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Physicochemical origins of electrochemical promotion of LSM/YSZ

V. Roche [a,b], A. Hadjar [a], J.P. Deloume [a], T. Pagnier [b], R. Revel [c], C. Roux [b], E. Siebert [b], P. Vernoux [a,*]

[a] *Université Lyon 1, CNRS, UMR 5256, IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon, 2 Avenue Albert Einstein, F-69626 Villeurbanne Cedex, France*

[b] *Laboratoire d'Electrochimie et de Physico-chimie des Matériaux et des Interfaces de Grenoble (LEPMI), UMR 5631 CNRS-INPG-UJF, ENSEEG, BP 75, 38402 St Martin d'Hères, France*

[c] *IFP-Lyon, Rond-Point de l'échangeur de Solaize, BP3, 69360 Solaize, France*

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ABSTRACT

A complex route provided powders of $La_{1-x}Sr_xMnO_3$ ($x = 0$, 0.15, 0.3 and 0.4) from the thermal decomposition of the chelated nitrate precursors. The catalysts were characterized by XRD, BET, SEM, and temperature-programmed techniques. Electrochemical catalysts based on $La_{0.7}Sr_{0.3}MnO_3$ (LSM) were deposited on yttria-stabilized zirconia (YSZ) pellets. Electrochemical characterizations of these samples evidenced two redox processes assigned to the existence of different environments around Mn^{4+} in LSM in good agreement with the peaks observed by temperature programmed reduction (TPR). In situ O_2 temperature programmed desorption (O_2-TPD) and temperature programmed oxidation (TPO) of propane were performed on LSM/YSZ to investigate the influence of the polarization on oxygen and propane chemisorption on LSM/YSZ. O_2-TPD experiments have shown that the electrical polarization during adsorption process has no significant impact on gaseous oxygen adsorption on LSM thin film. TPO experiments suggest an increase in the adsorption strength of propane on LSM that could be at the origin of the electrochemical promotion effects observed upon polarization conditions.

1. Introduction

Propane is a fuel of great interest as a major component of liquid petroleum gas (LPG). Its catalytic oxidation appears to be one of the crucial points for the clean production of energy [1]. Noble metal catalysts exhibit the best activity to perform this reaction. However, they present deactivation and high volatility at high operating temperatures in addition to an excessive cost [1]. To overcome these drawbacks, perovskite-type oxides with the general formula ABO_3 are proposed as alternative catalysts especially lanthanum manganites. The stability of the perovskite structure allows partial substitution on both the lanthanum (A) and manganese (B) sites. These substitutions generally enhance the activity of the catalyst [1]. Arai et al. [2] reported that $La_{0.6}Sr_{0.4}MnO_3$ materials exhibited higher activity for the methane combustion than unsubstituted $LaMnO_3$ and so did Batis et al. [4] for $La_{0.4}Ca_{0.6}MnO_3$. Many recent studies [3–6] are available to explain the modification of catalytic behaviour induced by partial substitution in the perovskite structure. For instance in case of $LaFeO_3$ catalysts Ciambelli et al. [3,6] observed a combined effect induced by the insertion of calcium on the lanthanum site attributed to the creation of oxygen vacancies and the partial oxidation of Fe^{3+} to Fe^{4+} resulting in an increase in the bulk oxygen mobility. Indeed, two mechanisms involving two kinds of oxygen species are proposed for methane oxidation on perovskite catalysts in the literature. They are named intrafacial and suprafacial respectively [7], depending on the operating temperature. The suprafacial mechanism prevails at low temperature (300 °C) and involves the reaction of surface oxygen adsorbed on the catalyst. The intrafacial mechanism occurs at high temperature (600 °C) when the concentration of adsorbed species becomes low. Bulk oxygen species coming from the perovskite lattice are then believed to be more active and could react with the hydrocarbons. Several parameters can influence the catalytic activity for the deep oxidation of alkanes on perovskites such as specific surface area and amount of oxygen vacancies. The active site is very often thought to be related to the B site. Buciuman et al. [8] reported that the reaction site is most probably associated with manganese cations Mn^{3+} in case of $LaMnO_3$-based catalysts.

