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RESEARCH PAPER

Effect of Copper Substitution and Preparation Methods on the LaMnO$_{3\pm\delta}$ Structure and Catalysis of Methane Combustion and CO Oxidation

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Abstract: LaMn$_{1-x}$Cu$_x$O$_{3\pm\delta}$ perovskite oxides (x = 0, 0.2, 0.4, 0.6, 0.8, 1) were prepared by two different methods, the Pechini and sol-gel methods. The catalysts were characterized by Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), X-ray fluorescence spectroscopy, N$_2$ adsorption, and temperature-programmed reduction. Their catalytic activity in the oxidation of methane and CO was evaluated. EDS and SEM results showed that the Pechini samples had more homogeneity and smaller particles (higher specific surface area). The catalytic activity for methane combustion was highest for x = 0.2. In CO oxidation, the oxides with x = 0.2 and x = 0.4 were the most active. The Pechini samples had higher activity and stability than the sol-gel samples.

Key words: perovskite; Pechini; sol-gel; methane combustion; carbon monoxide oxidation

Catalytic combustion is currently considered the best technology for the removal of hydrocarbons from off-gases because of its low energy consumption and the small amount of noxious byproducts such as thermal NO$_x$ [1]. Methane is a component in the exhaust of most combustion processes, and its increasing use as a fuel will increase methane emission unless more effective exhaust cleaning catalysts are developed. Methane is the main constituent of natural gas and is a small and stable molecule that is difficult to burn. The catalytic oxidation of methane is more difficult than the oxidation of most volatile organic compounds [1–4]. Therefore, methane has been chosen in many works as a model compound for catalytic oxidation studies because the catalytic combustion of most organic compounds will be ensured if methane combustion is catalyzed [1,5]. Carbon monoxide is another component in the exhaust of most combustion processes that must be converted to carbon dioxide to reduce exhaust gas pollution.

In internal combustion engines fueled by natural gas, the exhaust contains large amounts of unburned methane. For lean-burn engines, the gas slip is often in the region of 2%–4% of the feed fuel. Methane is the most difficult hydrocarbon to oxidize, and catalysts with increased activity at low temperature are required to effectively decrease the methane content in the exhaust, especially during engine start-up. It has been reported that temperatures of more than 600 °C are required for the steady conversion of more than 50% of the methane. In the current study, the methane oxidation activity of various supported metal catalysts was measured [5].

Perovskite-type oxides with the general formula ABO$_3$, where A and B represent metals in 12- and 6-coordinated sites, respectively, are interesting catalysts for CO oxidation and methane combustion. They are cheaper, have comparable activity, and are much more resistant to deactivation than the traditional noble-metal-based catalysts [1,6,7]. Because the catalytic properties of perovskite-type oxides are determined by the nature of the B-site cations [8], their selection is of primary importance in the design of perovskite catalysts and in modifying their catalytic properties. The activity of perovskite catalysts for methane combustion can be enhanced by partially substituting the metal in position A and/or B of the perovskite with a metal of the same or different valency [9]. The most frequently used B-site cations are Co and Mn because their simple metal oxides are very active for total oxidation reactions [10–12]. Also, the thermal stability of perovskite oxides has

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been found to depend on the nature of the cation at the B position, with $LaBO_3$ (B = Mn, Co, Ni) showing high stability [13].

Although perovskite-type catalysts performed well in many reactions, their low surface area is a disadvantage. There are many different methods for preparing perovskite oxides. The conventional method based on the solid-state reaction between metal oxides at high temperature is not suitable for catalytic applications because the high temperature synthesis leads to a material with a low surface area and low catalytic activity [14]. Some solution techniques, such as the sol-gel, Pechini, and co-precipitation methods, exist and can produce high surface area perovskites. In these methods, temperatures less than 800 °C are used for the preparation. Prior to this work, among the perovskites, lanthanum manganite has been investigated intensively [15] because it is one of the few perovskite systems that display a wide range of non-stoichiometry (oxygen excess). The deviation from stoichiometry can be modified by partial substitution of the A and B cations, which gives rise to significant changes in physical and chemical properties [16]. Lanthanum manganite is also of special interest due to its oxygen-transport property [17,18].

