Diethanolamine-Controlled Hydrothermal Synthesis of Submicron Spherical CoAl2O4 Pigment Postprint

Authors: Zhong Xingfuzi, Lu Xilong, Cao Chun' e, Chen Yunxia, Huarong Shen

Date: 2023-03-18T00:00:00+00:00

Abstract

Using $CoCl_2 \cdot 6H_2O$ and $AlCl_3$ as starting materials, NaOH as a precipitant, and diethanolamine as a coating agent, submicron spherical $CoAl_2O_4$ pigments were synthesized via a hydrothermal method. The effects of reactant concentration, nCo/nAl molar ratio, and diethanolamine addition amount on the phase composition, particle morphology and size, and coloration of the synthesized pigments were investigated using XRD, TEM, and colorimetric analysis, and the mechanism of spherical particle formation under diethanolamine coating control was analyzed from the perspective of crystal growth kinetics. The results demonstrate that when the Co^{2+} concentration is 0.05 mol/L, the nCo/nAl molar ratio is 1:2, and the diethanolamine addition amount is 12% (V/V), submicron spherical $CoAl_2O_4$ particles can be prepared, with most particle sizes ranging from 100–230 nm. The added diethanolamine can directionally adsorb at the vertices and edges during grain nucleation and growth, generating a steric hindrance effect that causes the particles to develop into a spherical morphology.

Full Text

Diethanolamine Controlled Hydrothermal Synthesis of Submicron Spherical CoAl2O4 Pigments

ZHONG Xingfuzi[1], LU Xilong[1], CAO Chun' e[1], CHEN Yunxia[1,2], SHEN Huarong[1]

[1]School of Material Science and Engineering, Jingdezhen Ceramic Institute, Jingdezhen 333403, China
[2]Jiangxi Key Laboratory of Advanced Ceramic Materials, Jingdezhen 333000, China

Supported by National Natural Science Foundation of China No.51162016, and Graduate Innovation Foundation of Jingdezhen Ceramic Institute No.JYC1105.

ABSTRACT

Submicron spherical CoAl2O4 pigments were hydrothermally synthesized using $CoCl_2 \cdot 6H_2O$ and $AlCl_3$ as raw materials, NaOH as the precipitant and diethanolamine (DEA) as capping agent, respectively. The effect of the concentration of raw materials, the ratio of nCo/nAl and the amount of DEA on the phase composition, particle size and morphology as well as the chroma of the as-prepared pigments was investigated by means of XRD, TEM and calorimetric analysis. The results show that submicron spherical $CoAl_2O_4$ pigments with size in a range of 100-230 nm could be synthesized under the conditions of nCo/nAl = 1:2, Co^{2+} concentration 0.05 mol/L and DEA 12% (V/V). The formation of spherical particles was analyzed from the point of view of kinetically controlled crystal growth in the presence of DEA. It follows that during the nucleation and growth process of the crystalline particles, DEA molecules can be adsorbed onto the edges and vertices of the particles in a highly oriented manner thus causing steric hindrance, which enables the spherical growth of the crystalline particles to be possible.

KEY WORDS inorganic non-metallic materials, spherical $CoAl_2O_4$, hydrothermal method, diethanolamine, capping agent

Spinel-type $CoAl_2O_4$ exhibits strong coloration ability and stable color development, making it an important inorganic blue pigment. High-value cobalt blue pigments have become a research and application focus in the industry. Hydrothermally synthesized $CoAl_2O_4$ crystals typically develop well-defined edges and clear facets, which is unfavorable for pigment mixing and printing. In contrast, fine spherical particles provide better mixing and printing performance. Therefore, synthesizing spherical $CoAl_2O_4$ pigments holds significant theoretical importance and broad application prospects.

In hydrothermal synthesis, capping agents are commonly introduced to control crystal morphology and size. Capping agents are typically surfactants that adsorb directionally on crystal surfaces in solution, forming an oriented capping layer. The adsorption of capping agents exhibits energy and facet selectivity, reducing surface energy and thereby influencing crystal growth. Consequently, introducing appropriate capping agents in hydrothermal synthesis can guide preferential crystal orientation, regulate growth rates of different facets, and control particle size and morphology. Dinesh Rangappa et al. synthesized approximately 10 nm pseudo-tetragonal $CoAl_2O_4$ under supercritical hydrothermal conditions using cobalt and aluminum sulfates as starting materials, NaOH as precipitant, and caproic acid and n-hexylamine as capping agents. Cao Chun' e et al. prepared spinel-type $CoAl_2O_4$ with particle sizes around 80 nm using cobalt and aluminum chlorides as raw materials, NaOH as precipitant, and a mixture of triethanolamine and glycerol.

