

# Synthesis of Cobalt Chromite Nanoparticles by Thermolysis of Mixed $\text{Cr}^{3+}$ and $\text{Co}^{2+}$ Chelates of 2-Mercaptopyridin N-Oxide

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**Abstract:** Pure greenish-blue cobalt chromite ( $\text{CoCr}_2\text{O}_4$ ) nanoparticles with narrow particle range of  $4.1 \pm 1.9$  nm and surface area of  $78.2 \text{ m}^2 \cdot \text{g}^{-1}$  were synthesized through mixed chelates thermolysis of corresponding metals using 2-Mercaptopyridine N-oxide sodium salt as chelating agent. During the thermolysis procedure, high amount of gases were emitted that led to the formation of nanoparticles with high surface area. The product was characterized by TGA, DTG, XRD, TEM, SEM, LLS, BET and chemical analysis. Design of experiments was performed to fulfill the two levels  $L_4$  Taguchi design. It was found that the temperature and time of thermolysis process have significant effect on the particle size reduction. The Oxidation of trichloroethylene was carried out over  $\text{CoCr}_2\text{O}_4$  nanocrystallite. Catalytic activity analysis revealed that the synthesis  $\text{CoCr}_2\text{O}_4$  possesses high catalytic activity for this process.

**Keywords:**  $\text{CoCr}_2\text{O}_4$ ; Nanoparticle; Chelates Thermolysis; Taguchi experimental design; Combustion of trichloroethylene

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## Introduction

Cobalt chromite is a potential industrial material. It is an insulating and normal spinel compound [1-5] and has various catalytic activity such as water gas shift reaction, combustion of halogenated hydrocarbons, alkylation of phenol, dehydrogenation and hydrogenation [6-11]. It is also used as ceramic material, heat resistant pigment [12,13], substrate for epitaxial growths [14,15], high density magnetic memory media, etc [16-18]. Cobalt chromite have been synthesized by sonochemical route [19,20], coprecipitation technique and heating  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions with styrene maleic acid copolymer in DMF medium [21].

In this article we report a new and convenient method for preparation of fine nanoparticles of  $\text{CoCr}_2\text{O}_4$  with high specific surface area using themolysis of

mixed complexes of  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  chelates with 2-Mercaptopyridine N-oxide sodium salt (MPNO-Na). The mole ratio of Co/Cr in the mixed chelate was 1:2. In this method, several parameters such as thermolysis temperature, time of thermolysis and concentration of  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  in the initial materials affect the surface area and particle size of the metal oxide.  $L_4$  Taguchi experimental design was used to optimize the preparation conditions for the synthesis of cobalt chromite with low particle size [22]. To the best of our knowledge, there is no report about this process in the open literature.

## Experimental

### Materials

All chemicals used were AR grade and obtained

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from Sigma-Aldrich and used without further purification. The starting materials were  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  as cobalt and chromium precursor respectively. 2-Mercaptopyridine N-oxide sodium salt (MPNO-Na) was used as chelating agent. Ammonium hydroxide was used as precipitating agent. Distilled deionized water was used in all experiments.

### CoCr<sub>2</sub>O<sub>4</sub> preparation

#### thermolysis method

The following procedure is based on the L<sub>4</sub> Taguchi experimental design which is discussed later. Aqueous solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  were placed in 250 ml flask equipped with mechanical stirrer and thermometer. Then appropriate amount of MPNO-Na was added with stirring and the flask was heated up to 100°C with an IR heating lamp (the pH of solution 2-3.5). After 5 min digestion the precipitation was filtered, washed several times with distilled deionized water to remove the impurities and then calcined at different conditions. The product of thermal decomposition was the brilliant greenish-blue nano cobalt chromite. The experimental design was arranged for three factors: A (thermolysis temperature, °C), B (time of thermolysis, h) and C (coefficient of stoichiometric concentration of  $\text{Co}^{2+}$  and  $\text{Cr}^{+3}$  in the initial materials). Two levels assigned factor are shown in Table 1.