Ran et al. [19] prepared $La_{0.7}Sr_{0.3}Mn_{0.7}Cu_{0.3}O_3$ by the sol-gel method and investigated the effect of the pH in the precursor on the physicochemical properties. When the pH was about 1.16, the surface area and catalytic activity were both increased. The catalytic activity for CO oxidation on $LaCoO_3$ was investigated by Taguchi et al. [20] who showed that CO oxidation started above 70 °C and was complete below 200 °C. Porta et al. [21] used the sol-gel method to prepare $LaMn_{1-x}Cu_xO_3$ by metal citrate decomposition for methane combustion. They showed that all their samples catalyzed the combustion of methane in the temperature range 300–800 °C with total oxidation to CO_2 [22]. Mn-based perovskites were found to be more active than the corresponding Co samples with the same composition. Zhang et al. [13] used reactive grinding to prepare La, Mn, and Cu perovskites and investigated their activity for NO reduction. These perovskites showed good activity [23]. They also reported that the substitution of Cu into $LaMnO_3$ enhanced the activity for CO oxidation and CO–NO reactions. Tabata et al. [24] observed that in $LaMn_{1-x}Cu_xO_3$ prepared by amorphous acetate decomposition, the valence state of the substituted copper ion was Cu^{2+} and the manganese ion was in a mixed state of Mn^{3+} and Mn^{4+}. The non-stoichiometry of the surface lattice oxygen was also observed by X-ray photoelectron spectroscopy (XPS) [24].

In this study, the effect of the synthesis method on the properties of $LaMn_{1-x}Cu_xO_{3\pm\delta}$ oxides was investigated. The samples were prepared by both the Pechini and sol-gel methods. In the Pechini method, citric acid was used to chelate the metal ions. Ethylene glycol was used as the solvent for the process of polymerization between citric acid and ethylene glycol, which were used to initiate a polyesterification reaction. In the sol-gel method, only citric acid was used as a complexing agent. The Pechini method involves the formation of a rigid polymer network and was shown to result in better chemical homogeneity from Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), X-ray fluorescence rared spectroscopy (XRF), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), and N_2 adsorption analyses.

1 Experimental

1.1 Catalyst preparation

To determine the effect of the preparation method on the properties of the $LaMn_{1-x}Cu_xO_{3\pm\delta}$ (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) mixed oxides, two methods were used. The reactants used for preparing the perovskites were the nitrates of lanthanum ($La(NO_3)_3$), manganese ($Mn(NO_3)_3$), and copper ($Cu(NO_3)_2$). All starting compounds were purchased from Merck and more than 99% pure.

Samples prepared by the Pechini method were prepared as follows. Nitrate solutions were prepared by dissolving La, Mn, and Cu salts in deionized water. Citric acid as the complexing agent was weighed out in the amount corresponding to the molar ratio of citric acid/total metal ions of 2 and was then added to the nitrate solutions. Ethylene glycol with a mass ratio of 40 g to 60 g of citric acid was then added to the solution. The solution was heated to 80 °C with stirring. Ammonia was then added to the solution until the pH reached 1.15–1.2 [19]. Heating increased the rate of the polyesterification reaction between the acid and alcohol. The resin-like substance that formed after water evaporation was dried at 110 °C overnight in an oven and then calcined at 750 °C for 6 h.

In the second sol-gel method, the catalysts were prepared using citric acid as complexing agent. The same amounts of nitrate salts as in the Pechini method were used to prepare the $LaMn_{1-x}Cu_xO_{3\pm\delta}$ perovskites. Citric acid in the amount corresponding to the molar ratio of acid/total metal ions of 2 was added to the nitrate solution. The solution was heated to 80 °C with stirring until a gel-like substance was obtained. This was subsequently dried at 110 °C overnight and calcined at 750 °C for 6 h.

1.2 Catalyst characterization

In order to investigate the resin- and gel-like substances, FT-IR experiments were performed using a Shimadzu 8400s FT-IR spectrometer. The dried samples were dissolved in *n*-hexane and then frozen at –10 °C. The crystals obtained were then analyzed by FT-IR (3% in KBr matrix).

XRD experiments were performed on a Philips PW-1800 diffractometer using Cu-K_α radiation (λ = 0.154 2 nm) at 40 kV and 30 mA to determine the crystalline phases and calculate the lattice parameters. Scattering intensities were measured over