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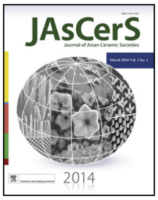

Full Length Article

Double perovskites La_2MMnO_6 as catalyst for propane combustion

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ABSTRACT

The synthesis, structural, spectroscopic and morphological characterization; as well as the evaluation of the catalytic properties, of a family of oxides La_2MMnO_6, with M = Co, Ni and Cu are presented in this work. The materials were obtained by solid state reaction and through citrate route. The structure was determined by X-ray diffraction and a correlation was found between the crystal cell parameters and the M(II) cation sizes, as a consequence of MO_6 and MnO_6 octahedral ordering. According to infrared spectroscopic characterization of the materials prepared by citrate route, a diminution of the M^{4+}-O bond strength was observed, according with M(II) sizes, in the sequence: Cu > Ni > Co. More labile O species should be present in La_2CoMnO_6-CIT. The electron microscopy morphology of this oxide confirmed the presence of agglomerated tiny particles. The presence of nanometic crystallites was confirmed by transmission electron microscopy. The catalytic tests, using propane as reaction test, were carried out in a fixed bed micro reactor, coupled with an "on line" chromatograph. The materials obtained by citrate route, despite M(II) cations, are better suited for propane combustion and the catalyst La_2CoMnO_6 is the most active of the investigated series with $T_{90} \sim 500\,^{\circ}C$.

1. Introduction

The need to control the pollution coming from hydrocarbon (HC) combustion used as fuels in industrial processes requires the reduction of gases and particulate emissions. A significant decrease in CO, NOx, and unburnt HC has been achieved through catalytic combustion [1–3].

Catalytic combustion is more convenient in comparison with conventional flame combustion due to its higher energy conversion efficiency and ultra low emissions of pollutants [4]. In presence of a catalyst the temperature at which combustion occurs is lower and the adverse conditions of the homogenous process can be controlled [5]. In addition, catalytic combustion is considered as one of the most effective treatments for the elimination of phenyl compounds from the air as they are an important type of volatile organic compounds (VOC's) air pollutants [6].

Until now a variety of catalytic materials has been reported as suitable. These include supported noble metals and metal oxides [7–9]. Supported noble metal oxides, particularly Pd oxides, are excellent catalysts for low temperature combustion but noble metals are expensive and have tendency to deactivation due to sintering, decomposition or undesirable interaction with supports [5]. Therefore transition metal oxides and mixed oxides have now been established as an inexpensive alternative to precious metal and noble metals containing materials [9].

Diverse transition metals mixed oxides of specific structures, such as spinels, perovskites, pyrochlores, and also hexaaluminate have been reported as suitable catalysts for HC combustion due to oxygen ion conductivity. Moreover, metal oxides and oxometallates are less expensive, more thermally stable and resistant to poisoning than noble metals [5].

Some MFe_2O_4 ferrites, belonging to the inverse spinel structural type, have been extensively investigated as combustion catalysts [10–15]. In a previous work MFe_2O_4 (M = Co, Ni and Cu) bulk catalysts, synthesized by solid state and citrate routes as nanosize particles scale, were investigated for propane combustion reaction [10,11]. The superior activity of $CoFe_2O_4$ ferrite was attributed to the largest amount of Fe active octahedral sites and low Fe—O bond strength giving rise to more labile O surface species necessary for the reaction. On the other hand, the catalytic performance of M(II) ferrites can be enhanced by supporting on porous ceramic supports, such as Al_2O_3, ZrO_2 and zeolites [12]. $NiFe_2O_4$ obtained at low temperature by co-precipitation procedure, exhibit a good catalytic activity for methane combustion [13]. In addition a new efficient

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high surface area nano crystalline Co_3O_4 spinel obtained by a non-conventional soft reactive grinding procedure is among the most active propane combustion catalyst [14]. Recently the conductivity and redox properties of substituted $CuFe_{2-x}Mn_xO_4$ spinels were correlated with the catalytic behaviour for the total oxidation of methane [15].

Mixed oxides belonging to perovskite structural type, with the general formula ABO_3, have been studied extensively for complete HC oxidation, decomposition of NO, and non-selective reduction of NO by CO, H_2 and HC [16]. Most of them contain a combination of rare earth or alkaline earth cations located in the A site and 3d transition metal ions at the B sites [17]. Moreover, the role of physico-chemical characteristics of substituted perovskites $La_{1-x}Sr_xM_{1-y}M'_yO_3$ (M and M′ are transition metals) catalysts for methane and propane combustion have been investigated [18].

The simple ABO_3 perovskite structure can be appropriately modified by incorporating two types of B ions with suitable differences in charge and size. A great number of combinations have been reported, but the most frequent substitution $A_2BB'O_6$ have been described so far [19]. This subclass of perovskites, also called double perovskites, display novel interesting physico-chemical behaviour which give rise to interesting and valuable technological applications. The possible combination of cations gives rise to a wide range of compositions and ordering which are very attractive from the catalytic point of view. Double perovskites are so versatile among mixed oxides materials suitable for catalysts design due to its greater compositional range and ordering which may promote catalytic chemistry [20].

