Effect of fuel type on structural and physicochemical properties of solution combustion synthesized CoCr$_2$O$_4$ ceramic pigment nanoparticles

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ARTICLE INFO

Keywords:
Combustion synthesis
Nanopigment
Cobalt chromite
Physicochemical properties
Fuel

ABSTRACT

Due to importance and wide applications, CoCr$_2$O$_4$ ceramic pigment nanoparticles were synthesized via low-temperature solution combustion route by different fuels including ethylenediamine/oxalic acid, ethylenediamine/citric acid, oxalic acid/citric acid and ethylenediamine/oxalic acid/citric acid. Physicochemical properties of the synthesized samples were determined by different techniques such as fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM) and energy dispersive X-ray spectroscopy (EDX) and color/optical properties were evaluated based on CIELAB system by spectrophotometer. Moreover, thermodynamic considerations of combustion reactions for CoCr$_2$O$_4$ nanoparticles formation in terms of calculated adiabatic flame temperature and enthalpy of combustion reaction were studied. The Comparison of results and data showed that cobalt chromite pigment nanoparticles synthesized by using ethylenediamine/citric acid and ethylenediamine/oxalic acid/citric acid fuels exhibited higher purity, smaller crystallite size and lower degree agglomeration.

1. Introduction

The cobalt chromite greenish-blue pigment, CoCr$_2$O$_4$, is a normal spinel that crystallizes in a cubic Fd$ar{3}$m structure with lattice constant of $a_0 = 8.33$ Å [1].

The wide applications have been reported for cobalt chromite such as usage as industrial inorganic pigment [2], dye substrate for film growth [3], solar absorber [4], a multiferroic material [5–10], electrode in solid oxide fuel cells (SOFCs) [11,12], gas sensor [13], catalyst support [14], and catalysts for catalytic combustion of dichloromethane [15,16], total oxidation of trichloroethylene (combustion of chlorinated organic pollutants) [17], the ortho-selective alkylation of phenol with methanol [18], in the complete oxidation of methane [19], the removal of NOx and diesel soot [20] and the oxidation of 2-propanol [21].

Various techniques were used to synthesize CoCr$_2$O$_4$ including classical ceramic [22] and conventional co-precipitation approaches [23] and new chemical methods of sol-gel [24,25], solution combustion (fuels: urea, tetraformal trisazine, glycine and hexamethylentetramine) [26–31], citrate gel combustion [32], precursor thermolysis [33–35], hydrothermal/solvothermal [36–39] and sonochemical [40].

The combustion route involves an exothermic chemical reaction between the fuel and oxidizer (usually metal nitrates) to produce high purity product. In this method, physicochemical properties of product such as particle size, crystallinity, composition, purity, surface area, morphology, degree and nature of the aggregate can be influenced by fuel type [41–46]. In general, combustion approach is easy, safe and cheap and its main advantage is to reduce the time and energy required for the synthesis. Moreover, it is no requirements to complex tools, special reaction chamber and high-temperature furnaces for synthesis.

In present work, nanoparticles of CoCr$_2$O$_4$ spinel-type pigment were synthesized through low temperature combustion method by using different fuels and their physicochemical and color properties compared, indicating investigation of fuel type influence.

2. Experimental

2.1. Materials

For synthesis of samples used the following starting materials without purification: oxalic acid dihydrate (Merck), citric acid non-hydrate (Merck), ethylenediamine (LOBA Chemie), cobalt nitrate hexahydrate (RANKEM.LOBO), chromium nitrate nonahydrate (RANKEM.LOBO).

2.2. Synthesis of samples

CoCr$_2$O$_4$ nanopowders were synthesized using low-temperature solution combustion route by different fuels including ethylenediamine.
To synthesize samples through this method, first the stoichiometric amounts of metal nitrates and fuel were weighed and poured in the reaction flask containing deionized water. Then, the obtained mixture was aged at 90 °C for 2 h. After homogenization, the temperature was rapidly increased to 300 °C to occur self-ignition of the solution. The ignition reaction was occurred less than 3 min as a significant amount of gases was released and it was created a fluffy foamy sample. In order to complete combustion, the resulting sample was maintained at 300 °C for 15 min. Finally, the sample was annealed at 600 °C for 3 h to obtain final product.

