

Surface properties of Sr- and Co-doped LaFeO₃

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Abstract

The surface properties of Fe-based perovskite-type oxides with the formula La_{0.6}Sr_{0.4}Co_yFe_{1-y}O_{3-δ} for $y = 0.1, 0.2,$ and 0.3 were investigated. Using methanol as a probe molecule, the amounts of basic and Lewis surface sites were determined. The types of sites were confirmed using DRIFTS. The surface basicity, as well as the reducibility, oxygen storage capacity, transition metal surface concentration, and methanol oxidation activity, were found to progress through an extrema for the intermediate Co level; that is, the behavior and performance of the samples are nonlinear with respect to increasing Co content. An electronic structural transition is proposed as the explanation for the observed trends.

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1. Introduction

Perovskite-type (ABO₃) oxide catalysts have been widely researched due to their unique properties which have led to applications in a number of reactions [1–3]. These applications include various total and partial oxidation reactions (e.g., CO, NH₃, and organics), hydrogenation, dehydrogenation, hydrogenolysis, photocatalysis, and environmental applications (e.g., SO₂ reduction, de-NO_x). For methane oxidation, several formulations displayed performance similar to that of Pt on Al₂O₃ [2]. In addition to these purely catalytic reactions, perovskite-type materials have been used in several applications in which both their unique surface and bulk properties are exploited. Oxygen separation membranes are a prime example [4,5]. Because only oxygen (as oxide ions) is transported across the dense membranes, high-purity separations of air can be achieved. These devices can be combined with catalytic applications, and oxide ions can be used as the oxidant source for ethane dehydrogenation and oxidative coupling of methane [6,7]. The present work focuses on formulations of interest for solid oxide fuel cell (SOFC) applications.

All four major SOFC components (cathode, electrolyte, anode, and interconnects) are commonly made from perovskite-type oxides [8]. This fact attests to the wide variety of potential behavior of perovskite-type oxides, because the components require very different properties. For example, the electrolyte must be an electronic insulator, and the interconnects must be catalytically inactive, whereas the electrodes must be electronic conductors and have catalytic activity. In particular, perovskite-type oxides are especially important as electrode materials, because cathode alternatives are limited to cermets containing precious metals, such as Pt, and conventional anode materials (Ni-YSZ) deactivate due to sulfur impurities and carbon-based fuels. Whereas Co-based materials were the first proposed perovskite-type oxides as SOFC cathodes, Mn-based materials quickly became popular because of their increased stability under harsh conditions [8]. However, because there was a desire to lower the SOFC operation temperature (mainly achieved by decreasing the thickness of the electrolyte), more active materials were needed at intermediate temperatures (500 to 800 °C). At this range of operating temperatures, materials based on Fe and Co and mixtures thereof are expected to provide improved performance at lower temperatures through increased ionic conduction abilities.

As the ionic conductivity increases, the active reaction area for oxygen reduction expands. When this expansion occurs, the role of interfacial oxygen reduction kinetics becomes increas-

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ingly important. As demonstrated through the work of several researchers, surface processes that are chemical in nature, such as surface oxygen exchange and oxygen surface diffusion, influence the performance of mixed conducting perovskite-type materials [4,9–13]. For SOFC cathodes, Adler has proposed that the performance of mixed conductors is co-limited by ionic diffusion and the activation of molecular gas-phase oxygen. However, despite their newfound importance, few studies have focused on the characterization of the surface of these materials.

The bulk oxygen pathway makes an exclusive study of the surface difficult. For example, oxygen temperature-programmed desorption is truly a bulk technique, because oxygen evolves from the anionic matrix to form oxygen vacancies. During heterogeneously catalyzed reactions, the mechanisms can be intrafacial (involving mobile lattice oxygen) rather than suprafacial (involving adsorbed oxygen). At temperatures high enough for bulk oxygen to become mobile, methane oxidation is an example of an intrafacial reaction [2].

