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Nanocrystalline Cr_2O_3 and amorphous CrO_3 produced by solution combustion synthesis

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Abstract

The synthesis of chromium oxides by solution combustion synthesis was investigated. Ammonium dichromate, glycine, urea and ammonium nitrate dissolved in aqueous solution 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. Amorphous CrO_3 and crystalline Cr_2O_3 were synthesized. The results suggest that glycine is a better complexing/combustible agent for ammonium dichromate than urea. Addition of extra ammonium nitrate to stoichiometric compositions improved the specific surface area and reduced the crystallite size. The smallest crystallite size ($\approx$20 nm) of Cr_2O_3 was obtained with glycine as fuel/complexant agent in fuel-lean mixtures. The highest specific surface area (63 m^2/g) was observed with urea in fuel-rich mixtures, forming amorphous CrO_3.

Keywords: Powders-chemical preparation; Grain size; Wear parts; Cr_2O_3

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1. Introduction

The technique of combustion synthesis is an inexpensive method to produce oxides and mixtures of submicrometric or nanometric powders. This method consists of heating an aqueous solution made of inorganic salts, usually nitrates which act as oxidant agent and an organic combustible, which can be also a complexant agent of the metallic ions. Firstly, it is necessary to ensure the homogeneity of the system with the complete dissolution of the components. After that, the solution is heated until its ignition, giving rise to a fast exothermic reaction that leads to oxides formation. The complexant/combustible agent plays a fundamental function preventing the precipitation of the individual precursors prior the ignition.

One of the cheapest amino acids, glycine (NH_2CH_2COOH), is known to act as a complexant agent for a great number of metal ions because it contains a carboxylic acid group at one end and an amino group at the other end.[1] When in solution, amino acids act as zwitterionic molecules with both positive and negative charges. Such kind of zwitterionic character of a glycine molecule can effectively complex metal ions of several ionic sizes and help preventing their selective precipitation, maintaining the homogeneity among the constituents. On the other hand, glycine can also act as fuel during a combustion reaction, being oxidized by nitrate ions.[2]

Urea is largely employed in techniques of combustion synthesis due to its high exothermicity and low cost, mainly used in aluminum oxides synthesis.[3] Moreover, the presence of an amino groups in its molecule leads to a good complexation of transition metals cations.[1]

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). The addition of an organic complexing/combustible agent could improve the synthesis of the Cr_2O_3 accelerating the decomposition reaction, reducing the exposition of the formed oxide to the high temperatures and

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precluding the sintering and the grain growth. Besides that, the addition of organic material to the mixture increases the gas generation during the combustion reaction, leading to an increase of the superficial area.[1,2]

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. Generally, a suitable fuel reacts non-violently, produces non-toxic gases, and acts as a good complexant for metal cations.[4]

Ultra fine chromium oxide (eskolaite) is used as a catalyst in oxidation reactions, hydrogenation reactions, isomerization of olefins, dehydrogenation of alkanes and pigments production. Furthermore, it is an important refractory material due to its high melting temperature (about 2435 °C) and oxidation resistance. Small particles (below 200 nm) are preferred for pigment applications in order to increase the opacity. Cr_2O_3 particles below 50 nm can be used as transparent colorants. Reduction of particle size is also important to improve sintering abilities, i.e., to decrease sintering temperature and to increase density of sintered powders. This is of particular interest for Cr_2O_3, which is difficult to be sintered up to high densities due to its high vaporization rate, leading to a grain coarsening without densification.[5]

Microstructured chromia exhibits an excellent performance as plasma sprayed coatings in applications that require high wear resistance, because of its good tribological properties, even in high temperatures or in the absence of lubrication.[6–9] The use of nanostructured materials to produce thermal sprayed coatings probably will increases hardness, fracture toughness and consequently wear resistance.

Despite the existence of several reports concerning chromates like $LnCrO_3$[10] produced from combustion synthesis technique, it was not encountered any article regarding the synthesis of Cr_2O_3 that investigate the influence of parameters such as the complexant nature, fuel/oxidant ratio, the reaction character (fuel rich, stoichiometric, fuel-lean) and the extra addition of oxidant (ammonium nitrate) on the final properties of the oxides produced by combustion synthesis.

