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Combustion synthesis of the cermet $LaCrO_3$–Ru

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Abstract

Perovskite-type chromites have been previously synthesized employing the combustion method; in the present work a ceramic–metallic composite $LaCrO_3$–Ru was also prepared by the same method. Employing the combustion synthesis, nanocrystalline powders composed by two different phases were achieved, being the particle size of the $LaCrO_3$ ceramic of 11–16 nm, and the average grain size of Ru metallic around 2–5 nm. The ruthenium was dispersed randomly and well distributed over the ceramic phase. TEM studies, revealed the formation of the cermet, finding two different types of particles, most of them dark coloured and with polygonal shapes associated with the ceramic support and others, smaller in size, rounded were assumed to be Ru phase. The cermet showed activity in the partial methanol oxidation, finding the maximum conversion of MeOH to H_2 at 327 °C.

Keywords: Nanocomposites; Ceramic matrix composites; $LaCrO_3$–Ru

1. Introduction

The preparation of $LaCrO_3$ by different methods has been well reported in the literature.[1,2] Although these oxides exhibit two different crystal structures, the perovskite-type chromites are of great importance due to their elevated electronic conductivity (p type) and their stability at high temperatures. This oxide has been proposed as an interconnector in the planar design of SOFC, as $LaCrO_3$ exhibits an increase in the electronic conductivity when the oxide is doped with alkalines.[3] However, $LaCrO_3$ shows low sinterability in air, as a consequence of the high vapour pressure of Cr_2O_3, formed at 1400 °C. For this reason, most of the efforts concerning the development of this material deal with the study of the sintering process[4] of this compound, or alternatively, the preparation of $LaCrO_3$ by different synthesis methods[5] in some cases to achieve a particular morphology or reactivity that enhance its further sintering.

Combustion synthesis has been widely used to prepare powders with specific applications, such as catalysts[6–8] or ceramic glides,[9] because it promotes small-sized particles and thus, higher catalytic activity. The preparation of $LaCrO_3$ by this method has been reported before,[10] being its synthesis and the reactions involved in it, deeply studied.

Here we proposed an alternative material synthesized rapidly by the combustion method in a single step procedure. This work aimed to obtain a nanocomposite material based on $LaCrO_3$ with a metallic phase, Ru, finely dispersed over the ceramic matrix. $LaCrO_3$ ceramic has been modified adding a 25 mol% of Ru precursors to obtain a cermet with nanocrystalline morphology able to be used as electrocatalyst in hydrocarbon electrochemical reforming devices, producing CO-free H_2 from methane reforming.

2. Experimental

The combustion method is based on the generation of a highly exothermic and self-sustaining reaction; with this aim a stoichiometric mixture of reactants was placed into an open-air reactor. The cation precursors used in these synthesis were $La(NO_3)_2{\cdot}xH_2O$ (99%), $Cr(NO_3)_3{\cdot}nH_2O$ (99%) and $(CH_3–CO–CH{=}C(O^-)CH_3)_3Ru$ (97%) all supplied by Aldrich. $CO(NH_2)_2$ (98%, Aldrich) was used as fuel, mixed with an oxidizing aid; in this case NH_4NO_3 (Aldrich, 98%) was used to achieve the adequate equivalent ratio $\Phi e = \Sigma$(oxidant elements)/Σ(reducing elements) = 1, which will be responsible of the mixture ignition.[11] The reactants were highly

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homogenised and heated up to 100 °C to melt the nitrates. The temperature was then increased up to 300 °C while the reaction mass increases its viscosity until the ignition takes place.

DTA–TG was used to characterize the raw materials; these analysis were conducted in dry air using a NETZSCH STA-409 instrument, with a temperature NETZSCH TASC 414/2 controller. For the characterization of the as-prepared powders, a Siemens D5000 diffractometer was used for phase identification. BET specific surface area was determined employing a Monosorb Surface Area Analyzer (Quantachrome Corporation, model MS-13). Direct observation of the nanosized perovskite crystals, and the differences between phases was examined employing transmission electron microscopy (TEM) with a Hitachi H-7000 instrument operating at 125 kV. Scanning electron microscopy (SEM) studies were performed with a JEOL Superprobe (JXA-8900H-WD/ED), combined microanalyzer equipment. Catalytical activity of this catalyst towards methanol reforming was evaluated placing 300 mg of the powder inside a homemade reactor, which was heated between 237 and 327 °C, while a flux of gaseous methanol was flowing through it. A mass spectrometer was connected to the reactor to analyze the composition of the outlet stream. The flux used was 0.257 g s cm^{-3} with a $H_2O/MeOH = 1.5$, being the MeOH concentration in the inlet of 5%.