Fabien Hubert et al. noted that short-chain surfactants as capping agents yield

spherical or short rod-like products. Among amine surfactants, short-chain primary, secondary, and tertiary amines can control crystal morphology. Triethanolamine, a tertiary amine, is an effective capping agent for hydrothermal synthesis of spherical $CoAl_2O_4$. Diethanolamine, a secondary amine, possesses similar properties. Therefore, this study employs diethanolamine as a capping agent to prepare $CoAl_2O_4$, investigating the effects of reactant concentration, the molar ratio of $CoCl_2 \cdot 6H_2O$ to $AlCl_3$ (nCo/nAl), and diethanolamine addition amount (volume fraction) on the synthesized $CoAl_2O_4$ pigments.

1.1 Sample Preparation

Based on preliminary experimental results, the following process parameters were selected: filling degree of 70%, pH value of 13, reaction temperature of 230°C, and holding time of 20 h. The effects of reactant concentration, nCo/nAl ratio, and diethanolamine addition amount on the synthesized $CoAl_2O_4$ pigments were investigated under diethanolamine control.

Cobalt chloride ($CoCl_2 \cdot 6H_2O$, analytical grade) and aluminum chloride ($AlCl_3$, analytical grade) were weighed according to the desired ratio and dissolved in 30 ml deionized water. While maintaining constant temperature stirring at 20°C using a magnetic stirrer, 3 mol/L NaOH (analytical grade) solution was added dropwise. After complete precipitation, different volume fractions (V/V%) of diethanolamine were added, and stirring continued for 30 minutes. Additional NaOH solution was then supplemented to control the precursor pH at 13. The precursor was transferred into a 100 mL autoclave at 70% filling degree and maintained at 230°C for 20 h to synthesize $CoAl_2O_4$. After reaction completion, the product was washed with deionized water and dried at 80°C to obtain pigment samples. The effects of reactant concentration, nCo/nAl ratio, and diethanolamine addition amount were investigated separately. To ensure comparability within each experimental group, optimal condition tests were conducted for each group, with specific experimental arrangements shown in .

1.2 Sample Characterization

Phase analysis was performed using a Bruker D8 Advance X-ray powder diffractometer. Microstructure and particle size were observed using a JEM-2010 transmission electron microscope. Colorimetric properties were measured using a KONICA MINOLTA CM-5 spectrophotometer.

2.1 Effect of Reactant Concentration under Diethanolamine Control

Figure 1 [Figure 1: see original paper] and Figure 2 [Figure 2: see original paper] present the XRD patterns and TEM images of samples prepared with different reactant concentrations at a fixed diethanolamine addition level of 12%, respectively. Colorimetric test results are listed in Table 2 .

As shown in Figure 1, spinel $CoAl_2O_4$ diffraction peaks appear at a Co^{2+} concentration of 0.05 mol/L without any impurity phase peaks. At 0.1 mol/L Co^{2+} concentration, weak γ-AlO(OH) diffraction peaks emerge in addition to spinel $CoAl_2O_4$ peaks. When Co^{2+} concentration increases to 0.15 mol/L, the γ-AlO(OH) diffraction peaks intensify further. At 0.3 mol/L Co^{2+} concentration, the pattern shows not only $CoAl_2O_4$ peaks but also diffraction peaks of γ-AlO(OH) and Co-Al-LDHs. According to CHEN Zhi-Zhan et al., the formation of γ-AlO(OH) and Co-Al-LDHs can be expressed as:

(aq) + $3OH^-$(aq) = $Al(OH)_3$(s)
(aq) + (2 - 3)$Al(OH)_3$(s) + (1 - x)Co^{2+}(aq) + Cl^-(aq) + nH_2O(l) = Co_1 Al $(OH)_2$ · nH_2O(s)
$Al(OH)_3$(s) = γ-AlO(OH)(s) + H_2O(l)

In reaction (1), $Al(OH)_3$ is generated during precursor preparation when $AlCl_3$ mixes with NaOH solution, before diethanolamine addition, and the reaction proceeds rapidly and completely. During the subsequent hydrothermal process, the introduction of diethanolamine and increased precursor concentration hinder the diffusion and migration of participating ions in reaction (2), suppressing the reaction and leaving unreacted $Al(OH)_3$, which transforms into γ-AlO(OH) under certain conditions via reaction (3). Additionally, the introduction of diethanolamine and increased precursor concentration raise the system viscosity, making diffusion and mass transfer difficult, preventing Co^{2+} from reaching the vicinity of γ-AlO(OH) microcrystals, affecting $CoAl_2O_4$ nucleation and precipitation, with the unprecipitated portion forming Co-Al-LDHs. During experiments, when Co^{2+} concentration was below 0.05 mol/L, the small product quantity after drying was insufficient for subsequent analysis, so lower concentrations were not tested.