In this paper, we present results on the preparation and characterizations of lanthanum manganites and some substituted parents synthesised in nanosized powders. Different compositions of lanthanum manganite nanosized powders were synthesized. The physicochemical properties of the catalysts were characterized by temperature-programmed techniques. The effect of partial substitution on the physicochemical properties of the catalysts characterized by thermal-programmed techniques is discussed. Then, the most suitable composition is selected to be deposited as

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[*] Corresponding author. Tel.: +33 4 72431587; fax: +33 4 72431695.
E-mail address: philippe.vernoux@ircelyon.univ-lyon1.fr (P. Vernoux).

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thin films on an ionic conductor. As already observed [9] the catalytic activity of doped lanthanum manganites thin films interfaced with an O^{2-} conducting solid electrolyte could be slightly enhanced by using the concept of electrochemical promotion of catalysis (EPOC) also called non-Faradaic electrochemical modification of catalytic activity (NEMCA) effect [10]. This concept, discovered and developed by Vayenas et al. [10], involves the use of an electrochemical catalyst composed of an electronic conductor catalyst and an inert counter electrode both deposited as thin films on each side of a solid electrolyte support. The application of small potentials or currents through the catalyst/electrolyte interface can affect the activity of the catalyst, in a reversible manner. This phenomenon is related to the migration of ions (called promoters) supplied by the current at the surface of the catalyst. The applied polarization is expected to result in a pronounced rate enhancement, superior to the electrochemical rate of supplied ions or ionic current. Indeed, a single ion could activate the reaction of more than one gaseous adsorbed species. The supply or the removal of the promoting ions modifies the binding energy of the reactants on the catalyst. In our previous work [9], the behaviours of strontium substituted lanthanum manganite deposited on Yttria-stabilized zirconia (YSZ) were investigated for the deep oxidation of propane upon anodic polarizations at different temperatures and for various applied potentials. Low electrochemical promotion effects were obtained at temperatures inferiors to 400 °C. The promotional impacts on propane conversion were weak. The magnitude of the effects observed was found to decrease when the temperature and the applied potential increased as it enhanced the oxygen electrochemical reaction kinetic and therefore decreased the lifetime of the promoters on the catalyst. The goal of the present study was to investigate the origins of EPOC on lanthanum manganites deposited on an oxygen ionic conductor via temperature programmed oxidation or reaction as well as solid state electrochemistry characterizations and to link the observed electrochemical promotional effects to the reaction mechanism of propane oxidation on lanthanum manganites.

2. Experimental

2.1. Preparation of lanthanum manganite catalyst powder

Powders of lanthanum manganite, $La_{1-x}Sr_xMnO_3$ ($x = 0$, 0.15 and 0.30), were prepared by a complex route [11] from the thermal decomposition of the chelated nitrate precursors. The following reagents were used $La(NO_3)_3$, $6H_2O$ (p.a. Alfa Aesar), $Sr(NO_3)_2$ (p.a. Acros organics), $Mn(NO_3)_2$, $6H_2O$ (p.a. Alfa Aesar) and maleic acid ($C_4H_4O_4$, p.a. Alfa Aesar). Contents in lanthanum and manganese in the hydrated salts were accurately determined by conventional methods. The nitrate precursors were dissolved in a 10% aqueous solution of maleic acid. Lanthanum nitrate was firstly introduced in the solution, then strontium nitrate was added and finally manganese nitrate. The molar ratio of La/Sr/Mn/maleic acid was the following $1 - x/x/1/8.6$. After the dissolution of the salts, the pH of the mixture was raised at 8 by adding NH_3 solution. Most of the water was then evaporated on a heating plate. The mixture was put overnight in an oven at 130 °C and produced a powder precursor. This last was heated at 500 °C for 2 h to remove the organic compounds and finally calcined at 800 °C for 4 h.

