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Correlation of carbon monoxide sensing and catalytic activity of pure and cation doped lanthanum iron oxide nano-crystals

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ABSTRACT

For nano-crystalline cobalt (Co) and cobalt/lead (Pb) co-doped lanthanum ferrite ($LaFeO_3$) ceramics, we have investigated the carbon monoxide (CO) sensing characteristics. The catalytic activities toward CO oxidation were investigated for $LaFeO_3$ and $LaFe_{0.8}Co_{0.2}O_3$ powders. At an operating temperature as low as 175 °C, Co doped $LaFeO_3$ sensors exhibit excellent low concentration (<100 ppm) CO gas sensing characteristics. Also, $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LPFC) ceramics selectively senses CO at 150 °C. For $LaFe_{0.8}Co_{0.2}O_3$, 0.056 mmol of CO conversion per gram of catalyst was measured at 200 °C. On the other hand, for $LaFeO_3$ ceramics, CO conversions per gram of catalyst were recorded to be 0.004 mmol. The superior low temperature CO sensing characteristics of nano-crystalline $LaFe_{0.8}Co_{0.2}O_3$ ceramics correlates well with its excellent catalytic activity toward CO oxidation. For perovskite $LaFe_{0.8}Co_{0.2}O_3$ sensors it was demonstrated that lower metal-oxygen binding energy, favorable d-orbital electron configuration of Co cation, and nature of surface composition are the three dominant factors control its superior catalytic activity and the CO sensing characteristics.

1. Introduction

Hazardous carbon monoxide (CO) emission is common in a variety of combustion processes. Thus, apart from automobile and industrial exhaust, significant CO emission has also been reported from solid fuel (firewood, coal, cow-dung cake, crop residues etc.) combustion. Solid fuel combustion for cooking is commonly practiced in the rural parts of many of the developing countries like India. In majority of these rural households solid fuels are burnt either in earthen/metal stoves, or using open pits in poorly ventilated kitchens. This results in very high concentrations of CO and other indoor air pollutants in rural houses. Through this practice, it is estimated that more than 2.5 billion people are exposed worldwide to high concentration of CO, un-burnt hydrocarbons and particulate matters [1,2]. Apart from this, combustion type water heaters in poorly ventilated bathrooms also emit significant CO gas. It is well known that CO interacts with haemoglobin and reduces the cellular respiration of human being. Detection of CO and control of its emission has therefore been a subject of major environmental and health concerns. In view to this, it remains a subject of immense interest to improve the CO sensing and catalytic activities of ceramic materials. It is important to synthesize highly sensitive oxide materials that not only detect low concentration (<100 ppm) CO gas but also exhibit superior catalytic CO oxidation activities. However, using oxide sensing materials, it remains an open challenge to detect CO gas selectively at lower operating temperature (<200 °C). Additionally, to control indoor emissions from solid fuels, it would be very appealing if these sensing oxides can simultaneously be used as catalyst for efficient CO oxidation. Reports on such dual use of oxide materials (both as CO sensor and its catalytic conversion) are scanty. If successfully developed, such low cost oxide materials will be an effective alternative to noble metal based catalysts for air quality monitoring in automobile and aviation industries. The catalytic activities of many of the perovskite oxides are explained to be due to supra-facial and/or intra-facial mechanisms. Therefore, scientifically it will be very interesting to study the sensing and catalytic properties simultaneously for selected perovskite oxides.

Perovskite lanthanum manganates and cobaltates are reported to be excellent catalysts for CO oxidation [3,4]. In these perovskites 'A' site ions (e.g. La, Pb etc.) are generally catalytically inactive. The CO oxidation activity of these perovskite oxides are mostly governed by 'B' site transition metal ions (e.g. Mn, Fe, Co, Ni etc.) [5]. Also, the symmetry and coordination of A and B site elements are lost on these perovskite surfaces, and, as a result, the surface is saturated with adsorbed oxygen and hydroxyl ions [6]. These

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adsorbed species make the perovskite surface catalytically active and thus, the CO oxidation is favorable at relatively lower operating temperature. It is presumed, that for these perovskite oxides, the CO sensing characteristics are closely related to their CO oxidation activity. The CO sensing characteristics has been described by Langmuir–Hinshelwood mechanism. By accepting electrons from its conduction band, the ambient oxygen is chemi-absorbed on the sensor surface at elevated temperature. This leads to the increase of the surface resistance of 'n' type perovskites, whereas, for 'p' type perovskites the surface resistance is decreased. When these perovskites are exposed to reducing gas (say CO), the gas molecules react with adsorbed oxygen to form oxidized product (say CO_2). The oxidized product eventually desorbs from the sensor surface and the electrons are transferred back to the conduction band. This results in a sharp decrease of resistance for 'n' type perovskites, whereas, for 'p' type perovskites the surface resistance is increased on exposing the perovskite to reducing gas environment. Thus the sensor response is directly related to the catalytic activity of the sensor surface toward the oxidation of reducing gases.

In the sensor operating temperature in the range of 30–650 °C, temperature programmed desorption (TPD) studies were performed to identify various oxygen species on SnO_2 sensor surface [7]. From these TPD chromatograms, molecular type adsorbates (O_2, and O_2^-) (α-type) are identified at low operating temperature (30–200 °C) of the sensor surface. Dissociative type oxygen (O^-) (β-type) is detected above 500 °C, and surface (lattice) oxygen (O^{2-}) (γ-type) is detected above 600 °C [8]. It is known that the sensitivity of chemi-resistive type gas sensor is highest for γ-type oxygen adsorbate [9]. However, for γ-type oxygen adsorbate, higher sensor operating temperature is required. Unfortunately, with the increase in sensor operating temperature, more and more CO molecules are desorbed from the sensing surface. Since the available adsorbed CO molecules are decreased at higher operating temperature, the advantage of having more reactive oxygen species (γ-type) for efficient CO oxidation is grossly minimized. Therefore, it will be beneficial to have γ-type oxygen available at relatively lower operating temperature. In view to this, we feel that it will be fruitful to modify the perovskite sensing surface so that the presence of γ-type oxygen species is abundant at lower operating temperature.

