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Nanocrystalline pirochromite spinel through solution combustion synthesis

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Abstract

The production of magnesium–chromium oxides by solution combustion synthesis was investigated using glycine and urea for the first time. Ammonium dichromate, urea/glycine and ammonium nitrate aqueous solutions were used as the precursors of the oxides. The effect of different reaction parameters, such as fuel richness, stoichiometry and fuel leanness was evaluated; such parameters were modified by changing the reagents and the fuel/oxidant ratio. The results suggest that glycine is an interesting complexing/combustible agent for ammonium dichromate to produce chromite spinel. Addition of extra ammonium nitrate to stoichiometric compositions improved the specific surface area and reduced the crystallite size. The highest specific surface area (153.40 m^2/g) was obtained for the stoichiometric fuel/oxidant mixtures containing glycine as combustible in combination with ammonium nitrate; however, the smallest crystallite size (approximately 9 nm) of Pirochromite ($MgCr_2O_4$) was synthesized using urea as combustible.

Keywords: A. Nanostructures; A. Oxides; B. Chemical synthesis; C. X-ray diffraction; C. Electron microscopy

1. Introduction

The spine1 structure encompasses a large family of compounds showing a wide variety of physical properties. These properties have, in many cases, of practical interest. Metal oxide spinels (AB_2O_4), such as Pirochromite ($MgCr_2O_4$), are binary oxides that have important technological applications, including the use as magnetic materials [1], high temperature ceramics [2], as well as strengthening agents [3], sensor elements [4–10], interconnection material for solid oxide fuel cells [11], combustion catalysts [12–15] and catalysts-support [16].

$MgCr_2O_4$ spinel has a cubic structure and belongs to the space group $O^7{}_h$ ($Fd3m$), with 56 atoms per unit cell ($Z = 8$) [17]. Mg and Cr ions occupy the tetrahedral and octahedral sites, respectively. Picrochromite is highly refractory (melting point, 2250 °C), but Cr_2O_3 slowly volatilizes when the material is heated to 2000 °C.

However, extremely high temperatures (1600 °C) are necessary to obtain Pirochromite from its oxides [18,19]. In this context, many other precursors and alternative routes have been of special interest to develop some high temperature oxides [20–29].

$MgCr_2O_4$ was obtained from the suspension of $Mg_5(CO_3)_4(OH)_2{\cdot}4H_2O$ in an aqueous $Cr(NO_3)_{3.9}H_2O$ solution at 600 °C in air by Zaki et al. [30]. An aerogel of magnesiochromite spinel with a surface area of 53 m^2/g was also

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developed by Finocchio et al. [15]. However, the highest surface area obtained was 72 m^2/g trough combustion synthesis of the respectively nitrates and maleic hydrazide in appropriate mole ratios at 375 °C by Chandran and Patil [31].

Combustion synthesis seems to be interesting to produce oxides and mixtures of submicrometric or nanometric powders with relative high surface area with a relative low cost technique [29]. The high temperature required for the formation of these oxides is achieved by the exothermicity of the redox reactions between the decomposition products of metal nitrate (oxidizer) and urea (fuel) during combustion. It consists of heating an aqueous solution made of inorganic salts until its ignition. The complexant/combustible agents play a fundamental role in preventing the precipitation of the individual precursors prior to ignition. Maleic hydrazide, urea and glycine are the more common ones. Generally, a suitable fuel reacts non-violently, produces non-toxic gases and acts as a good complexant for metal cations.

According to some previously published papers [32,33], urea (COH_4N_2) seems to be a good complexant/fuel for chromic oxide. Glycine ($C_2O_2H_5N$) presents zwitterionic character, acting as a complexant agent for a great number of metal ions of several ionic sizes and prevent their selective precipitation [34]. Furthermore, it can also act as fuel during a combustion reaction, being oxidized by nitrate ions and is one of the cheapest amino acids.

Ammonium dichromate, $(NH_4)_2Cr_2O_7$, is known to undergo exothermic autocatalytic decomposition to produce Cr_2O_3, N_2 and H_2O. This salt has major advantages over the chromium nitrate: its decomposition begins at a lower temperature (170 °C) and it is exothermic (ΔH -476.4 ± 0.4 kJ/mol).

Actually, the mechanism of the combustion reaction is quite complex. The parameters that have the greatest influence on the reaction include: nature of fuel, fuel to oxidizer ratio and use of auxiliary oxidizer.

Despite the existence of some reports concerning chromium oxide [32] and chromates [31,35–38] produced from combustion synthesis technique, no articles regarding the synthesis of nanocrystalline $MgCr_2O_4$ using glycine/urea as combustibles were found in the literature. We have not found papers describing the influence of parameters such as fuel/oxidant ratio, the reaction character (stoichiometric, fuel lean) and the extra addition of oxidant (ammonium nitrate) on the final properties of the oxides produced by combustion synthesis as well. Furthermore, it was not encountered any report concerning on high surface area powders of $MgCr_2O_4$, which is of great interest as catalyst-support and humidity sensors.

2. Experimental procedures

$MgCr_2O_4$ was produced through the decomposition of ammonium dichromate salt $(NH_4)_2Cr_2O_7$. Its decomposition is exothermic and autocatalytic, with a heat of reaction of 476.4 ± 0.4 kJ/mol together with glycine combustion [34]. In some cases NH_4NO_3 was utilized as an auxiliary oxidant agent.

In order to take advantage of the exothermic reaction, its important to achieve the proper composition of the oxidizer/fuel mixture. The different mixtures employed in this work (Table 1) were used to evaluate the deviation of the stoichiometry and the influence of the amount of gases and heat produced by the addition of extra quantities of ammonium nitrate. Reagents grade were used for all formulations.

Oxidant character. The deviation from stoichiometry in the combustion reactions was made through the addition of ammonium nitrate.

Effect of the ammonium nitrate addition. Keeping the same combustible-to-ammonium nitrate ratio, the effect of higher amounts of combustible and ammonium nitrate was tested in the stoichiometric formulations.

Table 1
Tested formulations

Test	Magnesium nitrate, P.A. 100% (g)	Dichromate ammonium, P.A. 97% (g)	Urea, P.A. 100% (g)	Glycine, P.A. 100% (g)	Ammonium nitrate, P.A. 100% (g)	pH
Ox.	7.6857	7.791	–	–	–	2.09
U.St	7.6857	7.791	3	–	–	3.04
U.Ox.N.	7.6857	7.791	3	–	23.991	2.94
U.St.N.	7.6857	7.791	6	–	23.991	3.31
G.St.	7.6857	7.791	–	2.5	–	4.01
G.Ox.N.	7.6857	7.791	–	2.5	23.991	3.83
G.St.N.	7.6857	7.791	–	5	23.991	4.31

Example of nomenclature: U.St.N, stoichiometric formulation with urea and ammonium nitrate; Ox., oxidant character, without combustible; U.Ox.N, oxidant character with Urea and ammonium nitrate.