3. Results and discussion

3.1. Powders synthesis

The as-prepared powders obtained in the synthesis had the appearance of ashes, being very fine; they were grounded in an agathe mortar and sieved through a 63-μm mesh. The use of $(CH_3\text{–}CO\text{–}CH{=}C(O^-)CH_3)_3Ru$ enhanced significantly the reducing valences considered in the mentioned equivalent ratio [i.e. (total amount of reducing elements/total amount of oxidizing elements)], thus requiring a higher content of oxidants to equilibrate it, added by means of ammonium nitrate. The decomposition in air of this Ru precursor has been studied by DTA–TG found to be highly exothermic by itself, increasing the total exothermic energy released. The whole reaction synthesis considered in a simplified view, is as described in reaction (R1). Due to the lack of thermodynamical data related with $[CH_3COCH{=}C(O\text{–})CH_3]_3Ru$ the total energy involved in this synthesis cannot be calculated.

$$\begin{aligned}&La(NO_3)_3{\cdot}6H_2O_{(c)} + Cr(NO_3)_3{\cdot}9H_2O_{(c)}\\&+ [CH_3COCH{=}C(O\text{–})CH_3]_3Ru_{(c)} + m\,CO(NH_2)_{2(c)}\\&+ m\,NH_3NO_{4(c)} + (9.7 + 0.5m)O_{2(g)} \rightarrow LaCrO_3\text{–}Ru_{(c)}\\&+ (15 + m)CO_{2(g)} + (25.5 + 4m)H_2O_{(g)} + (3 + 2m)N_{2(g)}\end{aligned} \tag{R1}$$

Thermal analysis of the precursors involved has been done, observing that all nitrates decompose endothermally with temperature, while $[CH_3COCH{=}C(O\text{–})CH_3]_3Ru$ exhibits an exothermic peak placed at 250 °C; this exothermic decomposition, Fig. 1, together with the result in the reaction between the urea and the nitrates are responsible of the energy released that generates the ignition of the reaction mixture. Biamino and Badini[12] published the synergetic exothermic effect of the urea with an oxidant compound, as a nitrate, in the preparation of lanthanum chromites approached by combustion synthesis. They showed how separate DTA curves were endothermic for both compounds, but when they were placed together the DTA showed an exothermic peak.

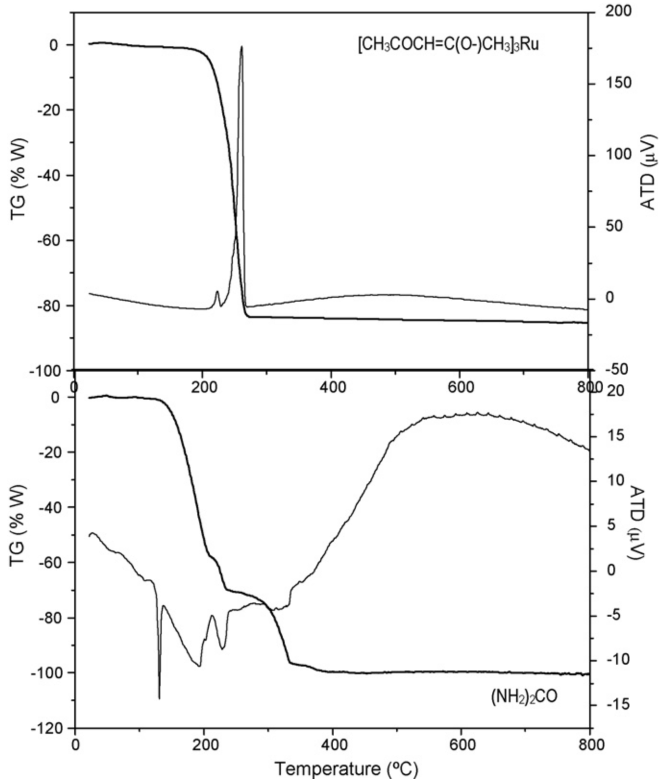

Fig. 1. DTA–TG of (a) urea and (b) $[CH_3COCH{=}C(O\text{–})CH_3]_3Ru$.

3.2. Powder characterization

Fig. 2 shows the X-ray diffraction (XRD) pattern of the as-prepared powders; $LaCrO_3$ phase was formed being the reflections indexed corresponding to the JPCDS card, PDF 83-1328. Ru metallic reflections present a very low intensity comparing with those belonging to the ceramic phase. The small size and the low amount of Ru particles make difficult its detection by XRD. No reflections associated with RuO_2 were found, as well as, no peaks of the raw materials appears in the XRD pattern or SEM-EDX analysis; a fact that gives an indication of a complete reaction.

