Electrical and CO gas sensing properties of nanostructured La$_{1-x}$Ce$_x$CoO$_3$ perovskite prepared by activated reactive synthesis

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ABSTRACT

A series of nanostructred La$_{1-x}$Ce$_x$CoO$_3$ perovskite-type (*x* ranging from 0 to 0.2), with a crystallite size of around 10 nm and a specific surface area of up to 55 m^2/g were prepared using the activated reactive grinding method. XRD results showed that Ce segregates as CeO$_2$ when the addition level exceeds 10 at%. CO was chosen as a typical reducing gas and its interaction with surface oxygen was investigated. TPD-O$_2$ was used to investigate the effect of Ce-doping on total surface oxygen. The experimental results confirmed a positive effect of Ce-doping of up to 10 at% on total surface oxygen (α-O$_2$). TPD-CO and XPS analyses were performed to find the total carbon adsorption (i.e. related to the adsorption of CO) on the surface of the synthesized samples. Both methods confirmed that more carbon adsorbs on the surface of doped formulations compared to the pure LaCoO$_3$. Ce-doping increases the surface oxygen, thereby facilitating the adsorption and oxidation processes. CO gas sensing properties of thick La$_{1-x}$Ce$_x$CoO$_3$ films were performed. La$_{0.9}$Ce$_{0.1}$CoO$_3$ showed the highest conductivity and the lowest activation energy. The optimum CO sensing temperature for doped formulation was found to be 100 °C compared to 130 °C for pure perovskite. Ce-doped samples showed a maximum response ratio of 240% with respect to 100 ppm CO in air compared to 60% obtained with pure LaCoO$_3$.

1. Introduction

Recently, a number of mixed-metal oxides with a perovskite-type structure and the overall formulation of ABO$_3$ have received considerable attentions as catalyst and gas sensor materials because of their thermal and chemical stability [1–4]. The activity of perovskites is practically determined by the nature of their cations, which play an important role in adsorption of gas species and their catalytic activities. The electronic properties and catalytic activity of the perovskite-type oxides can be modified by substitution of ions into the A or B sites [5].

Most of the published reports on gas sensing properties of perovskites have been reviewed by Fergus [6]. As a CO gas sensor, a variety of undoped perovskites including titanates [7], ferrites [8], cobaltates [9] and doped formulations [9–11] have been reported. Partial substation of A or B site cations in some cases resulted in a positive effect on the gas sensing performance. For example, in LaFeO$_3$ system substitution of Pb on the La site [12] and/or of Co on the Fe site [13] increased the sensing performance while

substitution of Sr on the La site [14] or of Mg on the Fe site [14] did not result in a significant improvement in gas sensing properties. On the other hand, the response of LaCoO$_3$ to CO was improved by doping Sr on the La site and Cu or Ni on the Co site [15].

Cerium doping (up to 10 at%) on the A site in cobalt or manganese-based perovskites usually leads to an increase in oxidation catalytic activity [16–21]. Oxidation of CO on perovskite-type materials is a superficial reaction where the gas species react with the surface oxygen. The availability of more oxygen on the surface may result in higher catalytic activity. The consequences of partial substitution of Ce(IV) on the La(III) site are the reduction of a fraction of Co(III) to Co(II) and/or a change in oxygen stoichiometry to ensure the charge compensation. Oxygen can be adsorbed and reduced on the Co(II) sites to produce Co(III)/O$'_2$ species [34] An increase in the Ce doping on the structure is expected to increase the number of surface oxygen, thus facilitating the oxidation reaction. However, the solubility limitation of Ce doping on the La$_{1-x}$Ce$_x$CoO$_3$ structure results in a saturation point in the structure. More Ce doping after the saturation point may increase the level of impurities and decrease the overall activity.

In addition to the chemical composition, the structural features of perovskite materials have a significant influence on their

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response with respect to gas species. Nanostructured metal oxides with a higher surface area and a smaller crystallite size offer the potential for a substantial increase in the performance of gas sensors as compared to that offered by conventional microcrystalline materials [22]. In the synthesis of nanocrystaline perovskite oxides, a number of techniques have been used to reduce particle size to the extent possible [23–25]. However, in order to form a perovskite structure and to remove the organic precursors, high calcination temperatures (typically above 600 °C) are usually required. A high calcination temperature enhances solid-state diffusion, reducing the specific surface area and increasing the mean crystallite size which grows with calcinations temperature and time. Some researchers have reduced the calcination temperature to reach higher SSA and lower particle size by using complex or expensive methods. For example, spray-freezing/freeze-drying [26] and Schiff base complex sol–gel [27] have been used to prepare $LaCoO_3$ with an average crystallite size of 20 nm and SSAs of 24 and 11.7–18.6 m^2/g, respectively, with the calcinations temperature kept as low as 500 °C. Both traditional and new methods of synthesis of nanostructured perovskites have considerable manufacturing issues basically due to low production rates, high costs, and expensive waste treatment.

