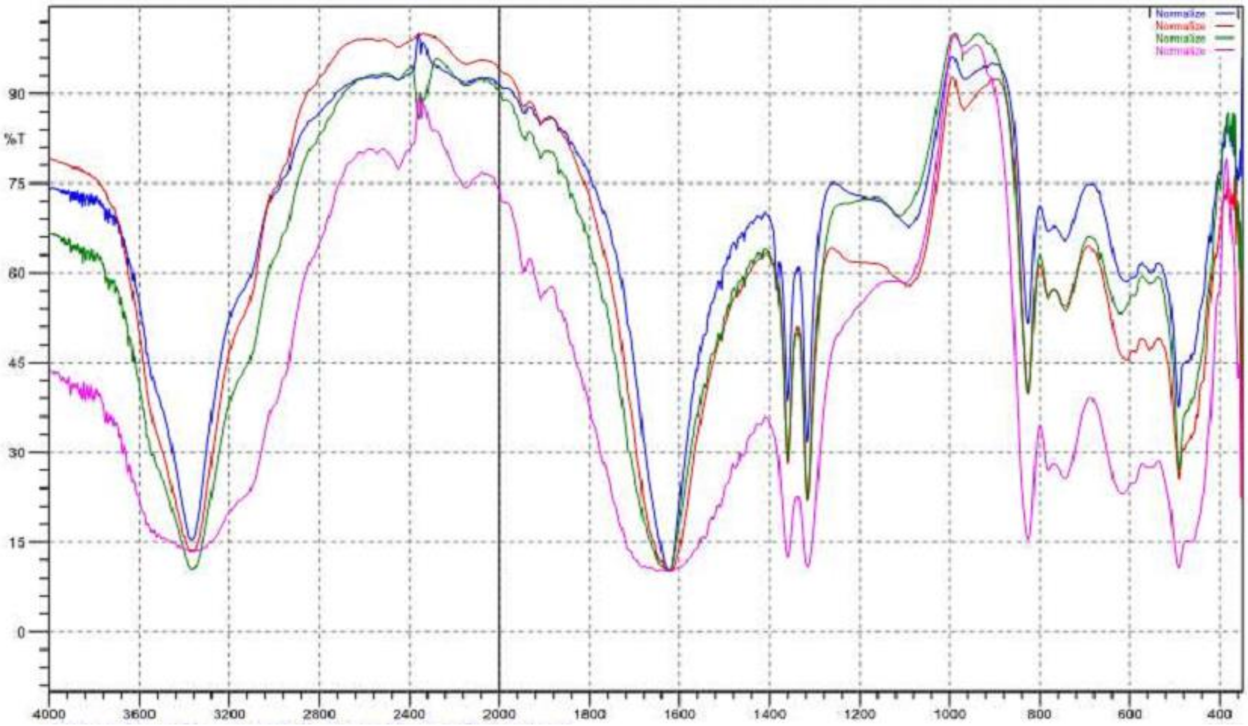

Figure 2. FTIR spectra of products from all solvents using straight tube method

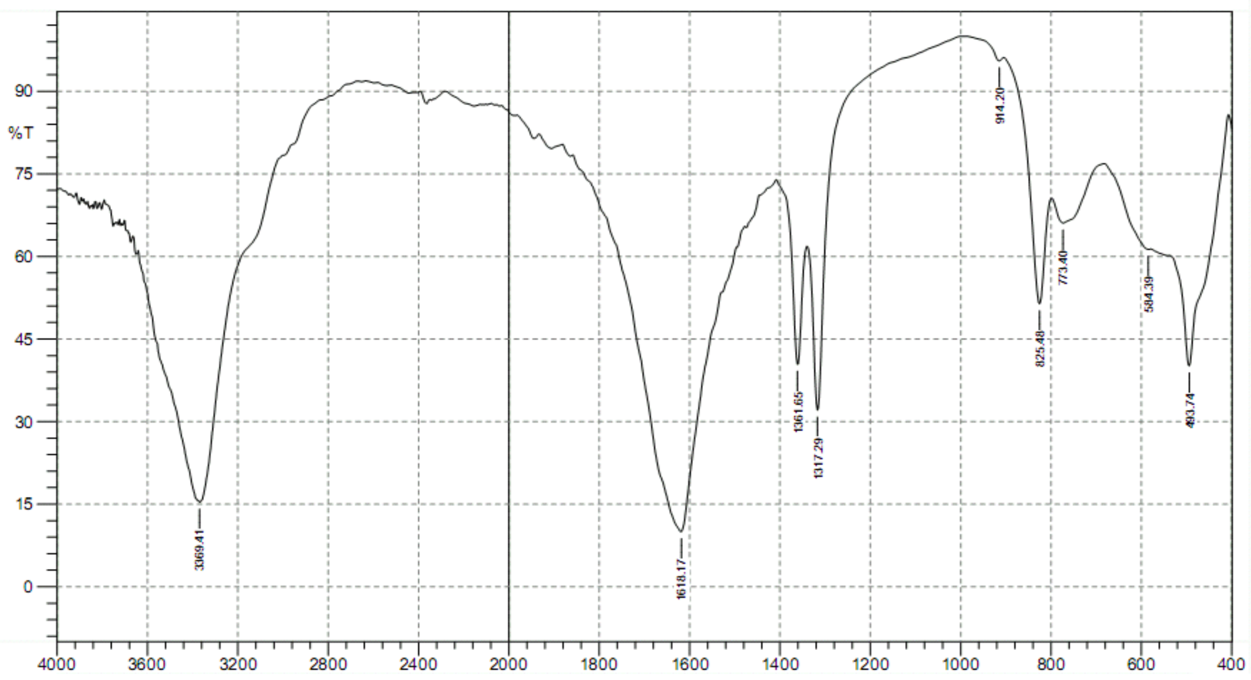

Figure 4. FTIR spectra of products obtained from U-tube method

1:1. Based on visual examination, red block crystals were started to grow in gel after 8 weeks in the middle pathway of both supernatants and continuing to grow bigger until week 12 (Figure 3). This crystal has bigger size than those obtained from straight tube method. However, crystal growth for U-tube method takes more time compare to that of straight tube method, due to the diffusion pathways of U-tube is longer than in straight tube. Moreover small concentration of both reactants, which was 0.034 M, also causes low diffusion rate of both oxalate and cobalt (II) ions in gel, hence it takes more time for both reactants to interacts and form crystal nuclei in gel.

An infrared spectrum of product obtained from U-tube method is presented in Figure 4, while details of selected bands are given in Table 1. Similar to those observed from product obtained from straight tube method, analysis by FTIR reveals that U-tube product shows characteristic bands which confirm the presence of oxalate in the crystal. In general, there is a sharp peak around 1620 cm^{-1} which correspond to carbonyl stretch vibration, while two identical sharp peaks around 1300 – 1400 cm^{-1} correspond to asymmetric and symmetric stretch of C–O, respectively. Moreover, a peak at 825 cm^{-1} belongs to asymmetric vibration of O–C–O. Finally, the presence of Co–O is confirmed from a peak occur around 490 cm^{-1}. In addition, FTIR of all products were identical with FTIR of cobalt (II) oxalate reported by Wang *et al.* [4] as seen in Figure 5.