**Table 1 Factors and their experiment levels**

| Level 1 | Level 2 | Factors   |
|---------|---------|---|
| 800     | 600     | A (thermolysis temperature, °C)   |
| 5       | 3       | B (time of thermolysis, h)  |
| 0.6     | 0.2     | C (coefficient of stoichiometric concentration of $\text{Co}^{2+}$ and $\text{Cr}^{+3}$ in the initial materials) |

#### Precipitation method

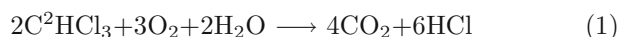
For comparison, a cobalt chromite sample was prepared with conventional co-precipitation method with following procedure: initially, aqueous solutions of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$  were placed in 250 ml flask equipped with mechanical stirrer and thermometer. Then precipitation was carried out by adding aqueous ammonia to the above stirred solution. The pH of solution was adjusted to about 8.9. After that, the precipitate was washed and filtered and dried at 100°C overnight. The final solid was then calcined in a flow of air from room temperature to 600°C with a heating rate of  $2^\circ\text{C} \cdot \text{min}^{-1}$ , and kept at this temperature for 3 h. The obtained powder was named as sample 6.

### Characterization

An automatic C H N analyzer (CHN- Micro, Karlkolb 267-48) was used to analyze the cobalt and chromium chelates. Thermogravimetric (TGA) and differential TG (DTG) analyses were carried out in a Netzsch STA 409 system in a static air atmosphere at a heating rate of 10°C per minute. The XRD patterns were recorded on an X-ray diffractometer (Shimadzu XD3A) using a  $\text{Cu-K}\alpha$  monochromatized radiation source and a Ni filter in the range  $2\theta = 10^\circ$  to  $80^\circ$ . The surface areas (BET) were determined by nitrogen adsorption at  $-196^\circ\text{C}$  using an automated gas adsorption analyzer (The Tristar 3000, Micromeritics). The diagram of particle size distribution of sample was obtained with laser light scattering (LLS) instrument, (SEMATECH 230v, 50 Hz). Transmission electron microscopy (TEM, Ziss EM 900) and scanning electron microscopy (SEM, Philips XL30) were used to observe the size and morphology of  $\text{CoCr}_2\text{O}_4$  nanoparticle. Atomic absorption spectrophotometry (Philip, U9100) was used to analyze  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions in synthesized cobalt chromite. The catalytic reaction products were identified by a gas chromatograph coupled with mass spectrometry (GC-MS, TRACE GC Ultra, column THERMO TR-5MS 30 m-0.25 mm ID, quadrupole MS TRACE DSQ).

#### Catalyst evaluation

Removal of volatile trichloroethylene (TCE) pollutants has been known as challenging technology [23-27]. In this work combustion of TCE was carried over cobalt chromite nanoparticles. This compound is nonflammable and it is used in metal degreasing and drycleaning industries. TCE in the presence of catalyst is oxidized to  $\text{CO}_2$  according to the following reaction,



Oxidative decomposition process was conducted in a glass-tube fixed bed reactor (I.D.=0.8 cm and Length=40 cm) at 330°C under atmospheric pressure with weight hourly space velocities (WHSV) of  $60 \text{ Lg}^{-1} \cdot \text{h}^{-1}$ . The reaction feed was a mixture of 1500 ppm of TCE and 15000 ppm of  $\text{H}_2\text{O}$  with balance air. The reaction products were analyzed by an on-line gas chromatograph (GC) equipped with TCD and FID.

### Results and discussion

MPNO-Na reagent form insoluble stable five-membered ring chelates with  $\text{Co}^{2+}$  and  $\text{Cr}^{+3}$  ions according to following reactions:



where  $\lambda$  is the wavelength of radiation,  $\theta$  is the Bragg's angle,  $B$  and  $b$  are the FWHM observed for the sample and standard, respectively. Results are presented in the response column of Table 3. The experiment was carried out by random order.

**Table 3** The  $L_4$  Taguchi design for 3 main factors at 2 levels

| Average Crystallite Size (nm)=<br>Response | Factors levels |   |   | Experiment No. |
|--|----------------|---|---|----------------|
|  | C              | B | A |                |
| 4.1 (Y1)                                   | 1              | 1 | 1 | 1              |
| 6.9 (Y2)                                   | 2              | 2 | 1 | 2              |
| 7.2 (Y3)                                   | 2              | 1 | 2 | 3              |
| 7.2 (Y3)                                   | 1              | 2 | 2 | 4              |