2. Experimental procedure

Cr_2O_3 was produced through the decomposition of ammonium dichromate salt $(NH_4)_2Cr_2O_7$ together with glycine or urea combustion. In some cases NH_4NO_3 was utilized as an auxiliary oxidant agent. The theoretical main reactions were:

$$(NH_4)_2Cr_2O_7 \rightarrow Cr_2O_3 + N_2 + 4H_2O \tag{1}$$

$$C_2O_2H_5N + \tfrac{9}{4}O_2 \rightarrow 2CO_2 + \tfrac{5}{2}H_2O + \tfrac{1}{2}N_2 \tag{2}$$

$$C_2O_2H_5N + \tfrac{9}{2}NH_4NO_3 \rightarrow 2CO_2 + \tfrac{23}{2}H_2O + 5N_2 \tag{3}$$

$$CO(NH_2)_2 + \tfrac{3}{2}O_2 \rightarrow CO_2 + N_2 + 2H_2O \tag{4}$$

$$CO(NH_2)_2 + 3NH_4NO_3 \rightarrow 4N_2 + 8H_2O + CO_2 \tag{5}$$

The decomposition reaction of ammonium dichromate reaction (1) is exothermic and autocatalytic, neither consuming nor liberating O_2.The addition of organic material in the mixtures requires an extra addition of oxidant agent in order to maintain the stoichiometry (burning the complexant agent). In this case, NH_4NO_3 was used, which is a cheap chemical product and does not produce any residual solid material after its decomposition. Besides testing the influence of the complexing/combustible agent (urea or glycine) used on the process, it was also evaluated:

Effect of the deviation of the stoichiometry: The deviation of the stoichiometry in the combustion reactions was carried out trough the addition of combustible (glycine/urea) or oxidant (ammonium nitrate). Due to the fact that the decomposition of ammonium dichromate is autoredox, the combustible additions are arbitrary. The amount of combustible was set to the equivalent compositions (G0 and U0, G1 and U1, etc.) in order to produce the same amount of gas after the complete combustion reaction. In the reductive formulations (G0 and U0) was added arbitrarily 1 mol of glycine combustible for each mol of dichromate ammonium and the urea was added obeying the gas generated criteria. In the stoichiometric formulations G1 and U1 the combustible was added in the same amount of the reductive formulation but a proportional amount of ammonium nitrate was added to burn completely the organic material. For the oxidant formulations (G3, U3), was added the double of amount of ammonium nitrate necessary to oxide the combustible.

Effect of the combustible/oxidant addition: In order to evaluate the effect of the addition of more complexing/combustible agent and oxidant (keeping the stoichiometry), it was added the double of glycine/urea and ammonium nitrate in formulations G2 and U2 than in formulations G1 and U1.

Another formulation denominated “0”, composed of pure ammonium dichromate, was tested for comparison purpose.

To calculate the theoretical adiabatic flame temperature and the gas volume generated by each mixture, the combustion was admitted to be complete, and the combustible excess was burned by the atmospheric oxygen. Heat loss by radiation or conduction was ignored. The adiabatic flame temperature of each mixture was approximately calculated by the following equation:[11]

$$T_f = T_0 + \frac{\Delta H_r - \Delta H_p}{c_p} \tag{6}$$

where ΔH_r and ΔH_p are the enthalpies of formation of the reactants and products, respectively; c_p is the heat capacity of products at constant pressure, and T_0 is 298 K. Using the thermodynamic data for the various reactants and products listed in the Table 1, the enthalpy of combustion and the theoretical adiabatic flame temperatures as a function of glycine-to-nitrate molar ratio could be calculated. Nevertheless, the

Table 1
Relevant thermodynamic data[12]

Compound	ΔH_f (kcal/mol)	c_p (cal/mol/K)
$NH_4Cr_2O_7$ (c)	−429.93	–
NH_2CH_2COOH (c)	−126.22	–
$CO(NH_2)_2$ (c)	−79.56	–
NH_4NO3 (c)	−87.40	–
Cr_2O_3 (c)	−271.020	28.510
CO_2 (g)	−94.051	$10.34 + 0.00274T$
N_2 (g)	0	$6.50 + 0.0010T$
O_2 (g)	0	$5.92 + 0.00367T$
H_2O (g)	−57.796	$7.20 + 0.0036T$

(c), Crystallite; (g), gas; T, absolute temperature.

measured flame temperatures are typically much lower than calculated values, because of loss by radiation, incomplete combustion, and heating of air.

