



## Structural, magnetic and catalytic properties of cobalt chromite obtained through precursor method



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### ABSTRACT

Cobalt chromite ( $\text{CoCr}_2\text{O}_4$ ) was synthesized through the precursor method. The precursors:  $(\text{NH}_4)_3[\text{CoCr}_2(\text{C}_4\text{O}_6\text{H}_4)_4(\text{OH})_3] \cdot 4\text{H}_2\text{O}$ ,  $(\text{NH}_4)_3[\text{CoCr}_2(\text{C}_6\text{O}_7\text{H}_{10})_4(\text{C}_6\text{O}_7\text{H}_9)] \cdot 5\text{H}_2\text{O}$  were characterized by elemental chemical analysis, infrared (IR) and ultraviolet–visible (UV–vis) spectroscopy, and thermal analysis. The final oxides were characterized by X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM/TEM), UV–vis, IR, Raman spectroscopy (RS), magnetic measurements,  $\text{N}_2$  adsorption–desorption analyses and X-ray photoelectron spectroscopy (XPS). XRD confirmed the cubic  $\text{CoCr}_2\text{O}_4$  phase only and determined average crystallite sizes between 14 and 21 nm. Electron microscopy revealed morphology corresponding to the complete crystallization into cubic  $\text{CoCr}_2\text{O}_4$ . All the samples presented ferrimagnetic ordering below the Currie temperature ( $T_c$ ), and a phase transition at  $T_s \sim 26$  K attributed to the onset of long-range spiral magnetic order. The  $\text{CoCr}_2\text{O}_4$  nanoparticles generated through the gluconate route following calcination at  $700^\circ\text{C}$  for 1 h were found to have the best catalytic activity in the total oxidation of methane.

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## 1. Introduction

The cobalt chromite ( $\text{CoCr}_2\text{O}_4$ ) – member of the chromite spinel family – has been used as a highly active catalyst in the treatment of diesel exhaust gases, for the simultaneous removal of  $\text{NO}_x$  and soot [1,2], and in the complete oxidation of methane [3].

It is well known that the methane emission from natural gas vehicles (NGVs), a larger contributor to global warming than  $\text{CO}_2$ , needs to be reduced. This can be achieved by catalysis after-treatment of exhaust gases which consists in the complete oxidation of methane. Indeed, cobalt-based catalysts, especially cobalt chromites, were found to be one of the best candidates for the catalytic combustion of methane [4,5].

The cobalt chromite,  $\text{CoCr}_2\text{O}_4$ , crystallizes in a cubic  $Fd\bar{3}m$  spinel structure. It is a normal spinel due to the large octahedral ligand field stabilization energy of  $\text{Cr}^{3+}$ . This means that the  $\text{Co}^{2+}$  ions

occupy all of the tetrahedral A sites and the  $\text{Cr}^{3+}$  ions occupy all of the octahedral B sites [6].

$\text{CoCr}_2\text{O}_4$  shows both ferrimagnetic and spiral magnetic ordering below  $T_c = 97$  K (Curie temperature) and  $T_s \sim 26$  K, respectively [6,7].

$\text{CoCr}_2\text{O}_4$  was synthesized by various classical methods, such as the ceramic and the coprecipitation techniques [1,7] and also by new chemical routes such as the sol–gel/citrate gel combustion [8], the hydrothermal process [9–11], the low temperature solution combustion [2,12,13] and the thermolysis of polymer metal/polynuclear metal precursors (precursor route) [14–16].

The precursor route has a number of advantages: (i) the distribution of the chemical species is homogeneous at molecular level; (ii) the decomposition of the complex compounds occurs simultaneously with, or is immediately followed by the formation of the mixed oxide; (iii) the oxide is formed at a much lower temperature than in the ceramic processes.

The precursor route involves: (i) a detailed study of the parameters influencing the synthesis of the multimetallic complex compounds (the nature of the ligand, the  $M^{n+}:L$  ratio, the pH of the reaction medium, the temperature, etc.); (ii) a physico-chemical characterization of the multimetallic complex compounds as

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precursors of the mixed oxides; (iii) a complex study of the thermal decomposition of the precursors; (iv) the characterization of the oxides.