Electron microscopy was employed to characterize and study the cermet obtained by combustion. SEM micrographs shown in Fig. 3(a) and (b) indicate that the powders exhibit a fine and foamy morphology, being the agglomerates studied formed by smaller particles. The Ru dispersion was evaluated employing mapping, finding it randomly and well dispersed over the ceramic phase.

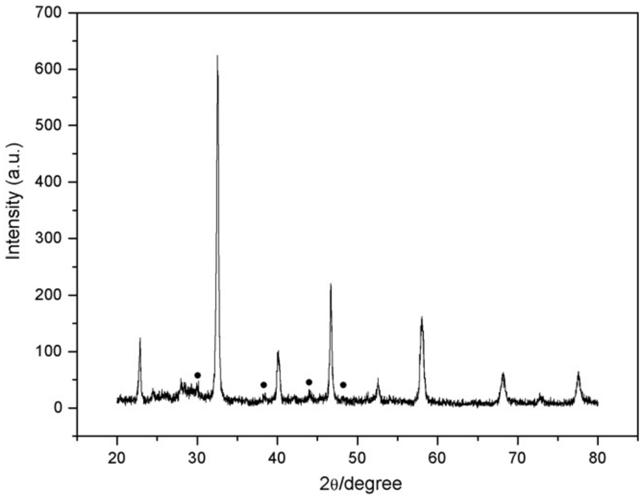

Fig. 2. XRD of the as-prepared powder $LaCrO_3$–25 mol% Ru. (●) Metallic Ru.

The crystalline size was calculated from the patterns above employing the Scherrer equation, ceramic phase $LaCrO_3$ particle size was 11–16 nm. The crystalline size of the metallic phase Ru was calculated from TEM images (Fig. 4). The average grain size of Ru metallic particle size could be estimated in 2–5 nm. Specific surface area of the as-prepared powders were also determined in 8 m^2/g employing the BET method; the addition of Ru seems to produce higher surface areas.

TEM studies, revealed the formation of the cermet; finding with two different types of particles, most of them were bigger in size, with a distribution in the range of 30–300 nm, dark coloured and with polygonal shapes. The second ones, pointed with an arrow in Fig. 4, were even lighter than the previous, smaller in size (∼3 nm), rounded and assumed to the Ru phase. It was observed to be distributed over the ceramic matrix, but randomly.

Combustion synthesis produces directly and in one single processing step material formed by two different phases, a pure oxide matrix, with a second phase, randomly and well-dispersed metallic Ru. The energy released in the combustion reaction is used for the ceramic matrix synthesis, thus preventing Ru particles from agglomeration and the subsequent growth. Combustion synthesis, produces the adequate powder morphology, when dealing with catalysts. However, the final yield of Ru dispersed onto the ceramic matrix, was less than expected. This lost has not been quantified, but it was noticed during the experimental procedure, and explained as a partial oxidation of Ru to RuO_{2+x}, which volatilizes at temperatures higher than 800 °C.

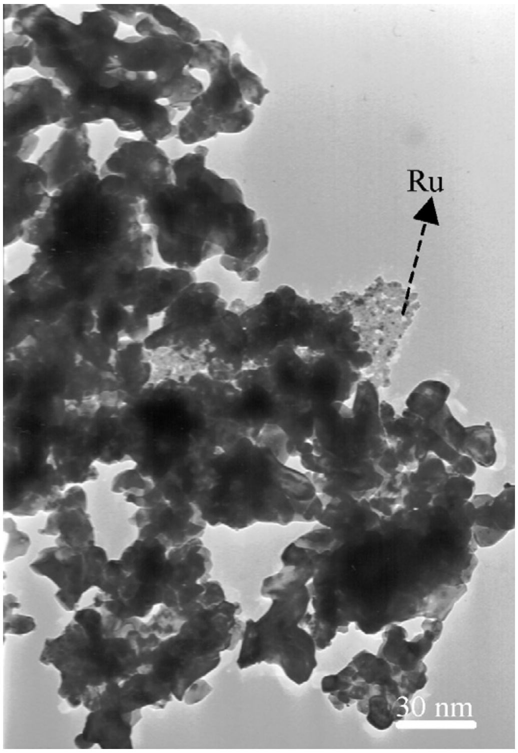

Fig. 4. TEM micrograph of the cermet $LaCrO_3$–25 mol% Ru.