Each mixture was completely dissolved in 100 ml of water and this solution was heated in a stainless steel beaker with a Bunsen burner until water evaporation and subsequent combustion of the material. Temperature was measured with a type K thermocouple of 1.5 mm diameter inserted into the reagent mass. The resulting material was crushed in a mortar with ethylic alcohol and dried in a stove. The specific area of the produced powder was measured by Brunquer–Emmett–Teller (BET) technique with N_2 adsorption using Autosorb Quantachrome Instrument (model Nova 1200). The diameter of the produced particles was calculated from the superficial area using Eq. (7), as follows:

$$D_{\mathrm{BET}} = \frac{6}{S_{\mathrm{BET}}\rho} \tag{7}$$

where S_{BET} is the superficial area (m^2/g) measured by BET analyses and ρ is the density of the powder (5.21 g/cm^3).

Before the combustion, small portions of each mixture were reserved for thermal gravimetric (TG) and differential thermal analyses (DTA), in order to determine the ignition temperature of the mixture. The solution was previously dehydrated in a stove at 105 °C for 24 h. Thermal analyses were carried out in platinum crucibles with 34 ± 4 mg of material and heated until 700 °C at a rate of 10 K/min in an air gas flow. A JEOL JEM2010 TEM, with point resolution of 0.25 nm at 200 kV was used for evaluation of the particle morphology and crystallite size of the produced oxide.

2.1. X-ray diffraction analysis

WinFit 1.0 software was used to determine the crystallite size of the synthesized powders. The profile shape function used was a split Pearson VII function and the single line variance approach of Toth[13] and Arkai and Toth[14] was considered for the crystallite size calculation. The Kα2 contribution was removed by the Rachinger correction, and the Stokes deconvolution method was employed to remove the instrumental contribution of the experimental peaks after introducing the profile shape function of pure-line standard. A sample of chromia, which was annealed at 1500 °C for 4 h, was used as standard. Very sharp and well defined peaks were obtained with this procedure (Fig. 1). From the Pearson exponent of the profile shape function, the contribution of Gaussian and Lorentzian components could be calculated. Such contributions are assumed to be proportional to the amount of crystallite size broadening and strain broadening, respectively. Finally, Fourier analysis was used to calculate size and strain parameters.

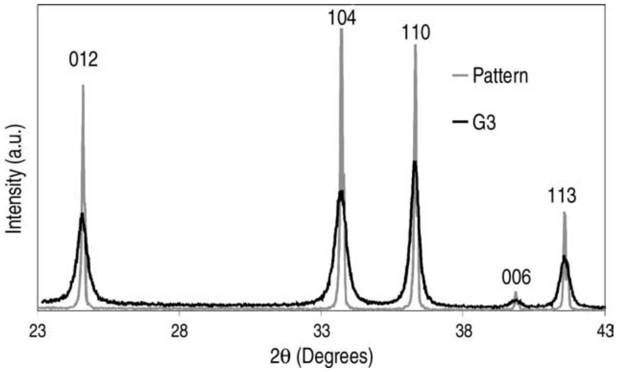

Fig. 1. Powder X-ray diffraction pattern of Cr_2O_3 annealed at 1500 °C for 4 h and G3 mixture after combustion.

All the samples were analyzed with Philips (model X'Pert MPD) diffractometer, equipped with a graphite monochromator and a rotative anode of copper operating a 40 kV and 40 mA. All measurements were made using Cu Kα radiation; the scanning rate was 1°/min for phase analysis and 0.4°/min for crystallite size determination.