Figure 3. Crystal growth of cobalt (II) oxalate using U-tube method

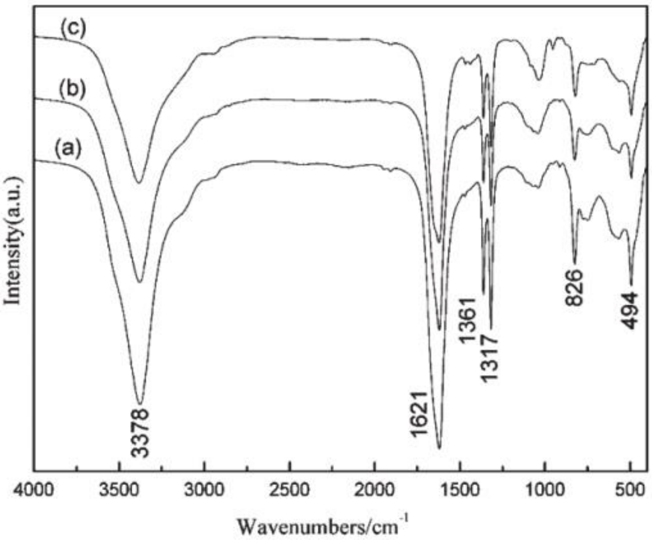

Figure 5. FTIR spectra of cobalt(II) oxalate as reference [4] (Note: a = Layered Parallel Folding (LPF) nanostructures; b = nanorods; c = nanowires)

Table 1. Details of selected bands shown in Figures 2 and 4

Absorption bands (cm^{-1})					**Inter-pretations**
(1)	**(2)**	**(3)**	**(4)**	**(5)**	
3369.41	3344.34	3367.48	3336.62	3369.41	υ OH (hydrate)
1623.95	1616.24	1623.95	1643.24	1618.17	υ C=O
1359.72	1359.72	1359.72	1359.72	1361.65	υ_{asym} C–O
1317.29	1317.29	1315.36	1317.29	1317.29	υ_{sym} C–O
825.48	825.48	825.48	825.48	825.48	υ_{asym} O–C–O
491.81	491.81	491.81	491.81	493.74	υ Co–O

Note: (1) ethanol; (2) methanol; (3) water; (4) acetonitrile; (5) U-tube

Based on the FTIR analysis and discussion, it is suggested that products from both methods have identical composition of hydrated cobalt (II) oxalate.

4. Conclusions

Pink crystalline powder was directly formed using straight tube method. The use of different solvents in straight tube method affects crystallization and could delay direct precipitation of the product. In contrast, bigger and better shape of red block crystal was yielded from U-tube method; however, longer growth time was needed to grow the crystal. FTIR studies suggest that both growth method produces identical compound of hydrated cobalt (II) oxalate.

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