3.3. Catalytic activity $LaCrO_3$–Ru

The catalytic activity of this $LaCrO_3$–Ru cermet was evaluated towards methanol reforming, considering the preparation of an electrocatalyst matrix for this application in order to combine with Ni or Cu metal to obtain better performance in hydrocarbon

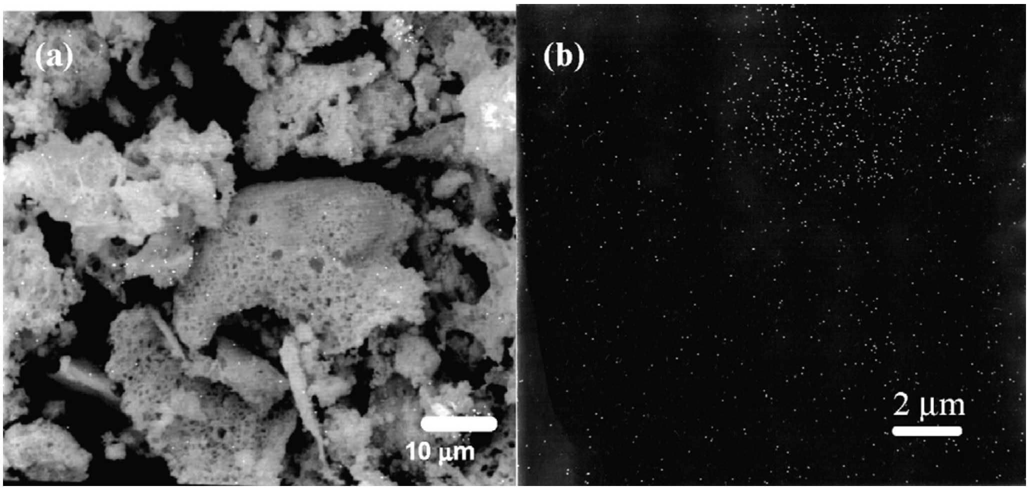

Fig. 3. (a) SEM micrograph of the $LaCrO_3$–25 mol% Ru powders and (b) Ru mapping.

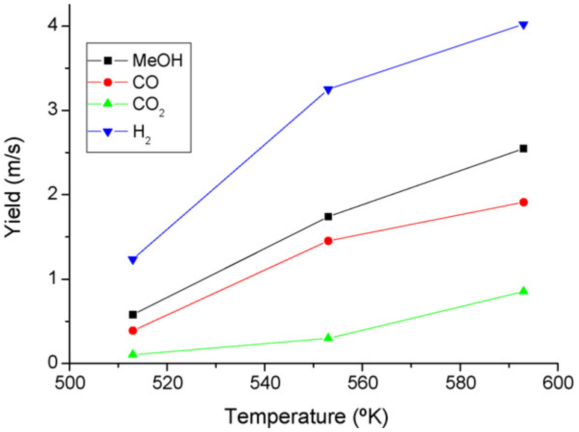

Fig. 5. Catalytic activity of ($LaCrO_3$)–25 mol% Ru towards methanol reforming.

electrochemical devices. The procedure described in Section 2, promotes the results obtained by using the following reactions:

$$CH_3OH \rightarrow 2H_2 + CO \tag{R2}$$

$$CH_3OH + 0.5O_2 \rightarrow H_2 + CO_2 \tag{R3}$$

From Fig. 5 it was concluded that both CO and CO_2 were detected as by-products of both reactions, (R2) and (R3), being the amount of the latter significantly minor that the CO production. The maximum conversion of MeOH to H_2 was found at 327 °C, but exhibit a low yield, only about 4%, produced at the same time, CH_3OH un-reacted. This result is promising since a cermet ($LaCrO_3$)–Ru can be used as matrix in anodic hydrocarbon reforming, optimizing its properties.

The significant catalytic activity of this cermet has been ascribed to the low Ru content in the samples, comparing with the values of other catalysts such as CeO–Cu (with a 50% metal content).[13] All these values, however, are far away from the results published by Chinarro[14] who employed the $SmCoO_{3-d}$ perovskite achieving conversions of 45% at 375 °C, being this values increased to 75% at 325 °C, when the powder was impregnated with Pt. Changes in the synthesis of this cermet have been proposed, which have to be adjusted in order to obtain the $LaCrO_3$–Ru composite, pure, but with higher Ru content. For this reason, changes in fuel and precursors nature have been proposed with the idea of reducing the maximum temperature reached in the synthesis. In this concern, sucrose, which has been employed before as fuel in combustion reaction could be a feasible reactant as its decomposition reaches less temperature, which could avoid the oxidation reaction of Ru, and thus, volatilization, that takes place above 800 °C.

4. Conclusions

$LaCrO_3$–Ru cermet has been synthesized by combustion synthesis. This cermet has been obtained as a pure, nanometric powder, composed by a ceramic matrix $LaCrO_3$ (11–12 nm) with Ru metallic particles randomly distributed. This material exhibits catalytic activity towards methanol oxidation, being the maximum conversion yield of 4%. This was due to the amount of Ru in the material; that result is promising since the nanoparticle cermet can be used as an anodic matrix in hydrocarbon electrochemical devices.

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