3. Results and discussion

3.1. Adiabatic flame temperature and volume of gases produced

The calculated adiabatic flame temperatures are shown in Fig. 2. It is possible to observe that the calculated flame temperature is higher for mixtures containing glycine as fuel/complexing agent. It is important to note that the quantity of combustible and nitrate were adjusted in order to produce quite the same volume of gases for analogous mixtures of

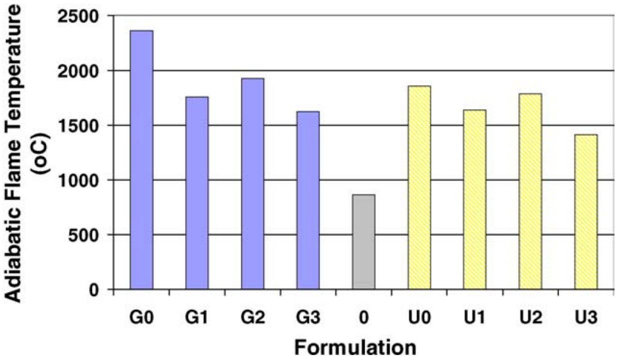

Fig. 2. Calculated adiabatic flame temperatures.

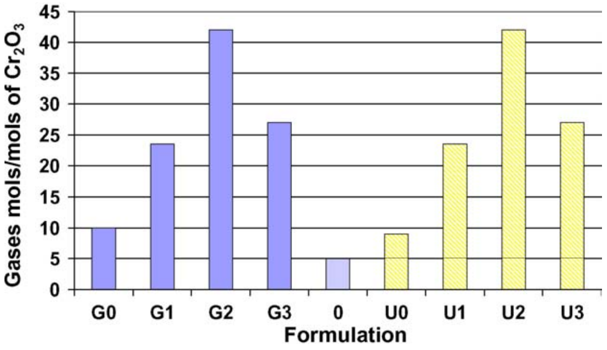

Fig. 3. Calculated volume of gases produced at room temperature and pressure.

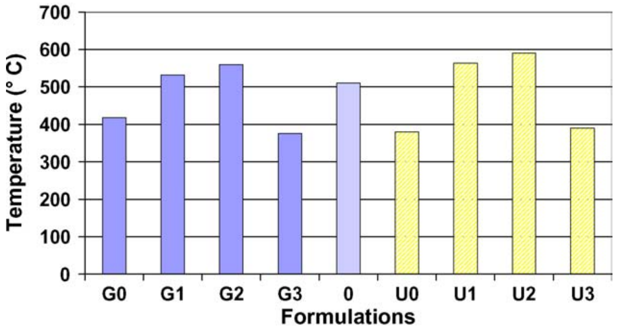

Fig. 4. Maximum temperatures reached during the combustion measured with thermocouple.

glycine and urea (Fig. 3). In order to maintain this equivalency in volume of gases of the products, a slightly smaller amount of glycine than urea was used (Table 2). Even so it is possible to note a lower adiabatic temperature in the mixtures containing urea. The characteristics of the resulting oxide are influenced by the generated gas in combustion reactions, which causes the dissipation of the combustion heat, decreases the temperature in the reagents mass, may increase the specific volume of the resulting material and may increase the superficial area of the oxides. In opposition to this effect, elevated temperature during the combustion might cause the sintering of the products, reducing their surface area and increasing the crystallite size.[15]

During the combustion some differences were observed: while in the fuel-rich mixtures (G0 and U0) there was not any flame during the ignition, only an incandescence of the reagents mass was observed. On the other hand, mixtures G1, G3, U1 and U3 produced flames during ignition, while for G2 and U2 mixtures an explosion-like reaction was observed. The powder resulting from mixture U0 showed a black coloration, probably due to the presence of residual carbon. In contrast to this, all the others powders had a green coloration. Despite higher temperatures were calculated for the combustion of mixtures G0 and U0, its aspect did not indicate so. Maximum temperatures reached by the mixtures during combustion are represented in Fig. 4. It can be noted that the maximum temperatures of the fuel-rich mixtures are among the lowest ones. Besides the fact that the temperatures measured by the thermocouple during the combustion of stoichiometric and reductive mixtures were much lower than the calculated ones, it is interesting to observe that for the other mixtures the temperatures show the same tendency—for mixtures G2 and U2 the temperatures were the highest, while for G3 and U3 they were the lowest ones.

For calculation purposes, it was assumed that the atmospheric oxygen caused the combustion of the excess of urea and glycine (reactions (2) and (4)), since the ammonium dichromate have auto-redox decomposition, neither providing nor consuming oxygen. However, burning of the excess combustible by atmospheric oxygen is not efficient, because of its slow diffusion into the reagents bulk mass and heterogeneities issues. Such assumption could be a possible explanation for the fact that reductive mixtures (G0 and U0) reached much lower temperatures during combustion.