The selection of the ligand is the most important aspect of this technique since it is necessary to obtain complex compounds that can easily decompose at low temperatures and form non-toxic volatile products. The ligands that largely satisfy this requirement are the anions of carboxylic/polycarboxylic and polyhydroxycarboxylic acids, such as the oxalate, citrate, tartarate, gluconate etc.

The aim of this research is to obtain  $\text{CoCr}_2\text{O}_4$  spinel nanoparticles through the precursor method *via* the tartarate and gluconate routes. The precursors in these routes are the polynuclear tartarate and the gluconate multimetallic compounds, respectively. All the precursors and the cobalt chromites were characterized. The catalytic performance of the cobalt chromites was investigated in the total oxidation reaction of methane.

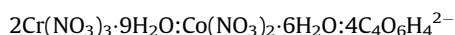
## 2. Experimental

### 2.1. Reagents

All chemicals  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , tartaric acid ( $\text{C}_4\text{O}_6\text{H}_6$ ),  $\delta$ -gluconolactone ( $\text{C}_6\text{H}_{10}\text{O}_6$ ) were of reagent quality (Merck).

### 2.2. Precursor method

The following systems were investigated for the preparation of the complex precursors:



where  $\text{C}_4\text{O}_6\text{H}_4^{2-}$  = tartarate anion,  $\text{C}_6\text{O}_7\text{H}_{11}^-$  = gluconate anion.

The chromium(III) nitrate and cobalt(II) nitrate were dissolved together in a minimum amount of water and mixed under continuous stirring with an aqueous solution of tartaric acid (in a 2:1:4 ratio) and gluconic acid (in a 2:1:8 ratio), respectively. Ethanol was added to the final solution in each of the two systems until a lavender precipitate was formed. The pH was raised to ~6 for the complete precipitation by adding  $\text{NH}_4\text{OH}$ :ethanol (in a 1:1 ratio). After 24 h at 4 °C the compounds were filtered and dried over  $\text{P}_4\text{O}_{10}$ .

The elemental analysis was consistent with the formula:

$(\text{NH}_4)_3[\text{CoCr}_2(\text{C}_4\text{O}_6\text{H}_4)_4(\text{OH})_3] \cdot \text{H}_2\text{O}$  I: Anal.: Calcd.: Cr%: 11.16; Co%: 6.33; C%: 20.60; N%: 4.50; H%: 4.18; found: Cr%: 11.49; Co%: 6.52; C%: 20.30; N%: 4.46; H%: 4.02.

$(\text{NH}_4)_3[\text{CoCr}_2(\text{C}_6\text{O}_7\text{H}_{10})_4(\text{C}_6\text{O}_7\text{H}_9)] \cdot 5\text{H}_2\text{O}$  II: Anal.: Calcd.: Cr%: 8.15; Co%: 4.62; C%: 28.21; N%: 3.29; H%: 5.56; found: Cr%: 8.33; Co%: 4.73; C%: 27.87; N%: 3.51; H%: 5.68.

To study the formation of  $\text{CoCr}_2\text{O}_4$  spinel, the gluconate and tartarate compounds were annealed at two different thermal treatments.

### 2.2. Characterization techniques

The metal content of the complex compounds was determined by atomic absorption spectroscopy with a SAA1 instrument; the C, N and H values were obtained using a Carlo Erba Model 1108CHNS elemental analyzer.

The IR spectra of the polynuclear coordination compounds and spinel chromites were recorded on KBr pellets with a JASCO FTIR 4100 spectrophotometer in the 4000–400  $\text{cm}^{-1}$  range. Absorption spectra were made with a JASCO V-670 spectrophotometer.

The thermal behavior of the precursors was evidenced by TG-DSC with a Netzsch TG 449C STA Jupiter apparatus. The samples were placed in an open crucible made of alumina and heated at 10 °C  $\text{min}^{-1}$  from room temperature up to 900 °C, under a dried air flow of 20  $\text{mL min}^{-1}$  dried air.

