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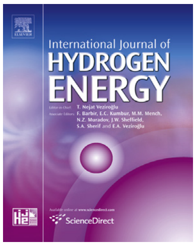

Nanostructured metal oxides obtained by means polymerization-combustion at low temperature for CO selective oxidation

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ABSTRACT

We investigated the synthesis of nanosized Co_3O_4, NiO and CuO oxides by the polymerization-combustion method and evaluated in the selective oxidation of CO. These materials were characterized before and after catalytic test under specific conditions by X-ray diffraction, scanning electron microscopy, temperature programmed reduction, Raman spectroscopy and Diffuse reflectance infrared Fourier transform spectroscopy. For isoconversion the activity follows the order: Co_3O_4>NiO > CuO. The intrinsic activities under isothermal conditions at 100 °C are: $0.20 \times 10^{-3}\ s^{-1}$ for the Co_3O_4 and $0.08 \times 10^{-3}\ s^{-1}$ for NiO and CuO. Therefore, the activity of the Co_3O_4, is 3 times higher than for NiO and CuO. The XRD and Raman analyses after catalytic test confirm the existence of a partial reduction of oxides to the metallic phase and no evidence of carbon deposition over surface materials. In the case of nickel oxide the analyzed sample shows the metallic phase of nickel and in the case of copper oxide the sample presents a high grade of reduction. XRD results confirm the presence of Cu_2O and metallic Cu. Finally, results showed that these oxide catalysts present a high resistance to carbonaceous formation under present reaction conditions and confirm the effectiveness of polymerization-combustion technique for synthesis of active high catalyst in the selective oxidation of CO.

1. Introduction

Fuel cells are devices that convert chemical energy directly into electricity from hydrogen and oxygen feedings. Among various advantages this kind of devices operates at low temperatures, present high power density and easy start-up [1]. However, the principal requirement for the ideal performance is promoting the on-board reforming, removing the residual CO to a hydrogen-rich stream, because CO can damage the electrochemical performance of anodic components severely, even at ppm levels [2]. It is generally recommended CO concentrations less than 10 ppm [2,3]. For the CO removal the catalyst is important and depends on the syntheses of these materials and improvements of specific catalytic properties. The most conventional method is based on a solid–state reaction, where metal oxides are mechanically mixed, resulting in finely divided powders. However, these materials present low surface areas, need high calcination temperatures and long reaction times [4]. On the other hand, the co-precipitation method can easily produce materials with high surface area, around

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100 m^2 g^{-1}, but an enormous effort is necessary to ensure a homogeneous material with uniform particle sizes and composition [1]. Sol-gel routes have been used to synthesize a lot of interesting materials with large surface areas, but this method requires expensive metal alkoxide precursors [2,5].

The combustion method has been proposed to synthesize nanosized materials and is particularly useful in the production of ultrafine ceramic powders with small average particle size. This is an easy and fast method, with the advantage of using inexpensive precursors, producing homogeneous nanosized crystallites and highly reactive materials [6]. The combustion synthesis technique needs the contact of a saturated aqueous solution of a desired metal salt and a suitable organic fuel boiling until the mixture ignites and a self-sustaining and fast combustion reaction takes off, resulting in dry crystalline fine oxide powders [7–9]. The large amount of gases released during the reaction produces a flame that can reach temperatures above 1000 °C, which help in the consolidation of desired crystalline phases.

Kingsley et al. [10] described the preparation of oxides with various metal nitrates (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu and Zn) using urea or carbohydrazide as fuel. The surface area depends on both the metal nitrates and fuel. The surface areas of the prepared materials using carbohydrazide are higher, varying from 45 to 85 m^2 g^{-1}, compared with the materials prepared with urea (1–20 m^2 g^{-1}). Mimani [11], evaluated different fuels (hexamethylenetetramine, urea, carbohydrazide and glycine) for production of MAl_2O_4 (M = Mn, Cu and Zn). In the case of manganese aluminate, urea was the best fuel, producing porous materials with high surface area. The copper and zinc aluminates prepared with carbohydrazide and glycine presented the best results for mesoporous materials. The fuel/oxidizer ratio was evaluated by Alinejad et al. [12] in the combustion synthesis of $MgAl_2O_4$ by using sucrose and PVA solution as fuels. The increase of fuel/oxidizer ratio caused agglomeration of materials with average crystallite sizes in the range of 12.7–17.5 nm [13]. Chandradass et al. [13] synthesized alumina zirconia nanopowder oxides with high surface area by means of citrate auto-combustion method, evaluating the effect of nitrate/citrate (N/C) ratio and the use of chelant agent. The use of a stoichiometric U/N ratio resulted in a material with high surface area and homogeneous nanocrystallites, while the excess of citrate resulted in a non-porous material with low surface areas. The formation of superficial metal nanoparticles resulted in an excellent stability for low temperature CO oxidation [14]. Thus, the aim of this paper is to investigate the synthesis of nanosized Co_3O_4, NiO and CuO oxides by the polymerization-combustion method and evaluated in the selective oxidation of CO, which permit to identify some of the most important characteristics in the performance of nanostructured fuel cell components.