Other factors that contribute to such temperature discrepancy are the fact that the combustion reaction is not completely adiabatic (radiation/conduction losses) and the thermal inertia of the thermocouple; furthermore, remaining water in the precursor solution at ignition temperature lowers the flame temperature, because this residual liquid water must be converted to the vapor and be heated to the flame temperature.[10]

3.2. DTA/TG analysis

The ignition temperatures of the dehydrated mixtures measured in the ATD indicated a low and well defined ignition temperature for the stoichiometric and oxidant mixtures,

Table 2
Investigated mixtures

Test	Reaction character	Ammonium dichromate (g)	Glycine (g)	Urea (g)	Ammonium nitrate (g)
0	Stoichiometric	12.95	0	0	0
G0	Fuel rich	12.95	3.75	–	–
G1	Stoichiometric	12.95	3.75		18
G2	Stoichiometric	12.95	7.5		36
G3	Fuel-lean	12.95	3.75		36
U0	Fuel rich	12.95		4.25	
U1	Stoichiometric	12.95		4.25	17
U2	Stoichiometric	12.95		8.5	34
U3	Fuel-lean	12.95		4	31.9

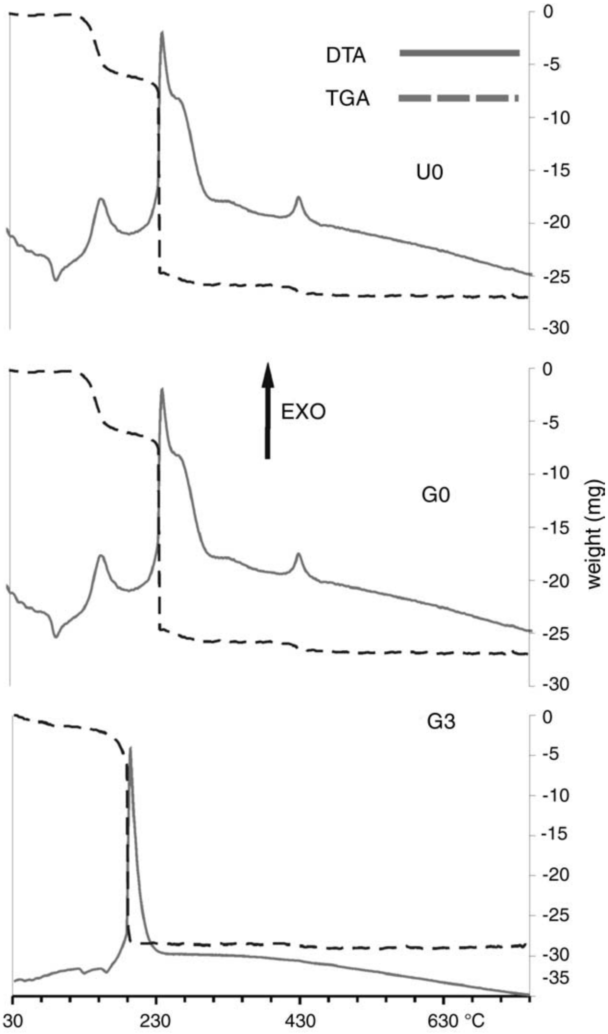

Fig. 5. Thermal analysis (DTA and TG) of the mixtures G and U.

all of them similar to the DTA/TG curve of the G3 mixtures showed in Fig. 5.

The DTA/TG curves for reductive mixtures (G0 and U0) are more complex. For mixture G0, three exothermic reactions could be observed: one of them at 250 °C, a great one 330 °C and small heat liberation at 418 °C. All of them were accompanied by mass loss. The first reaction could have been initiated by the fusion and decomposition of glycine (250 °C), and followed by the reaction of the products with the ammonium dichromate (strong oxidant agent), and inducing its decomposition.

Fig. 6 shows the ignition temperature of the mixtures, measured by DTA analysis. As can be seen, the decomposition of pure ammonium dichromate (mixture 0) occurred at 240 °C. Generally, this decomposition occurs at 170 °C[12] for pure ammonium dichromate. However, the heating rate and the amount of sample could change the decomposition temperature. The addition of combustibles/complexing agents (urea/glycine) to pure ammonium dichromate reduced the ignition temperature. However, for the reducing mixtures (U0 and G0) the ignition temperature was almost the same of that of pure ammonium dichromate.