X-ray diffraction data were collected using parallel beam geometry on Rigaku's Ultima IV X-ray powder diffractometer, with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ), CBO optics, operating at 40 kV and 30 mA, 0.02° step size and 5°  $\text{min}^{-1}$  scan speed. Phase identification and Rietveld analysis were performed using Rigaku's PDXL software, with whole pattern fitting (WPF) module, connected to ICDDPDF-2 database.

The microstructure of the complex precursors and ceramic powders obtained was studied by scanning electron microscopy (SEM) in a FEI Quanta 3D FEG apparatus operating at 2 and 5 kV.

The low magnification conventional TEM images were obtained using a JEOL 200CX electron microscope and the high resolution images were obtained using a JEM ARM 200 F electron microscope. The specimens for the TEM observations were prepared by dispersion of the chromite powders in alcohol and deposition on holey carbon copper grids.

Raman spectra (RS) were measured with a Horiba Jobin-Yvon LabRam HR microscope-spectrometer with acquisition time of 40 s; the green line ( $\lambda = 514.5 \text{ nm}$ ) of an  $\text{Ar}^+$  laser was used to excite the RS with a power of ~20 mW; measurements were carried out in the backscattering geometry, at room temperature, with a 50× microscope objective; the laser spot size was around 1–2  $\mu\text{m}$ ; the RS covered the range between 50 and 2000  $\text{cm}^{-1}$ .

All magnetic measurements were performed using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7 T magnet. The samples were loaded into gelatine capsules. Field-cooled (FC) and zero-field cooled (ZFC) magnetisation data were collected in a warming mode with a magnetic field of 100 Oe. Field dependent magnetisation measurements were carried out at 5 and 300 K by cycling the field between 4 and –4 T.

The nitrogen sorption isotherms were recorded at 196 °C with a Micromeritics ASAP 2020 automated gas adsorption system. The samples were outgassed for 3 h at 300 °C under vacuum prior to the  $\text{N}_2$  adsorption. The specific surface areas ( $S_{\text{BET}}$ ) were calculated according to the Brunauer–Emmett–Teller (BET) equation using adsorption data in the relative pressure range between 0.05 and 0.30. The total pore volume ( $V_{\text{total}}$ ) was estimated from the amount adsorbed at the relative pressure of 0.99. The average pore diameters were obtained using the Barrett–Joyner–Halenda (BJH) method from the desorption branch.

The surface analysis performed by X-ray photoelectron spectroscopy (XPS) was carried out on Quanterta SXM equipment, with base pressure of  $10^{-9}$  Torr in the analysis chamber. The X-ray source was Al  $\text{K}\alpha$  radiation (1486.6 eV, monochromatized) and the overall energy resolution was estimated at 0.65 eV by the full width at half maximum (FWHM) of the  $\text{Au}4f_{7/2}$  line. In order to take into account the charging effect on the measured binding energies (BEs), the spectra were calibrated using the C1s line (BE = 284.8 eV, C–C (CH) *n* bondings) of the adsorbed hydrocarbon on the sample surface. A dual beam neutralizing procedure ( $\text{e}^-$  and  $\text{Ar}^+$  ion beams) was used to compensate the charging effect in the insulating samples.

The catalytic properties were tested in the methane combustion. The reaction was carried out in a quartz tubular flow microreactor under atmospheric pressure, volume rate air/ $\text{CH}_4$  gas mixture (10%  $\text{CH}_4$ , 5%  $\text{N}_2$ , 85% Ar) 2/1, the temperature range from 200 to 500 °C and increasing the temperature by steps of 50 °C. About 40 mg of the catalyst sample was loaded in a fixed bed reactor. The inlet and outlet gas compositions were analyzed by on-line gas chromatography.  $\text{CH}_4$  and  $\text{CO}_2$  in the effluent gas were periodically analyzed using Porapaq QS 80/100 and carbon

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