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Synthesis and characterisation of $La_{1-x}Ca_xFeO_3$ perovskite-type oxide catalysts for total oxidation of volatile organic compounds

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Abstract

$La_{1-x}Ca_xFeO_3$ perovskite-type oxides with $x = 0$, 0.2 and 0.4 were prepared by the citrate method and characterised by means of X-ray diffraction (XRD), X-ray fluorescence (XRF), surface area measurement BET, X-ray photoelectron spectroscopy (XPS), Fourier transformed infrared spectroscopy (FT-IR), laser Raman spectroscopy (LRS), oxygen temperature-programmed desorption (O_2-TPD) and temperature-programmed reduction (TPR). The citrate method shows to be simple and appropriate to obtain single phases avoiding segregation and/or contamination. Moreover, controlling the calcination temperature, specific surface areas adequate for catalysts to be used in oxidation reactions are achieved. The structure refinement by using the Rietveld method indicates that the partial calcium substitution modifies the orthorhombic structure of the $LaFeO_3$ perovskite towards a less distorted one. From XRF and XPS, a slight surface enrichment in lanthanum and calcium was detected. XRD, FT-IR and TPR results indicated that the electronic debalance caused by the partial substitution for La^{3+} by Ca^{2+} is compensated by an oxidation state increase of a part of Fe^{3+} to Fe^{4+}. O_2-TPD results revealed that at a substitution level higher than $x = 0.2$, oxygen vacancies are also formed to preserve the electroneutrality. Finally, an improvement of the catalytic activity in propane and ethanol combustion was observed on the substituted perovskites. Correlating this with the characterisation results, the active sites would be associated to the Fe^{4+} ions.

Keywords: Lanthanum iron perovskite; Calcium; XRD; XRF; XPS; FT-IR; Raman spectroscopy; O_2-TPD; TPR; Rietveld refinement; Propane combustion; Ethanol combustion

1. Introduction

An increasing interest has been shown in catalytic combustion processes during the last decades since they are a convenient way for emission prevention (the control of nitrogen oxides NO_x and unburned hydrocarbons in heat and power generation plants) as well as clean-up (volatile organic compounds removal, automobile exhaust converters) [1].

Perovskite-type oxides display prominent catalytic activities in many fields such as the total oxidation of methane and of volatile organic compounds [2]. This activity, coupled with a high thermal stability, postulates to pervoskite-type oxides as potential catalysts in substitution of very active noble metals such as Pt and Pd, which are more expensive and do not resist operating at high temperatures [1–3]. Perovskite oxides have general formula ABO_3, where the 12-coordinated A sites may be occupied by rare-earth, alkaline-earth, alkali or other large ions and the 6-coordinated B sites are usually filled with transition metal cations. A large number of metallic cations can occupy the A and the B sites. Furthermore, the great stability of the perovskite framework allows partial substitution at the A sites and/or the B sites modifying the catalytic, redox and structural properties. The substitution at A site with ions having lower valence can allow the formation of structural defects such as anionic or cationic vacancies and/or a change in the oxidation state of the transition metal cation to maintain the electroneutrality of the compound. When the oxidation state of B cation increases, the relative ease of the redox process generates larger quantities of available oxygen at low temperature and the overall oxidation activity enhances. Moreover, the oxygen vacancies favour the catalytic activity in oxidation reaction because they increase the lattice oxygen mobility.

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Perovskites with lanthanum in A site and transition metals in B site ($LaBO_3$) with B = Mn, Co, Fe, Ni have received much attention. Partial substitution of divalent ions, in particular Sr^{2+}, for lanthanum has been studied producing interesting results. For example, $La_{1-x}Sr_xFeO_3$ perovskites with $x = 0.1$ and 0.2 are more active in propane oxidation than the corresponding unsubstituted $LaFeO_3$ [4]. The calcium substitution in A site has been studied from the structural viewpoint [5–7] but few results about the catalytic applications have been reported. Ciambelli et al. [8] investigated a $La_{1-x}Ca_xFeO_3$ series as catalysts for methane combustion and they observed that the catalytic performance of the substituted samples has not been better than that of unsubstituted sample. In contrast, we have studied the effect of calcium substitution in $La_{1-x}Ca_xCoO_3$ perovskites for propane oxidation and it has been beneficial [9].

On the basis of these results, in this work we reported a study carried out on $La_{1-x}Ca_xFeO_3$ perovskites ($x = 0, 0.2, 0.4$) which have been evaluated in total oxidation of propane and ethanol. The aspects related to the synthesis process have been carefully controlled. The structural and redox features are determined from the results of the textural and physicochemical characterisation. Furthermore, an explication of the catalytic behaviour is proposed.

