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Effects of cerium incorporation on the catalytic oxidation of benzene over flame-made perovskite $La_{1-x}Ce_xMnO_3$ catalysts

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ABSTRACT

Perovskite-type $La_{1-x}Ce_xMnO_3$ ($x = 0$–10%) catalysts were prepared by flame spray pyrolysis and their activities during the catalytic oxidation of benzene were examined over the temperature range of 100–450 °C. The structural properties and reducibility of these materials were also characterized by X-ray diffraction (XRD), N_2 adsorption/desorption, H_2 temperature-programmed reduction (H_2-TPR) and X-ray photoelectron spectroscopy (XPS). The incorporation of Ce was found to improve the benzene oxidation activity, and the perovskite in which x was 0.1 exhibited the highest activity. Phase composition and surface elemental analyses indicated that non-stoichiometric compounds were present. The incorporation of Ce had a negligible effect on the specific surface area of the perovskites and hence this factor has little impact on the catalytic activity. Introduction of Ce^{4+} resulted in modification of the chemical states of both B-site ions and oxygen species and facilitated the reducibility of the perovskite. The surface Mn^{4+}/Mn^{3+} ratio was increased as a result of Ce^{4+} substitution, while a decrease in the surface-adsorbed O/lattice O (O_{ads}/O_{latt}) ratio was observed. The relationship between the surface elemental ratios and catalytic activity was established to allow a better understanding of the process by which benzene is oxidized over perovskites.

Introduction

Perovskite-structure oxides (ABO_3) are receiving significant attention in the field of catalysis, especially with regard to the catalytic oxidation of volatile organic compounds (VOCs), based on their exceptional catalytic activity and thermal stability (Pecchi, Reyes, Zamora, Cadus, & Fierro, 2008; Royer, Alamdari, Duprez, & Kaliaguine, 2005; Wen, Zhang, He, Yu, & Teraoka, 2007). To date, ABO_3 perovskites have been applied to the catalytic flameless combustion of methane (Buchneva et al., 2009; Campagnoli et al., 2005; Rossetti, Biffi, & Forni, 2010), the oxidation of ethanol (Najjar & Batis, 2010), the selective catalytic reduction of NO_x (Chiarello, Ferri, Grunwaldt, Forni, & Baiker, 2007), the removal of diesel soot particulates (Teraoka, Kanada, & Kagawa, 2001), and the catalytic removal of ethyl acetate (Niu et al., 2007), acetone (Spinicci, Faticanti, Marini, De Rossi, & Porta, 2003), isopropanol and benzene (Blasin-Aube, Belkouch, & Monceaux, 2003). Within this series of perovskites, $LaMnO_3$ exhibits superior properties and catalytic performance (Li, Wang, & Gong, 2009), and this may be attributed to the inherent high specific surface area (SSA) of this material, the presence of a stoichiometric excess of oxygen, a defective/cation-deficient lattice, and the presence of manganese in multiple oxidation states (Mn^{3+}/Mn^{4+}). These properties can be further enhanced by the doping of certain metal oxide species, such as Ce ions, into the $LaMnO_3$ structure, such that La ions are partly substituted by the dopant ions (Kaddouri, Gelin, & Dupont, 2009).

Ceria in its natural form is a poor catalyst. However, the activity of certain catalysts can be dramatically improved by the incorporation of Ce (Zhang-Steenwinkel, Beckers, & Bliek, 2002). Oxygen storage capacity (OSC) is a characteristic property of Ce^{3+}/Ce^{4+} ions and the synergistic effect between Ce^{3+}/Ce^{4+} and Mn^{3+}/Mn^{4+} has been shown to enhance catalytic activity (Royer et al., 2005).