Figure 2 shows TEM images of samples with different concentrations. At 0.3 mol/L Co^{2+} concentration, the sample consists mainly of spinel octahedra and rhombic particles of pseudo-tetragonal (111) facets with sizes exceeding 500 nm, accompanied by flake-like Co-Al-LDHs and γ-AlO(OH). At 0.15 mol/L Co^{2+} concentration, particle sizes range from 250-400 nm, while at 0.1 mol/L, most particles are 200-300 nm, predominantly hexagonal and tetragonal with some spinel octahedral morphology and minor impurity phases. These results indicate that at excessively high ion concentrations, diethanolamine cannot completely inhibit crystal growth.

At 0.05 mol/L Co^{2+} concentration, spherical $CoAl_2O_4$ particles form with sizes mostly between 100-230 nm and essentially no impurity phases. These TEM observations are consistent with XRD analysis. From the perspective of crystal nucleation and growth kinetics, crystal facets with low atomic density and high energy exhibit strong attraction to growth units and rapid growth rates, eventually disappearing, while the crystal becomes enclosed by low-energy, high atomic density facets. In the present system, diethanolamine preferentially adsorbs on high-interface-energy particle vertices and edges during $CoAl_2O_4$ spinel nucleation and growth, creating steric hindrance that affects ion diffusion and

migration, resulting in slower growth at vertices and edges. In contrast, facet centers with less adsorbate grow faster, leading to spherical particle formation after sufficient hydrothermal treatment at appropriate precursor concentrations.

Table 2 presents colorimetric test results for different precursor concentrations, where L* represents lightness and a* and b* are chromaticity coordinates. Higher L* values indicate greater lightness; +a* denotes red while -a* denotes green; +b* denotes yellow while -b* denotes blue. The results show that a* values change little with increasing Co^{2+} concentration, while L* values gradually increase, indicating progressively lighter color. The -b* value first decreases then increases, reaching maximum at Co^{2+} = 0.3 mol/L, indicating the bluest coloration.

These results can be explained through TEM analysis. Figure 2d (Co^{2+} = 0.05 mol/L) shows no non-colored intermediate phases, consisting entirely of spherical $CoAl_2O_4$, thus exhibiting relatively large -b* values. Figures 2c and 2b (Co^{2+} = 0.10 and 0.15 mol/L) contain non-colored intermediate phases, resulting in reduced -b* values. The highest blue value at Co^{2+} = 0.3 mol/L may be attributed to two factors: first, despite numerous non-colored intermediate phases, the $CoAl_2O_4$ crystals are well-developed and significantly larger (over 500 nm), contributing to higher blue intensity; second, blue light has a wavelength of approximately 450 nm, similar to the $CoAl_2O_4$ crystal size synthesized under these conditions, making blue light waves most easily scattered by the particles and enhancing the sample' s blue appearance. However, combined XRD and TEM analysis reveals intermediate products and non-spherical $CoAl_2O_4$ morphology. Considering the objective of preparing spherical $CoAl_2O_4$, the optimal starting reactant concentration is determined to be 0.05 mol/L Co^{2+}, corresponding to 0.1 mol/L Al^{3+}.

2.2 Effect of nCo/nAl Ratio under Diethanolamine Control

Figure 3 [Figure 3: see original paper] shows XRD patterns of samples with different nCo/nAl ratios at 12% diethanolamine addition, with colorimetric results presented in Table 3 . At nCo/nAl = 1:1.5, only Co-Al-LDHs diffraction peaks appear. At nCo/nAl = 1:1.75, Co-Al-LDHs peaks weaken while $CoAl_2O_4$ peaks emerge. This occurs because when Al^{3+} content is below stoichiometric ratio (Al^{3+} = 0.1 mol/L), the lower Al^{3+} concentration is unfavorable for γ-AlO(OH) formation, which subsequently affects Co-Al-LDHs combining with it to precipitate $CoAl_2O_4$, resulting in Co-Al-LDHs peaks. At nCo/nAl = 1:2 and 1:2.25, the XRD patterns show pure $CoAl_2O_4$ phase. However, at nCo/nAl = 1:2.5, weak Co-Al-LDHs and γ-AlO(OH) peaks appear in addition to $CoAl_2O_4$, likely due to excess Al^{3+} converting to γ-AlO(OH).