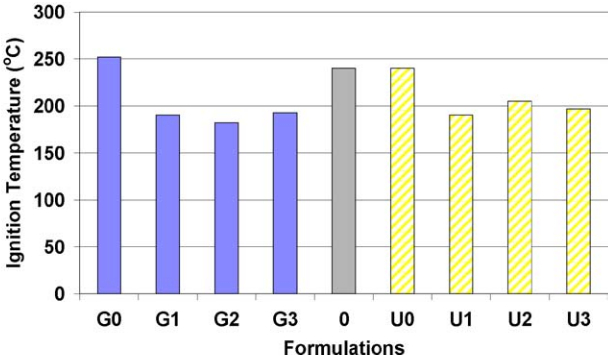

Fig. 6. Ignition temperature of the mixtures.

Mixtures U0 exhibited three exothermic peaks, the first one in a temperature below 160 °C. This is the same temperature in which the decomposition reaction of urea starts. Such reaction proceeds in a series of steps[16] and it is endothermic, but it is probable that part of ammonium dichromate reacts with some of the several sub-products resulting from the decomposition reaction of urea, such as isocyanic acid HCNO, cyanuric acid $[(HCNO)_3]$, ammonia NH_3, biruet $H_2NCONHCONH_2$, etc., leading to an exothermic reaction. However, great part of the reaction occurs when the temperature is sufficiently high, originating the highest exothermic peak, which in this case is at 240 °C. Both reductive mixtures (G0 and U0) presented an exothermic peak at 420–430 °C, associated to a mass loss. This temperature is the same of the exothermic decomposition of CrO_3 into Cr_2O_3 with oxygen liberation:[16]

$$2CrO_3 \rightarrow Cr_2O_3 + \frac{3}{2}O_2$$

It suggests that the fuel-rich mixtures U0 and G0 produced CrO_3 as primary product. When solution U0 was submitted to ignition inside the stainless steel becker, the resulting product was amorphous, while the G0 mixtures produced a crystalline material identified as Cr_2O_3. The low combustion temperature of the U0 mixtures (380 °C) was not sufficient to decompose the material in Cr_2O_3. However, the higher combustion temperature of G0 (420 °C) caused the decomposition of CrO_3 during ignition inside the stainless steel becker.

For the stoichiometric and oxidant mixtures, the ignition temperature was higher for mixtures containing urea than those ones containing glycine. For example, mixture G2 ignited at 182 °C (the lowest ignition temperature) and U2 at 205 °C. This may indicates a better complexation grade[10] of the metallic ion: chromium ions form charges transfer complexes with the nitrogen atom of glycine. As a result, water molecules of hydratation are displaced, thereby making the redox reaction between the metallic ion and the complexant/combustible easier and lowering the ignition temperature. G2 mixtures had the lowest ignition temperature probably due

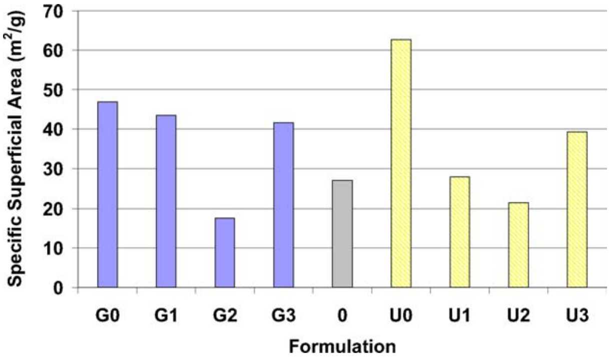

Fig. 7. Surface area measured by BET analysis.

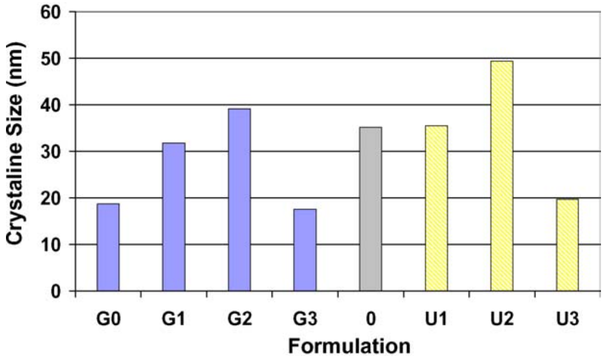

Fig. 8. Crystal size measured by X-ray diffraction.

to the higher proportion of glycine/ammonium nitrate in the mixture and the good complexation achieved by the use of glycine.