For calculation of the fuel stoichiometric amount the following equation [47] was used:

\[
\varphi_e = \frac{\sum \text{Coefficient oxidizing elements in the special formula} \times \text{Capacity}}{\sum \text{Coefficient reducing elements in the special formula} \times \text{Capacity}}
\]  

(1)

where \( \varphi_e \) is elemental stoichiometric coefficient defined as equivalence ratio (fuel to oxidizer ratio normalized by the stoichiometric fuel to oxidizer ratio). If \( \varphi_e = 1 \), mixture is fuel-stoichiometric, if \( \varphi_e > 1 \), mixture is fuel-rich and if \( \varphi_e < 1 \), mixture is fuel-lean. The stoichiometric mixture produces the maximum energy for combustion. In Table 1 is summarized the amounts of metal nitrates and fuels used for synthesis of the samples.

**Table 1**
The amounts of metal nitrates and fuels used for synthesis of the samples.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Co(NO(_3))(_2) 6H(_2)O (g)</th>
<th>Cr(NO(_3))(_3) 9H(_2)O (g)</th>
<th>C(_2)H(_2)O(_4) ox' (g)</th>
<th>C(_6)H(_8)O(_7) cit' (g)</th>
<th>C(_3)H(_8)N(_2) en' (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.291</td>
<td>1.8</td>
<td>1.26</td>
<td>=</td>
<td>0.1</td>
</tr>
<tr>
<td>2</td>
<td>0.291</td>
<td>1.8</td>
<td>1.26</td>
<td>=</td>
<td>0.7</td>
</tr>
<tr>
<td>3(a)</td>
<td>0.291</td>
<td>1.8</td>
<td>1.26</td>
<td>=</td>
<td>0.7</td>
</tr>
<tr>
<td>4</td>
<td>0.291</td>
<td>1.8</td>
<td>=</td>
<td>0.426</td>
<td>=</td>
</tr>
<tr>
<td>5</td>
<td>0.291</td>
<td>1.8</td>
<td>0.252</td>
<td>0.384</td>
<td>=</td>
</tr>
<tr>
<td>6</td>
<td>0.291</td>
<td>1.8</td>
<td>=</td>
<td>0.192</td>
<td>0.09</td>
</tr>
<tr>
<td>7</td>
<td>0.291</td>
<td>1.8</td>
<td>0.378</td>
<td>1.92</td>
<td>0.07</td>
</tr>
</tbody>
</table>

\(a\) For sample 3, only the addition method of two fuels is different compared to sample 2 (in the sample 2, at first, en was added to metal nitrates and ox added 15 min after the first reaction, while in the sample 3, at first, ox was added to metal nitrates).

**Table 2**
Effect of fuel type on moles of gases released, heat of combustion and adiabatic flame temperature.

<table>
<thead>
<tr>
<th>Sample no.</th>
<th>Used fuel</th>
<th>(\Delta H)(_{\text{combustion}}) (kJ/mol)</th>
<th>T(_{\text{ad}}) (K)</th>
<th>number of gases moles produced during combustion</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>cit</td>
<td>-1786.43</td>
<td>1265.62</td>
<td>50.2</td>
</tr>
<tr>
<td>5</td>
<td>cit/ox</td>
<td>-2760.41</td>
<td>1141.47</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>cit/en</td>
<td>-1932.67</td>
<td>1411.83</td>
<td>47.62</td>
</tr>
<tr>
<td>7</td>
<td>cit/ox/en</td>
<td>-3350.23</td>
<td>1839.93</td>
<td>60</td>
</tr>
</tbody>
</table>

Fig. 1. FT-IR Spectra for samples.

Fig. 2. X-ray diffraction patterns of synthesized samples 1-3 (o: Co\(_3\)O\(_4\); *: Cr\(_2\)O\(_3\); +: Co\(_2\)CrO\(_4\)).

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