Lu Xilong et al. found that without additives, pure-phase $CoAl_2O_4$ could be obtained at nCo/nAl ratios of 1:1.75 and 1:2. Under the present experimental conditions with diethanolamine addition, pure-phase $CoAl_2O_4$ was obtained at nCo/nAl ratios of 1:2 and 1:2.25. This is because $CoAl_2O_4$ formation fol-

lows a dissolution-precipitation mechanism: after Co_1 Al $(OH)_2$ $\cdot nH_2O$ forms and dissolves, Co^{2+} diffuses to γ-AlO(OH) microcrystal vicinity, and as water evaporates from the autoclave with increasing temperature, the solute reaches supersaturation, allowing $CoAl_2O_4$ nuclei to form and precipitate. The steric hindrance created by diethanolamine impedes ion migration in solution, and combined with low starting reactant concentration, makes the reaction even less favorable when Al^{3+} content is below stoichiometric ratio, producing intermediate phases.

Table 3 shows that at nCo/nAl = 1:1.5, the L* value is highest, indicating the lightest color with small -a* and -b* values. As Al^{3+} content increases, L* values decrease significantly while -a* and -b* values increase, reaching maximum -b* at Co^{2+}:Al^{3+} = 1:2, indicating the bluest coloration. Further Al^{3+} addition increases L* values (lighter color) and gradually decreases -b* values. Therefore, under these experimental conditions, nCo/nAl = 1:2 is determined to be optimal for synthesizing well-colored, pure-phase $CoAl_2O_4$.

2.3 Effect of Diethanolamine Addition Amount

Figure 4 [Figure 4: see original paper] and Figure 5 [Figure 5: see original paper] present XRD patterns and TEM images of samples prepared with different diethanolamine additions, respectively, with colorimetric results listed in Table 4 . The XRD patterns show that diethanolamine amount affects only diffraction peak intensity, not pure-phase $CoAl_2O_4$ formation. At 3% addition, diffraction peaks are strong, gradually weakening with increasing diethanolamine content. Stronger diffraction peaks indicate better crystal development, demonstrating that diethanolamine addition affects crystallinity. With smaller additions, crystals can develop completely, showing higher diffraction intensity, while larger additions inhibit crystal development, resulting in weaker diffraction peaks.

TEM images reveal that different diethanolamine amounts produce little variation in particle size (100-230 nm) but significantly affect morphology. At 3% addition, particles are mostly octahedral with some hexagonal shapes, indicating limited morphological control. Crystals tend to grow toward high surface energy facets, which are not preserved and eventually disappear, while low-energy, slow-growing facets remain. Diethanolamine preferentially adsorbs on octahedral vertices, hindering ion migration and diffusion while reducing surface energy at these sites, slowing vertex growth. At 6% addition, particles are primarily hexagonal and pseudo-hexagonal. At 9% addition, most particles become spherical, though some hexagonal particles remain. Pure-phase spherical $CoAl_2O_4$ is obtained at 12% addition, while 15% addition yields mostly spherical products with minor intermediate phases. This confirms the XRD results: smaller diethanolamine amounts allow more complete crystal development, mostly as well-formed octahedral crystals with strongest diffraction peaks; increased addition enhances growth inhibition, preventing complete crystal development and ultimately forming spherical particles with weaker diffraction peaks.

Under hydrothermal conditions, many factors influence final product morphology. In addition to spinel octahedra and basal tetragonal facets, hexagonal shapes were observed in the prepared samples. According to crystallography, spinel is an isometric mineral with highly symmetrical crystals, primarily exhibiting octahedral and octahedron-cube combination morphologies. The observed hexagonal shapes represent {111} facets of octahedron-cube combinations.

Table 4 shows that L* values generally decrease with increasing diethanolamine addition, though the reduction is small, indicating minimal color depth variation. The a* value changes little, while -b* first increases then decreases, reaching maximum at 12% addition, indicating optimal blue coloration. In summary, under constant other conditions, 12% (volume fraction) diethanolamine addition yields well-colored spherical $CoAl_2O_4$.

Conclusions

1. Adding diethanolamine as a capping agent in hydrothermal $CoAl_2O_4$ synthesis can control product particle morphology, enabling preparation of submicron spherical particles. The mechanism involves directional adsorption of diethanolamine on particle vertices and edges during nucleation and growth, creating steric hindrance that impedes growth unit migration. Facet centers with less adsorbate grow faster, gradually developing spherical particles.