3.3. *Specific surface area*

Fig. 7 shows the variation in the specific surface area of chromium oxide as a function of mixture composition. The higher surface area of the U0 mixtures is probably due to the residual amorphous carbon, as a result of the incomplete combustion of urea. The stoichiometric mixture containing extra amounts of glycine and ammonium nitrate (G2) exhibited the lower specific area, despite the great amount of gases generated in the combustion of this mixture (Fig. 3). The evolution of gases during combustion results in highly porous structures on the product. On the other hand, increasing the amount of combustible and oxidant results in higher flames temperature during the combustion and sintering and grain growth of the products. So, the surface area of the powder product seems to be influenced—in opposite directions—both by the effect of the flame temperature and the volume of gases generated during the process. In the stoichiometric mixtures containing urea, the surface area was affected by the addition of extra combustible and oxidant in the same way of the glycine mixtures.

3.4. *Crystal size measured by X-ray diffraction*

X-ray diffraction analyses showed that all mixtures resulted in crystalline Cr_2O_3 eskoalite (Fig. 1) after combustion, exception made for mixture U0 that resulted in amorphous material. The size of the crystals was also measured by X-ray diffraction, and they are shown in Fig. 8. It can be seen that crystal size and calculated adiabatic temperatures (Fig. 2) follow the same tendency, except for mixtures 0 and G0. Figs. 8 and 4 (maximum measured combustion temperature) present better equivalency. The most remarkable result found here was for mixture G3, which had the smallest crystal size: 18 nm. The lower amount of combustible/complexant in G3 and U3 oxidant mixtures decreased the flame temperature, while the excess of ammonium nitrate produced a sufficient amount of gases to provide a good dissipation of heat. Larger crystallites observed for mixtures U2 and G2 are probably related with higher temperatures reached during ignition, causing a great grain growth.

When comparing the particle diameter determined by specific surface area measurements (Fig. 9) with the crystal size determined by X-ray diffraction, it is possible to observe that the values are similar, thus showing that measurements made by both methods are in good agreement. Since Eq. (1) assumes that the powder particles are spherical, the concordance between the two measurement techniques indicates that the oxides have a spherical or quasi-spherical morphology, considering each particle as a monocrystal. In fact, TEM analysis agrees with this for G3 mixtures.

3.5. *Morphology and crystallite size measured by transmission electronic microscopy*

Mean particle size measured from TEM micrographs of G3 mixtures (Fig. 10) was 21 nm. Weakly bonded agglomerates of primary monocrystalline particles were observed (Fig. 11), and the diameter of 112 particles was measured from several agglomerates of the same micrograph. There was little difference in the crystal mean size among distinct agglomerates. When compared with the crystal size measured by X-ray diffraction (18 nm), a good agreement between both techniques could be noted.

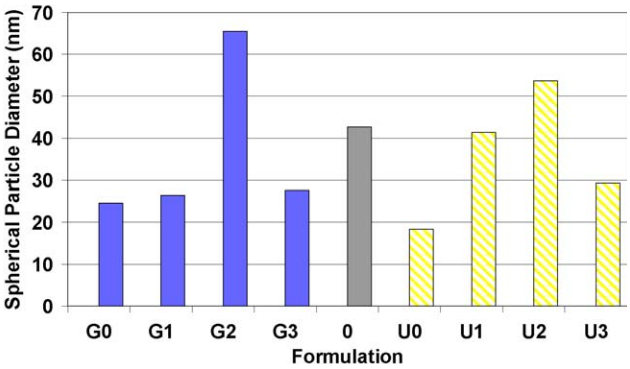

Fig. 9. Diameter of the particles calculated from the surface area.