Calculation of the average effects of factors follows,

$$\bar{A}_1 = \left( \frac{Y_1 + Y_2}{2} \right) = \left( \frac{4.1 + 6.9}{2} \right) = 5.50$$

$$\bar{A}_2 = \left( \frac{Y_3 + Y_4}{2} \right) = \left( \frac{7.2 + 9.2}{2} \right) = 8.20$$

$$\bar{B}_1 = \left( \frac{Y_1 + Y_3}{2} \right) = \left( \frac{4.1 + 7.2}{2} \right) = 5.65$$

$$\bar{B}_2 = \left( \frac{Y_2 + Y_4}{2} \right) = \left( \frac{6.9 + 9.2}{2} \right) = 8.05$$

$$\bar{C}_1 = \left( \frac{Y_1 + Y_4}{2} \right) = \left( \frac{4.1 + 9.2}{2} \right) = 6.65$$

$$\bar{C}_2 = \left( \frac{Y_2 + Y_3}{2} \right) = \left( \frac{6.9 + 7.2}{2} \right) = 7.05$$

The optimum combination of factors A, B and C and the lowest magnitude of the performance was calculated from the following equation,

$$Y_{opt} = \bar{Y} + (\bar{A}_x - \bar{Y}) + (\bar{B}_x - \bar{Y}) + (\bar{C}_x - \bar{Y}) \quad (6)$$

$\bar{Y}$  is the grand average,  $\bar{A}_x$ ,  $\bar{B}_x$  and  $\bar{C}_x$  are the lower calculated responses for A, B, C factors.

$$\bar{Y} = \left( \frac{4.1 + 6.9 + 7.2 + 9.2}{4} \right) = 6.85$$

$$Y_{opt} = 6.85 + (5.5 - 6.85) + (5.65 - 6.85) + (6.65 - 6.83) = 4.1$$

Therefore the optimum combination levels of A, B, C factors and the lowest average particle size belongs to the conditions of row 1 of Table 3 (i.e the preparation is robust). When the thermolysis of mixed chelates was carried out at 540°C which is less than 600°C, some oxides impurity were detected in the XRD spectrum of product (No. 5 in Fig. 2). To check the optimum value obtained for the average particle size (Row 1 in Table 3) the appropriate amount of cobalt chromite (0.1 g) was dispersed in 100 ml distilled deionized water containing

0.5 g pentaerythritol as dispersing agent by vigorous stirring. As can be seen, Fig. 3 shows that the size range obtained with laser light scattering (LLS) for optimum conditions was 2.2-6.0 nm. The mean diameter of particles was obtained from size distribution curve using RTG correlator software to be 4.2 nm (the result obtained from XRD spectrum was 4.1 nm). The estimated factor effects on the response were calculated from Table 3 by using the following equation [28,29],

$$\text{Effect estimate} = \left[ \left( \sum \text{level 2 results} \right) - \left( \sum \text{level 1 results} \right) \right] / \left( \frac{r}{2} \right) \quad (7)$$

where  $r$  is the number of experiments. Considering the absolute value of factor effects. The order of variable effectiveness is,

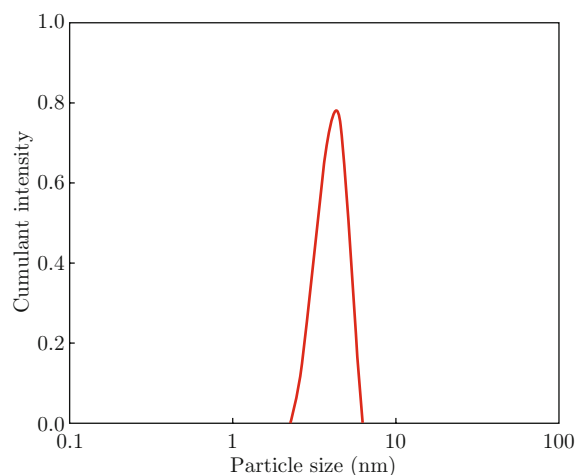


Fig. 3 LLS, mean and particle size distribution of cobalt chromite nanoparticles (particle size range of 2.2-6 nm).