The particle size of the sensing materials also significantly influences the gas sensing characteristics. Thus, during CO sensing, oxygen ions are chemi-absorbed on sensor particles (diameter, d_m) forming an electron depleted space charge layer (thickness, L). It has been reported that the response (%) of the sensor is grossly enhanced when $2L > d_m$ [8]. To exploit the particle size effect, the sensor operating temperature must be kept low to avoid particle growth. The particle growth at higher operating temperature induces drift in the measured resistance transients in air and test gas environments [10]. Therefore, if γ-type oxygen species could be made abundant at lower sensor operating temperature, it may results in improved response (%), sensitivity, and stability.

The aim of the present work is to modify the catalytic activity of nano-crystalline 'p'-type lanthanum ferrite sensing materials toward CO oxidation. The modification is done by selective B site (Co replacing part of Fe ions) doping. The rationale of dopant selection has been explained and it was demonstrated that the cobalt doped lanthanum ferrite exhibits selective CO sensing performance at a temperature as low as 175 °C. The catalytic activity of this sensing material has also been evaluated to study the correlation between sensing and catalytic properties. Our study highlights the potential of such low cost materials for making "Sense and Shoot" type CO detection cum control devices.

2. Experimental

Lanthanum and iron nitrates were used as raw materials to synthesize lanthanum ferrite precursor sol by a modified Pechini route. The details of the powder synthesis have been reported in our earlier publication [11]. The powder synthesis procedure is briefly described as follows. As a first step lanthanum and iron nitrate (in 1:1 mole ratios) were dissolved in warm (at 60 °C) distilled water through continuous stirring. Subsequently, aqueous solution of citric acid (C.A) (C.A: total cation (mole) ∼1.5) and ethylene glycol (E.G) (E.G: C.A (mole) ∼3) are added to the mixed precursor solution to form a polymer–metal cation network. Citric acid consists of three carboxyl groups and one hydroxyl group. It is a weak acid and easily decomposes in aqueous solution to its conjugate base, which acts as chelating agent to trap the cations of precursor materials. In this process cations are first bonded by citric acid followed by a temperature assisted hydrolysis reaction of citric acid with ethylene glycol to form an internal ester linkage. The complex precursor is stirred at 80 °C for 4 h and finally cooled down to room temperature to prepare lanthanum ferrite sol. In order to prepare lanthanum ferrite nano-particles, the sol is dried at 120 °C for 2 h to evaporate the liquid content and to produce a gelled mass. The gel is heated at 140 °C until the auto combustion is initiated. The combustion process includes the decomposition and auto-combustion of gel followed by the formation of dried $LaFeO_3$ (LFO) particles. The auto-combustion is considered as a thermally induced redox reaction in which the carboxylic group acts as reducing agent and nitrate ion (NO_3^-) plays the role of oxidant. Citric acid and ethylene glycol serve the role of organic fuel in this auto-combustion reaction. Since the process is completed within a very short period, the particle size of the synthesized powders remains in the nano-size regime. Following the identical processing route $La_{0.8}Pb_{0.2}FeO_3$ (LPFO), $LaFe_{0.8}Co_{0.2}O_3$ (LFCO) and $La_{0.8}Pb_{0.2}Fe_{0.8}Co_{0.2}O_3$ (LPFCO) nano-particles were also prepared using lead nitrate and cobalt nitrate as precursor salts.

The pore size distribution and the surface area of these perovskite powders (calcined at ∼700 °C), have been determined by analyzing Brunauer–Emmett–Teller (BET) N_2 adsorption–-desorption isotherm, using a gas sorption system (Autosorb-1, Quantachrome Instruments, USA). Prior to investigate the N_2 adsorption–desorption isotherm (at temperature ∼77 K) the samples are degassed at 300 °C for 4 h. The phase formation and microstructure of the synthesized powders are characterized by Rietveld refinement analyses of the respective X-ray diffraction (using CuK_α radiation) patterns and electron microscopy respectively. The core level spectra of atoms were studied by PHI 5000VERSA probe II, (ΦULVAC-PHI Inc., Japan) using an X-ray photoelectron spectrometer with a micro-focused (100 μm, 25 W, and 15 kV) monochromatic Al-$K_{\alpha 1,2}$ of 1486.6 eV), a hemispherical analyzer, and a multichannel detector.

To measure the gas sensing properties of the synthesized powders, few drops of 10% PVA solution is added as binder and pressed in the form of thin circular discs (12 mm diameter and ∼100 μm thick) using a hydraulic press. The discs are heated at 700 °C for 2 h in air, which ensures minimal particle growth, necking among particles, and sufficient handling strength. The gas sensing measurements are performed under dynamic condition in a reactor equipped with automated gas flow controllers and data acquisition system. The details of the set up and measurement protocol have been reported elsewhere [12]. From the measured value of equilibrium resistance in air (R_a) and gas (R_g), the response of the sensor toward CO and other reducing gases is calculated using the relation

$$\text{Response}\,(\%)\,(S) = \frac{R_g - R_a}{R_g} \times 100 \tag{1}$$