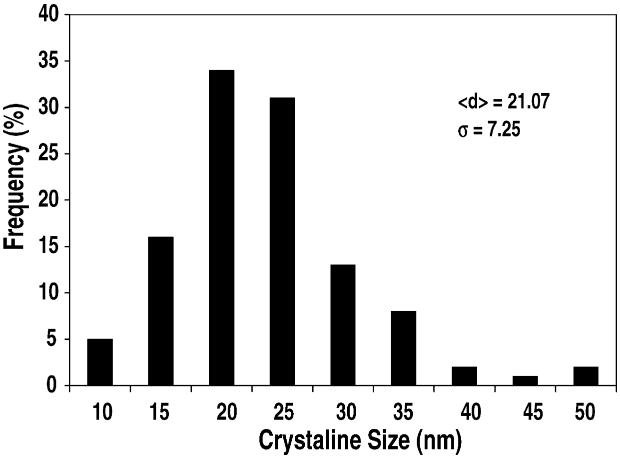

Fig. 10. Histogram of the distribution of crystal size obtained by TEM for the sample G3. The mean value (⟨d⟩) and the standard deviation (σ) are shown too.

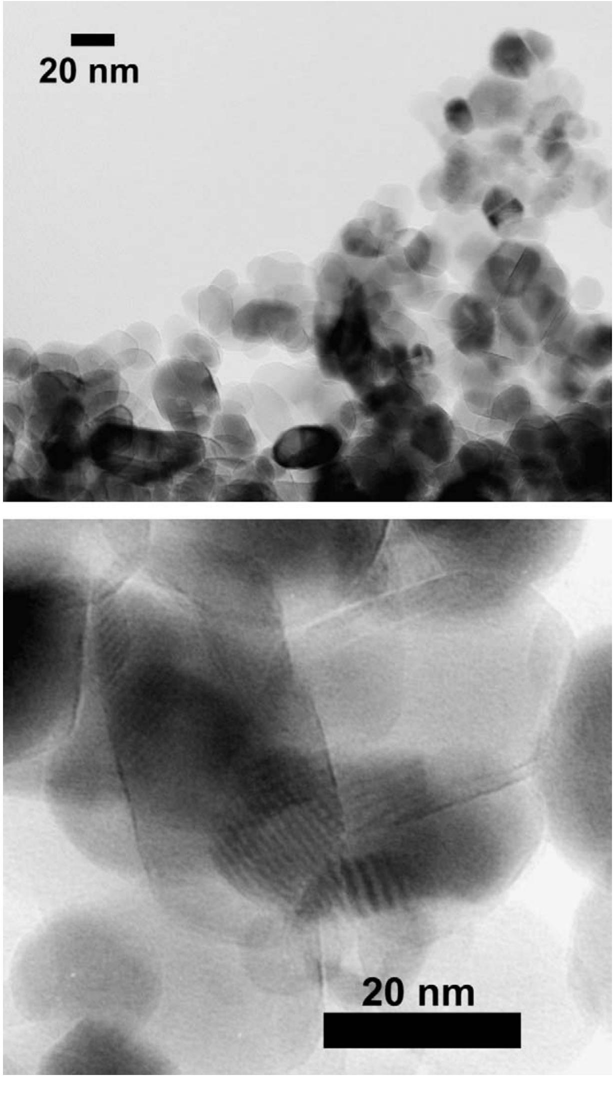

Fig. 11. TEM image of G3 mixtures after combustion.

4. Conclusions

The synthesis of chromium oxides by solution combustion synthesis using precursors containing ammonium dichromate, glycine, urea and ammonium nitrate dissolved in aqueous solution produced amorphous CrO_3 and nanocrystallite Cr_2O_3.

The smallest crystallite size of Cr_2O_3 was obtained with glycine in fuel-lean mixtures. The mean particle size calculated by BET was close to crystallite size measured by X-ray diffraction—18 nm, suggesting quite spherical primary monocrystalline particles. This fact was confirmed by TEM analyses.

Comparing the ignition temperature of the mixtures, the lowest one was exhibited by glycine-containing mixtures, that is probably associated to a greater complexation grade of the chromium by this compound than by urea. As a consequence, a better mixing of the components, a faster combustion reaction and lower flames temperatures probably due the higher water retentions are expected for such mixtures. These facts hinder the crystal growth, which is in agreement with the crystallite size measured by TEM and X-ray diffraction.

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