Since the Kobayashi report about the colossal magneto-resistance of Sr_2FeMoO_6 at room temperature, double perovskites have attracted great attention. A large number of research regarding electric, magnetic and transport properties of these materials dominates the literature at present [21]. The compounds seem to be key materials due to properties such as spin-polarized electron transport, high dielectric constant, low thermal conductivity, and multiferroicity [21,22,23].

The first report regarding the well known Sr_2FeMoO_6 as catalyst was for methane oxidation. This half metallic ferromagnet, prepared from citrate route, showed that at 800 K a 80% conversion was achieved [24]. And this was attributed to the presence of oxygen vacancies. In addition these perfectly ordered B—O—B′ perovskites are interesting from the catalytic point of view because of the possible electronic transfer through these linkages.

The catalytic activities of Mo- and W-containing double perovskites synthesized by nitrate route have been investigated for the reduction of NO by C_3H_8 in the presence of excess oxygen. In this paper, the crucial role of the cations on B sites was demonstrated [24].

The experimental results regarding the comparison of La_2CuNiO_6 and the mixture of $LaCuO_3$ with $LaNiO_3$ showed that double perovskites catalytic activities are much higher and this behavior could be correlated with the reducibility and the presence of surface adsorbed O species [25]. More recently an in-situ electrical conductivity study of LaCoFe-perovskites based catalysts in correlation with oxidation of methane has been published [26]. According to these results the reaction mechanism involves surface lattice O species.

Despite the promising results mentioned and the huge number of double perovskites formulations, there have been scarce reports about the application of RE containing materials as combustion catalysts. The application of La_2CuNiO_6 for methane combustion has been reported, in comparison with the related single perovskites [17]. The correlation between the physico-chemical and textural properties of this oxide with the catalytic behavior was shown. In addition, based on XPS and TPR measurements, it was demonstrated that $A_2BB'O_6$ display more active oxidic species than ABO_3 necessary for combustion.

Based on the results available in the literature, it seemed interesting to explore new catalytic materials belonging to double perovskites $La_2M^{II}MnO_6$, containing a combination of Mn with other first row transition metal such as M^{II} = Co, Ni and Cu, prepared by solid state reaction and citrate route. The aim of this paper is to correlate the observed catalytic performance with the physico-chemical properties measured, and in this way to connect the crystal chemistry of these materials with the catalytic activity.

2. Experimental part

2.1. Catalyst preparation

The samples La_2MMnO_6, with M = Co, Ni and Cu were prepared by different solid state and wet-chemical synthesis methods, i.e. Solid phase synthesis (SP) and Citric acid-aided process (CIT). The detailed synthetic procedures are described below.

2.1.1. Solid phase synthesis (SP)

The polycrystalline samples of the nominal composition La_2MMnO_6 (M = Co, Ni and Cu) were prepared by conventional solid state reaction, by firing intimate stoichiometric mixtures of the oxides La_2O_3 and MnO_2, and the M(II) oxides or carbonates involved in the formulations, $Co(NO_3)$, $NiCO_3 \cdot 2Ni(OH)_2 \cdot 4H_2O$ and CuO, respectively. The reactions were carried out in air, in platinum crucibles, at 1000 °C. The sample was maintained at this temperature, in the furnace, during 10 h. Heating was interrupted several times to grind the reaction mixture to facilitate the reaction progress. The samples were labelled as LaMMn-SP, where M indicates: Co, Ni or Cu.

2.1.2. Citric acid-aided process (CIT)

This chemical synthesis by citrate precursor involves the formation of the metal complexes with the transition metals in each formulation. Accordingly, in the first step, the aqueous solutions of the individual nitrates, $La(NO_3)_3 \cdot 6H_2O$, $Mn(NO_3)_2 \cdot 4H_2O$ and the M(II) nitrates of each cation, in concentration 0.1 M, in stoichiometric ratio, were prepared and then mixed with aqueous citric acid into 50 ml of a homogenous solution. One equivalent mole of citric acid was applied to each total equivalent mole of the metals, in order to obtain the chelate complex. In the second step, the aqueous solution was then concentrated by heating with vigorous stirring until viscous brown slurry was obtained at 70 °C. This slurry was dehydrated at about 80 °C in a sand bath for 2 h and the product was finally dried under vacuum in an oven at 95 °C. During this thermal treatment the volume of the gel increased markedly showing big pores and a puffy appearance. After grinding in a mortar, the dried gel was converted into a fine powder which was subjected to the following thermal schedule: 2 h at 150 °C, in order to decompose the nitrates and remnant citrate, 4 h at 400 °C and 4 h at 800 °C, with intermediate millings. Samples were taken from the furnace after the thermal treatment at each one of the mentioned temperatures, in order to study the pyrolitic decomposition of the precursor. These samples were labelled LaMMn-CIT, where M indicates the metal (M = Co, Ni, Cu).

2.2. Catalysts characterization

All the samples were characterized using different physico-chemical methods. The materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and electron microscopy (SEM, TEM).

A Philips PW 3710 diffractometer, with copper anode and graphite monochromated Cu Kα radiation was used for XRD mea-

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