2.2. Powdered catalysts characterizations

XRD measurements were carried out with a Siemens D5005 diffractometer, using the Cu Kα radiation at $\lambda = 0.15418$ nm. The BET specific surface areas of the catalysts were determined from nitrogen adsorption at 77 K by means of a Micromeritics TriStar 3000. Samples were outgassed at 300 °C for 3 h under primary vacuum (using a Micromeritics VacPrep. 061) before pressure measurements.

Temperature programmed desorption of oxygen (O_2-TPD) experiments were performed in a quartz fixed bed reactor with 0.2 g of powder. Each sample was pretreated in oxygen atmosphere at 500 °C for 1 h to adsorb gaseous oxygen on the surface of the catalyst and to remove carbonaceous species from the surface. In the next step, the sample was cooled down to room temperature still under pure oxygen flow. Then, the thermal desorption was carried out by heating the sample at 15 °C min^{-1} from room temperature to 600 °C in pure helium with a flow rate of 1.8 L h^{-1}. Desorption of oxygen was recorded by following the mass 32 with an Infincon transpector-cis mass spectrometer. The surface area of the oxygen desorption peak was calculated with Origin software (OriginLab Corporation) by considering Gaussian peaks.

Temperature programmed reduction (TPR) analyses with hydrogen were carried out on samples (0.1 g) in the reactor used for the O_2-TPD experiments. The catalyst was also pretreated in pure oxygen before running the analysis in the same way as for TPD. Then, TPR was performed with a flow of 1.8 L h^{-1} of 1 vol.% H_2 in He increasing the temperature from room temperature to 650 °C at a heating rate of 10 °C min^{-1}. The reduction profiles were obtained following mass $m/e = 2$ corresponding to H_2 with the mass spectrometer used for the O_2-TPD experiments.

2.3. Preparation of the electrochemical cells

Two types of samples (Fig. 1) were used for the experiments as already described elsewhere [9]. Temperature programmed analyses were performed for propane deep oxidation on an electrochemical catalyst called sample 1 composed of a thin layer of $La_{0.7}Sr_{0.3}MnO_3$ (LSM) (working electrode, W) deposited on one side of a dense YSZ pellet. A gold counter electrode was deposited on the opposite side of the pellet to act as the counter electrode (CE). YSZ pellets were 17 mm in diameter and 1 mm thick. For the electrochemical characterizations, a symmetric sample of LSM/YSZ/LSM was prepared (sample 2). The symmetrical cell was composed of a thick YSZ pellet (diameter = 16 mm and thickness = 1.5 mm) for the electrolyte, with LSM electrodes deposited symmetrically on both sides of the YSZ pellet. Two grids made of gold were used as current collectors. The reference electrode consisted of a silver wire which was fixed on the edge of the YSZ pellet.

The thin film preparation method was developed to obtain reproducible and adherent film of LSM as already reported elsewhere [9].

2.3.1. Characterization of sample 1

The two electrodes W (working electrode LSM), CE (Au counter electrode) were connected to a potensiostat–galvanostat Voltalab PGP 201 (Radiometer Analytical). Catalytic activity measurements under polarization were performed in the potentiostatic mode. The

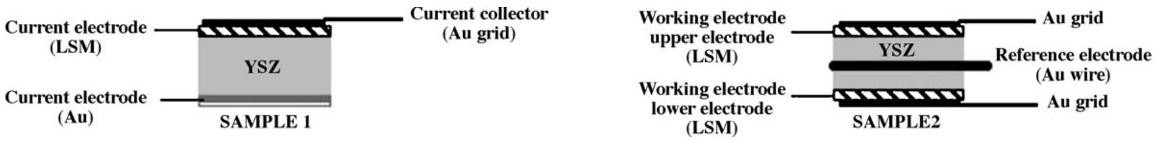

Fig. 1. Schematic drawings of the samples.