A=2.7 (temperature of thermolysis, °C) > B=2.45 (time of thermolysis, h) > C=0.4 (coefficient of stoichiometric concentration of  $\text{Co}^{2+}$  and  $\text{Cr}^{+3}$  in the initial materials). It is clear that the concentration of initial material have lowest effect on crystallite size of particles. This is maybe due to fast chemical reaction produces insoluble chelate. Furthermore the amount of thermolysed sample is low, therefore the temperature lag between inside and outside of sample for different sample size does not produce crucial effect on the particle size. The main effective factors on the particle size of product are temperature and time of thermolysis. Figure 4 shows changes in the crystallite size (responses) against the thermolysis temperature at two different thermolysis times. It is clear that, increasing the thermolysis temperature increases the crystallite size. The higher time of thermolysis (5 h) lead to bigger crystallite size. As the higher temperature causes sintering and aggregation of crystallite, therefore the crystallite size is increased significantly when the thermolysis temperature is increased from 600 to 800°C.

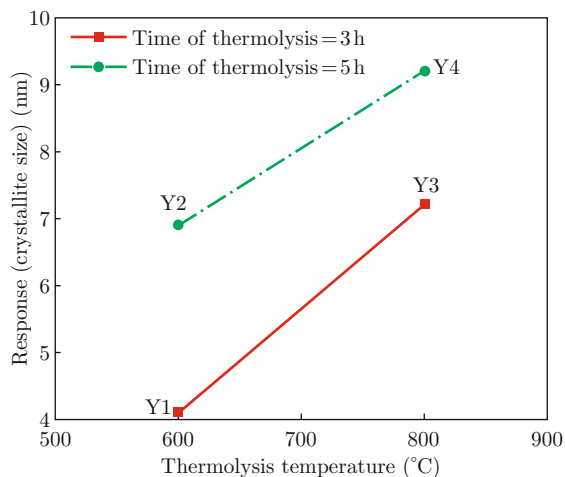


Fig. 4 Response (Crystallite size: Y1, Y2, Y3, and Y4) obtained against the thermolysis temperature.

Figure 5 shows the TEM analysis of the  $\text{CoCr}_2\text{O}_4$  nanoparticle obtained according to the recommended procedure (experiment 1 in Table 3). This image shows that the particles are roughly spherical having diameters in the range of 2.0-6.0 nm which agrees well with XRD and LLS results. Figure 6 shows the SEM analysis of the  $\text{CoCr}_2\text{O}_4$  obtained with conventional coprecipitation method (sample 6). As can be seen, the particles diameters are in the range of 30-60 nm. It is clear that the coprecipitation method causes the agglomeration of particle during precipitation. While the thermolysis method lead to the particles in range of 2-6 nm.

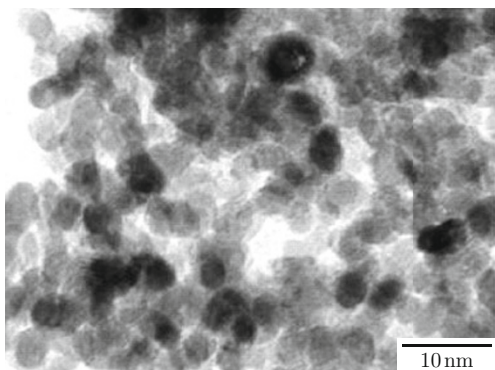


Fig. 5 The TEM image of the synthesized  $\text{CoCr}_2\text{O}_4$  nanoparticles.

The specific surface area (SSA) of sample1 (Table 3) was measured based on the principle of  $\text{N}_2$  sorption. The SSA obtained was high ( $78.2 \text{ m}^2 \cdot \text{g}^{-1}$ ). This is because of the generation of high volume of gases during thermolysis process. The evolution of hot gases causes the loss of heat from the solid phase and favours formation of small particle with high porosity.

To confirm the purity of  $\text{CoCr}_2\text{O}_4$ , about 0.2 g of sample was fused with ten times its weight of  $\text{Na}_2\text{O}_2$  flux and the melt was dissolved in  $\text{HNO}_3$  [30]. After

proper dilution the percentages of  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions in cobalt chromite were determined by atomic absorption spectrophotometry. The average of duplicate results for each case are given in Table 4.