2. The optimal conditions for synthesizing pure-phase submicron spherical $CoAl_2O_4$ pigment particles are: $CoCl_2 \cdot 6H_2O$ and $AlCl_3$ as raw materials, Co^{2+} concentration of 0.05 mol/L, nCo/nAl ratio of 1:2, diethanolamine addition of 12%, pH = 13, 70% filling degree, and holding at 230°C for 20 h, yielding spherical particles predominantly 100-230 nm in size.

3. When initial Co^{2+} concentration exceeds 0.05 mol/L or nCo/nAl ratio deviates from 1:2-2.25, the products contain γ-AlO(OH) and/or Co-Al-LDHs impurity phases. Different diethanolamine amounts can synthesize relatively pure $CoAl_2O_4$ without significant particle size variation, but diethanolamine addition significantly affects product morphology and crystallinity. Only at 12% addition can pure-phase spherical $CoAl_2O_4$ be synthesized.

References

1. LU Xilong, HU Qi, YU Feng, CHEN Yunxia, CAO Chun' e. Structure, properties and development trends of ceramic cobalt blue pigments. *Materials Review*, 24(8), 56 (2010)

2. MIAO Lifeng, HU Qi, CAO Chun' e, HONG Chen, CHEN Yunxia. Effect of organic additives on the $CoAl_2O_4$ pigments synthesized by hydrothermal method. *Journal of Synthetic Crystals*, 42(9), 1837 (2013)

3. D. Rangappa, S. Ohara, T. Naka, A. Kondo, M. Ishii, T. Adschiri. Synthesis and organic modification of $CoAl_2O_4$ nanocrystals under supercritical water conditions. *Journal of Materials Chemistry*, 17(41), 4426 (2007)

4. CAO Chun' e, HU Qi, CHEN Yunxia, LU Xilong, YU Feng, SHEN Huarong, HONG Chen. A method of spherical spinel nano cobalt blue pigment synthesized by hydrothermal methods. China Patent, C04B41/85, CN102241528A (2011)

5. F. Hubert, F. Testard, O. Spalla. Cetyltrimethylammonium bromide silver bromide complex as the capping agent of gold nanorods. *American Chemical Society*, 24(17), 9219 (2008)

6. T. Sugimoto, X. P. Zhou, A. Muramatsu. Synthesis of uniform anatase TiO_2 nanoparticles by gel-sol method 4. Shape control. *Journal of Colloid and Interface Science*, 259(1), 53 (2003)

7. LU Xilong, HU Qi, HONG Chen, CHEN Yunxia, SHEN Huarong, CAO Chun' e. Study on hydrothermal synthesis technique of spinel $CoAl_2O_4$ nanocolorants. *Journal of Synthetic Crystals*, 41(2), 419 (2012)

8. HU Qi, CAO Chun' e, CHEN Yunxia, SHEN Huarong, XIONG Chunhua. Effect of hydrothermal temperature and time on the properties of $CoAl_2O_4$ colorants. *Materials Engineering*, (Z2), 366 (2010)

9. CHEN Yunxia, HU Qi, CAO Chun' e, LU Xilong, HONG Chen, SHEN Huarong. Effects of Zn^{2+} and Cr^{3+} doping on nano-sized $CoAl_2O_4$ spinel pigments by hydrothermal processing. *Journal of Inorganic Materials*, 27(12), 1317 (2012)

10. Z. Z. Chen, E. W. Shi, W. J. Li, Y. Q. Zheng, J. Y. Zhuang, B. Xiao, L. A. Tang. Preparation of nanosized cobalt aluminate powders by a hydrothermal method. *Mater. Sci. Eng.*, 107(2), 217 (2004)

11. Y. D. Yin, A. P. Alivisatos. Colloidal nanocrystal synthesis and the organic-inorganic interface. *Nature*, 437(7059), 664 (2005)

12. TANG Shaoqiu. Ceramic color measurement. *China Ceramics*, (2), 33 (1984)

13. LIU Shuxin, GU Xingyong, CAO Chun' e. *Ceramic Mineral Raw Materials and Petrographic Analysis*. Wuhan: Wuhan University of Technology Press, 2007, p.189

14. A. Dadi, D. Pradhan, Y. Sohn, K. T. Leung. Nanoscale shape and size control of cubic, cuboctahedral, and octahedral Cu-Cu_2O core-shell nanoparticles on Si(100) by one-step, templateless, capping-agent-free electrodeposition. *American Chemical Society*, 4(3), 1553 (2010)

15. ZHANG Zhenyu, YE Danian, DAI Changlu, ZHANG Hongsheng, CUI Shushan, WANG Baoqiang. Research of mechanism of imitation cuprum metal luster glaze produce metallic luster. *China Ceramics*, (121), 5 (1991)