A common surface characterization technique is the use of probe molecules. Whereas simple molecules such as H₂, CO, CO₂, and H₂O are most common, hydrocarbons also have been used to gain insight into oxidation behavior and evaluate surface acid sites of perovskite-type oxides [2,3,14]. There has been considerable success in using oxygenated hydrocarbons (e.g., alcohols) as probe molecules for supported and bulk oxide materials. Methanol was shown as a useful compound for studying these surfaces. Product formation from methanol surface reactivity was related to the nature of the active sites [15]. Acidic surface sites led to dimethyl ether, whereas redox sites caused formaldehyde production. Basic sites, such as those examined for the perovskite-type oxides in the present study, resulted in the formation of carbon dioxide. Moreover, the ability of a surface to dissociate methanol yields information on the strength of the sites [16,17]. However, such surface studies have not been performed on perovskite-type oxides with stabilities relevant for SOFC cathodes.

Fe-based materials have been the least widely studied of the perovskite-type oxides, because they generally have lower activity than their Co counterparts. For example, studies focusing on the oxidation of propane [18], methanol [18], CO [2], propylene [2], and isobutene [2] have demonstrated that LaCoO₃ is more active than LaFeO₃. No studies have been performed on Fe-rich LaFeO₃ formulations doped with both Sr and Co. Fe-based formulations are desirable because of improved system compatibility, both in terms of lower thermal expansion coefficients (TECs) and lower chemical reactivity with the most common electrolytes (e.g., yttria-stabilized zirconia or YSZ), compared with Co-rich formulations. These materials also may catalyze oxidation reactions; recent work has shown that Fe doping provides structural stability in Co-based materials [19]. Moreover, the addition of Sr into La(Co,Fe)O_{3-δ} may lead to an activity increase, as was reported for butane oxidation over (La,Sr)CoO_{3-δ} [20]. On the other hand, an optimal Sr loading was observed for Fe-based materials used for ethanol and propane oxidation [21,22] and Co-based materials used for propane oxidation [18]. When La is doped with divalent

cations, catalytic properties (e.g., oxidation activity [23] and oxygen storage capacity [24]) tend to increase with Co content at the expense of stability [19] when Fe and Co are mixed on the transition metal site. However, evidence (maximum methane oxidation activity occurring for La_{0.8}Sr_{0.2}Fe_{0.6}Co_{0.4}O_{3-δ} compared with pure Co and Fe materials [20]) exists for complex behavior when these transition metals are used simultaneously.

The present work examines the surface properties of La_{0.6}-Sr_{0.4}Co_yFe_{1-y}O_{3-δ} for $y = 0.1, 0.2, \text{ and } 0.3$. In an extension of the work on simple metal oxides, the surfaces of these mixed perovskite-type oxides were characterized using methanol as a probe molecule. The site density was measured using dynamic chemisorption, whereas the nature of the sites was determined using the products from temperature-programmed desorption (TPD) and *in situ* diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS). Supporting surface information was obtained by X-ray photoelectron spectroscopy (XPS). The results were then used to explain the product distribution and activity differences for the different Co loadings during methanol oxidation.

In a previous study [25], we have reported the bulk characterization of the same materials. According to that work, all samples, due to the doping of Sr, have rhombohedral symmetry and are stoichiometric with respect of oxygen under ambient conditions. At elevated temperatures, the transition to cubic symmetry occurred, and the transition temperature dropped as the Co content increased, as was expected due to size arguments. For the reaction results discussed in this article, however, all three samples are expected to be of rhombohedral symmetry, because the lowest expected transition temperature is near 500 °C. The transition temperature is important because it may lead to significant differences in phase stability under reducing conditions [26,27]. Another important finding from our previous study [25] was that, in contradiction to what is generally perceived for formulations containing Fe and Co, oxygen vacancy formation was not proportional to Co content. This trend occurred under air up to 700 °C and for initial reductions under more reducing environments (e.g., He and 10% H₂/N₂). In addition, measured by *in situ* XRD under reducing conditions, the perovskite phase was the only one detected up to 800 °C in the presence of 5% H₂/N₂. This result indicates that the perovskite-type phase was the only one present under the reaction conditions used in this study.

2. Experimental

The La_{1-x}Sr_xCo_yFe_{1-y}O_{3-δ} samples were prepared by a conventional solid-state route. The preparation and the BET surface measurements were described previously [25]. The mass specific surface areas of all samples were between 1.5 and 2.0 m²/g.

2.1. Dynamic adsorption and temperature-programmed desorption of methanol

Dynamic methanol adsorption and sequential temperature-programmed desorption experiments were performed using a

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