Activated reactive synthesis is an alternative method to synthesize nanocrystalline metal oxide at quasi room temperature [28,29]. This method is essentially a combination of high energy and low energy ball milling steps. The former reduces the particle size while the latter enhances deagglomeration and increases the specific surface area. A wide variety of perovskites including simple perovskites and the doped ones with a crystallite size down to 10 nm and a SSA up to 100 m^2/g have been synthesized by this technique [29,30]. Royer et al. [31] showed the effect of high energy ball milling (HEBM) on bulk and grain boundary of perovskite oxides and their relation with oxidation reaction. HEBM creates nanostructured materials with a high density of grain boundaries, which can accelerate the diffusion of oxygen. Perovskites with a higher theoretical specific surface area have shown a higher grain boundary volume and subsequently a higher oxygen mobility and catalytic activity [31]. In our previous work [32], we used the activated reactive grinding method to synthesize nanostructured $LaCoO_3$ perovskite, which resulted in a surface area of 70 m^2/g and a small crystallite size (10 nm) accompanied by an improved CO sensing performance. $LaCoO_3$ synthesized using this method showed a better CO gas sensing behavior (lower temperature and higher sensitivity) as compared to the samples prepared using other methods such as the sol–gel and the solid-state reaction. The improved sensing performance was attributed to the higher oxygen mobility of the sensor.

In the study reported here, the effect of cerium doping on gas sensing behavior of $La_{1-x}Ce_xCoO_3$ prepared by activated reactive grinding method was investigated. The aim was to exploit the effects of both structural features and chemical composition in order to increase the oxygen mobility and consequently the gas sensing performance of LaCo-based perovskites. Five formulations with nominal compositions of $La_{1-x}Ce_xCoO_3$ ($x = 0$–0.2) were prepared. The principal objective of the study was therefore to provide new information on the mechanism through which the sensing properties of LaCo-based perovskite are influenced with respect to a typical reducing gas. CO was chosen as a typical reducing gas and its interaction with sensing material was investigated. Physicochemical characteristics of the sensing material were used to interpret the influence of Ce-doping on the samples' sensing behavior with respect to CO. Although the selectivity aspect was not addressed in this study, the behavior of the material under other reducing gas species was expected to follow the same trend, except for the maximum response temperature and amplitude.

2. Experimental details

$La_{1-x}Ce_xCoO_3$ ($x = 0$, 0.05, 0.1, 0.15, 0.2) nanostructured perovskites, labelled as Cex (x = mol fraction of doping in La-site), were prepared by the activated reactive synthesis method. La_2O_3, CeO_2 and Co_3O_4 with a purity of 99.8% were dehydrated at 550 °C to remove any hydrate from the oxides. They were subsequently weighed at the required molar ratio for each formulation and mixed together. This was followed by a heat treatment at 1000 °C for 2 h. Five grams of pre-mixed materials were introduced into a tungsten carbide (WC) crucible containing WC balls, and milled for 2 h. In order to deagglomerate the synthesized material, a second milling step was performed with a lower milling energy for 1 h. In this step, a laboratory attritor containing 4.5-mm hardened steel balls was used. Both milling times were the optimized times as reported earlier [32].

Powder X-ray diffraction (XRD) patterns were recorded using a diffractometer (SIEMENS D5000) with Cu/Kα radiation ($\lambda = 0.154$ nm) and a 0.05° step scan from 15° to 80° in 2θ angles. The average crystallite size (D) was calculated by means of the Debye–Scherrer equation $D = K\lambda/(\beta \cos \theta)$ after doing the Warner's correction for instrumental broadening. Phase identification was performed using the JCPDS data bank.

BET specific surface area of the powders was determined by adsorption/desorption isotherms of N_2 at −196 °C using Chem-BET Pulsar TPR/TPD/BET (Quantachrome). Before each BET test, the powders were degassed at 200 °C for 6 h under helium. Temperature programmed desorption of oxygen (TPD-O_2) was performed using the same equipment. A hundred and fifty mg of powder was placed in a quartz cell and calcined at 200 °C for 6 h. The sample was then pre-treated at a flow of 5% O_2 in He (20 ml/min) at 300 °C for 2 h, followed by cooling down to room temperature at the same flow. The gas flow was switched to pure He with a flow rate of 100 ml/min and the TPD-O_2 was carried by increasing the temperature. The temperature was increased from 25 to 900 °C with a heating rate of 5 °C/min, and kept at 900 °C for 15 min to obtain the complete desorption process. Desorption of oxygen was monitored and quantified using a thermal conductivity detector (TCD).

To obtain a thick sensing film on alumina rod substrates, the wash coating method was used. Ten percent of the perovskite powder was dispersed in DI water using an ultrasonic bath. The pH of the slurry was adjusted at 3. This pH value, one that allowed for a smooth and even coating, was achieved through trial and error. Some drops of prepared slurry were instilled on the alumina rod substrate (25.4 mm in length and 4.7 mm in diameter). Coated samples were dried overnight at room temperature and annealed at 400 °C for 2 h with a heating and a cooling rate of 10 °C/min. Metallic electrodes were then connected to the coated samples for gas testing.

CO gas testing was performed in a homemade system consisting of a stainless chamber with a capacity of 800 ml in which three samples can be hung up via a high temperature feed-through. This chamber was placed in the adjustable and programmable furnace with a precision better than 1 °C. The temperature of the chamber was monitored with a K-type thermocouple, which was placed close to the samples surface. A gas mixing system with a precision of 0.2% of the full scale provided the required CO concentration and flow rate. The gas flow was entering the chamber at the bottom and was exiting it from the top. For this experiment, resistance variations were recorded as a function of time, temperature and gas compositions. All resistances, temperature, gas flow and concentration were recorded every second using an Agilent 34970A data acquisition unit. For each gas testing procedure, coated samples were heated up to 350 °C under dry air to remove any adsorbed gases and humidity from the sensing film. They were then cooled down to, and maintained at, the desired temperature to stabilize the