2. Experimental

2.1. Catalyst preparation

$La_{1-x}Ca_xFeO_3$ perovskites with $x = 0$, 0.2, and 0.4 were prepared by the citrate method [10]. $La(NO_3)_3{\cdot}6H_2O$ (Fluka), $Ca(NO_3)_2{\cdot}4H_2O$ (Fluka), $Fe(NO_3)_3{\cdot}9H_2O$ (Aldrich) and citric acid (Mallinckrodt) were used as reagents. The aqueous solutions of the metal nitrates were added to an aqueous solution of citric acid with a 10% excess over the number of ionic equivalents of cations. The resulting solution was agitated for 15 min and concentrated slowly by evaporating water under vacuum in a rotavapor at 75 °C until the formation of a gel. This gel was dried in an oven, increasing slowly the temperature up to 250 °C and keeping it overnight, to yield a solid amorphous citrate precursor. The obtained precursor was milled and then decomposed in air at 400 °C for 30 min and calcined in air at 700 °C for 2 h. The perovskite catalysts are expressed by $La_{1-x}Ca_xFeO_3$ where $x = 0$, 0.2, and 0.4, although the actual composition may be non-stoichiometric in relationship to the oxygen and may not be of single phase.

2.2. Catalyst characterisation

2.2.1. Specific surface area

The specific surface area (SSA) of the catalysts was calculated by the BET method from the nitrogen adsorption isotherms obtained at 77 K on samples outgassed at 250 °C using a Micromeritics Accusorb 2100E apparatus.

2.2.2. X-ray diffractometry (XRD)

XRD patterns were recorded at room temperature by using a Rigaku diffractometer operated at 30 kV and 20 mA, employing Ni-filtered Cu Kα radiation ($\lambda = 0.15418$ nm). The data were collected at 0.02° with a counting time of 5 s per step, in the (2θ) range from 20° to 90°. The crystalline phases were identified by reference to the PDF data employing standard spectra software. The lattice parameters and the structure of the catalysts have been estimated from Rietveld's powder structure refinement analysis [11].

2.2.3. X-ray fluorescence (XRF)

The composition of every sample was determined by X-ray fluorescence on a PW1400 Philips instrument. The calibration was made by using calibration samples prepared with known amounts of La_2O_3, Fe_2O_3 and $CaCO_3$.

2.2.4. X-ray photoelectron spectroscopy (XPS)

XPS analyses were performed on a SSX 100/206 photoelectron spectrometer from Surface Science Instruments with a monochromatized microfocused Al X-ray source. Spectra were registered after purging the samples at ambient temperature in vacuum. The residual pressure in the analysis chamber during the analysis was about 10^{-6} Pa. The flood gun energy was adjusted at 10 eV. The data treatment was performed with appropriate software. Binding energies were calibrated with regard to the C(C, H) component of the C 1s peak fixed at 284.8 eV. The atomic ratios were calculated by using the atomic sensitivity factors provided by the manufacturer.

2.2.5. Raman spectroscopy

The Raman spectra were collected by using two different spectrometers: (a) JASCO TRS600SZP multichannel monochromatic spectrometer, and (b) Dilor LabRam Instruments. In both cases, the samples were pressed into self-supporting wafers and the spectra were recorded at ambient temperature. The excitation source was: (a) an Ar ion laser (514.5 nm) operated at a power of 50 mW, and (b) a He–Ne laser (632.8 nm) operated at a power of 10 mW.

2.2.6. FT-IR spectroscopy

FT-IR spectra were registered by using a Nicolet Protegé 460 spectrometer in KBr pellets. The spectra were the result of averaging out 32 scans obtained at ambient temperature in wavelength ranging from 4000 to 225 cm^{-1}.

2.2.7. Oxygen temperature-programmed desorption (O_2-TPD)

O_2-TPD experiments were performed in a quartz reactor using a TCD as detector. In each analysis, 500 mg samples were pre-treated with helium gas increasing the temperature from ambient temperature up to 700 °C at 10 °C min^{-1}. The samples were oxidised with a 20% O_2/He mixture at a total flow rate of 30 ml min^{-1} at 700 °C for 30 min. Then, they were cooled down to ambient temperature in the oxidising mixture and flushed by a stream of purified He for 30 min. The desorption was carried out in the same conditions as the pre-treatment, maintaining the temperature at 700 °C until the baseline of the chromatograph was stabilised.