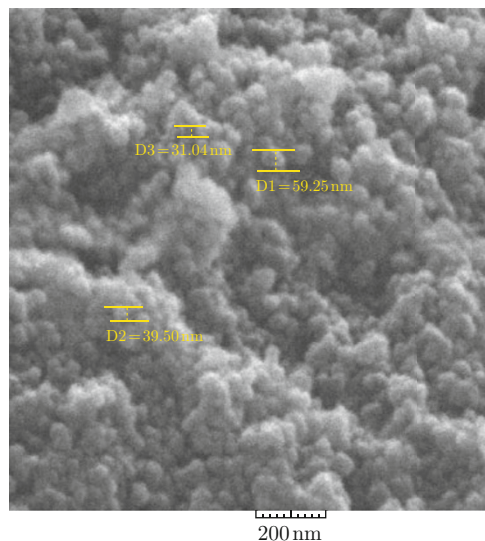


Fig. 6 SEM image of the synthesized  $\text{CoCr}_2\text{O}_4$  (sample 6).

Table 4 Analysis of cobalt and chromium in synthesized  $\text{CoCr}_2\text{O}_4$

| % Cr  | % Co  |              |
|-------|-------|--------------|
| 54.91 | 25.50 | Experimental |
| 54.83 | 25.79 | Theoretical  |
| +0.08 | -0.29 | Difference   |

Figure 7 shows the catalytic performance for the decomposition of TCE over  $\text{CoCr}_2\text{O}_4$  catalysts at  $330^\circ\text{C}$  and WHSV of  $60 \text{ L} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$  under steady-state conditions. As indicated in Fig. 7,  $\text{CoCr}_2\text{O}_4$  nanoparticle obtained according to the recommended procedure (experiment 1 in Table 3, average particle size is 4.1 nm)

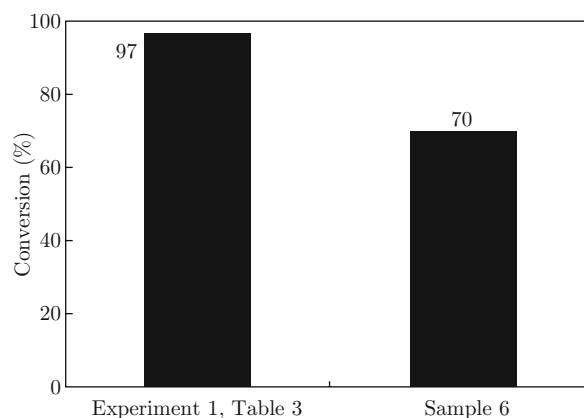


Fig. 7 TCE conversion over  $\text{CoCr}_2\text{O}_4$  samples prepared by optimized thermolysis procedure (experiment 1 in Table 3) and conventional coprecipitation method (sample 6) at WHSV:  $60 \text{ L} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$



showed higher conversion (97%) than sample 6 (particle size in the range of 30-60 nm) obtained with conventional co-precipitation method which gave 70% conversion. Comparison of catalytic activity and crystallite size of samples confirmed that the catalyst with smaller crystallite size gives more favorable active sites for the decomposition of TCE.

## Conclusion

A novel approach using new precursors is reported for the synthesis of cobalt chromite based on the decomposition of mixed chelates of  $\text{Co}^{2+}$  and  $\text{Cr}^{3+}$  ions with stoichiometric ratio using 2-Mercaptopyridine-N-Oxide Sodium salt as chelating agent. The characterization and the conditions for the complete conversion of mixed chelates to  $\text{CoCr}_2\text{O}_4$  nanocrystallite were confirmed by TGA, DTG, XRD, TEM, LLS, BET, SSA and chemical analysis. The  $L_4$  Taguchi design was implemented to optimize the experimental conditions for the preparation of  $\text{CoCr}_2\text{O}_4$  nanoparticles. The main factors having significant effect on the particle size reduction were found to be time and temperature of thermolysis process. The SSA of  $\text{CoCr}_2\text{O}_4$  synthesized by optimized method was effectively increased. This is because of generation and evolution of high amount of gases in the thermolysis process. The particle size of product was  $4.1 \pm 1.9$  nm. The lowest reported value is  $10 \pm 2$  nm [5]. The SSA of  $\text{CoCr}_2\text{O}_4$  was found to be  $78.2 \text{ m}^2 \cdot \text{g}^{-1}$ . Furthermore  $\text{CoCr}_2\text{O}_4$  nanoparticle with smaller crystallite size presented a better catalytic performance for oxidation of trichloroethylene.

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