2. Experimental

2.1. *Preparation of catalysts*

The nano-crystallite Co_3O_4, NiO and CuO oxides were prepared by the polymerization-combustion technique starting from the corresponding nitrates $Co(NO_3)_2.6H_2O$ 99.9%, $Ni(NO_3)_2.6H_2O$ 99.9%, and $Cu(NO_3)_2.9H_2O$ 99.99%. Similarly, solid citric acid monohydrate 99.99% was used. Stoichiometric quantities of each solid salt (0.01 mol) were added to 20 mL of deionized water in different glass vessels equipped with magnetic stirring (150 rpm), reflux system and controlled temperature. Once reached the total dissolution of each nitrate precursor, we added solid citric acid solution at 0.5:1 M ratio with respect to the total concentration of metal cations in solution. These mixtures were kept under reflux at 120 °C for 12 h, obtaining viscous liquids which were heated at 150 °C under air flux in an oven until complete solvent evaporation. The solid foams were treated in an alumina crucible at 300 °C for 30 min under air flow, using a ramp of 10 °C min^{-1} to start the auto-combustion stage. The obtained solids were maintained in a furnace at 350 °C for 6 h under oxygen flow (60 mL min^{-1}), to eliminate carbonaceous residues and then grounded and sieved.

The stoichiometric composition of the redox mixture was calculated based on the total oxidizing and reducing valences [15]. The stoichiometric ratio of nitrate to citrate (N/C), assuming complete combustion is described in reaction 1. Finally, the samples were calcined in flowing air at 400 °C for 3 h to clean the surface from carbon residues.

$$(NO_3)^- + C_6H_{18}O_7 \rightarrow 6CO_2 + N_2 + 9H_2O + \text{oxides} \quad (1)$$

2.2. *Characterization of catalysts*

The chemical composition was obtained using an X-ray fluorescence (XRF) apparatus, Rigaku Model RIX 3100. Samples were isostatically pressed in pellets and analyzed quantitatively to verify the purity of obtained samples. The specific area BET was evaluated by nitrogen adsorption isotherms at −196 °C, using the ASAP-2020 apparatus (Micromeritics). All samples were degassed at 300 °C overnight to remove humidity.

The crystalline structure was determined by X-ray diffraction, in a Miniflex Rigaku diffractometer, using Cu K_α radiation (λ = 1.54186 Å) between 10° and 90° with steps of 0.05° and a speed analysis of 0.15° min^{-1}. The refinement, indexing and the simulation of the structures were done with Cellref3.0® and Rietveld software that allowed us to establish the chemical composition and crystallographic structure of the oxides. The crystallite size estimation was done using the highest diffraction signals, using the Debye–Scherrer equation, taking the value of half peak width set by a Lorentzian function and using a constant of 0.89 as reference.

Temperature programmed reduction ($TPR-H_2$), was performed in a Micromeritics Pulse Chemisorb model 2705 equipment. The sample was heated at 200 °C for 2 h, flowing pure helium and then reduced with a mixture of 5% H_2/He (30 mL min^{-1}), rising the temperature up to 700 °C at 10 °C min^{-1} and the consumption of H_2 was measured in a thermal conductivity detector.

Analysis by scanning electron microscopy (SEM) was carried out in a LEO 440 microscope (Leica-Zeiss), equipped with an electron gun. The images were obtained with a focus distance of 10–25 mm, an accelerating voltage of 20 kV and a current of 100–200 pA, measurement time of 100 s and