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Extensive studies have examined the substitution of Ce into catalytic materials and the influence of the preparation method applied. Alifanti, Kirchnerova, and Delmon (2003) studied the effects of Ce incorporation on $La_{1-x}Ce_xMnO_3$ ($x = 0.1$, 0.2, 0.3, 0.4, and 0.5) catalysts, focusing on the relationship between physicochemical properties and catalytic activity. These catalysts were obtained by the citrate method and the study employed the combustion of 1% methane in air as a model catalytic reaction. It was determined that the substitution of cerium at the level of $x = 0.1$ had beneficial effects, whereas higher x values resulted in lower catalytic activity and higher cost. Kaddouri et al. (2009) reported the relationship between the physicochemical properties and catalytic performance of La–Ce–Mn–O perovskites obtained by different preparation methods. Samples prepared by the conventional hydrothermal and dielectric heating hydrothermal methods were tested for methane combustion. Higher CH_4 conversion and better sulfur tolerance were exhibited by the samples synthesized by the dielectric heating hydrothermal method. The superior catalytic performance was attributed to good dispersion of the various cerium oxide species as well as strong interactions between these cerium species and the $LaMnO_3$ host structure.

A catalyst that combines high surface area, high ionic mobility through the crystal lattice, and the potential for large-scale production is difficult to obtain by traditional methods. Recently, flame spray pyrolysis (FSP) was developed as a means of synthesizing various different kinds of metal oxides, either in lab-scale or large-scale quantities (Chiarello, Rossetti, & Forni, 2005; Chiarello, Rossetti, Lopinto, Migliavacca, & Forni, 2006). In general, FSP is a versatile, convenient, and cost-effective process for the production of ceramic nanoparticles. In a typical flame spray pyrolysis setup, a liquid precursor including a high or low combustion enthalpy solvent is aerosolized by a dispersion gas (oxygen or air) as it passes through a spray nozzle, and subsequently combusts in a support flame in the vicinity of the spray nozzle. The flame temperature in this process is thought to exceed 1000 °C in the main flame zone depending on the gas flow rate, the liquid precursor feed rate, the setup parameters, and the nature of the solvent (Liu, Yue, et al., 2013). Chiarello et al. (2005) reported the synthesis of nano-sized $LaCoO_3$ and its application to the catalytic combustion of methane. The effect of the solvent on the preparation of perovskites by FSP was also studied. In this work, Pd particles were systematically introduced into the $LaCoO_3$ simply by adding an appropriate metal precursor to the liquid precursor. Further studies on the catalytic performance during the reduction of NO by H_2 under lean-burn conditions have also been performed (Chiarello, Ferri, et al., 2007; Chiarello, Grunwaldt, et al., 2007). Additional structures, such as $MgAl_2O_4$ spinel (Roy, van Vegten, & Baiker, 2010), a NiO–Al_2O_3 core–shell structure (Azurdia et al., 2006) and a noble metal-loaded Pt/TiO_2 (Teoh, Madler, Beydoun, Pratsinis, & Amal, 2005), have been obtained by FSP or by variants of FSP.

Nano-sized catalysts formed by flame spray pyrolysis are characterized by high specific surface areas and high ionic mobility through the crystal lattice and they are also highly crystalline. In the present study, $LaMnO_3$ substituted with Ce was synthesized as a model catalyst to investigate the inherent relationships between structure, surface element composition, reducibility, and catalytic activity. Various characterization methods, such as Transmission Electron Microscopy (TEM), XRD, XPS, and H_2-TPR, were used to examine the nature of these flame-made catalysts. This study focused in particular on the physicochemical properties of the $La_{1-x}Ce_xMnO_3$ perovskites synthesized by flame spray pyrolysis and the catalytic performances of these materials for the complete oxidation of benzene.

Experimental

Materials

Propanoic acid (CP), lanthanum acetate (99.99%), cerium acetate (99.99%) and manganese acetate (99.9%) were purchased from the Sinopharm Company and used as received without any further purification.

Catalyst preparation

$La(CH_3COO)_3\cdot 6H_2O$, $Ce(CH_3COO)_3\cdot 6H_2O$, and $Mn(CH_3COO)_2\cdot 4H_2O$ were used as La, Ce, and Mn sources, respectively. Liquid precursors with a La to Mn molar ratio of 1:1 were obtained by dissolving the appropriate quantities of the corresponding metal precursors in propanoic acid, during which time the liquid precursor was stirred at 1200 rpm at 70 °C for 20 min. Stoichiometric $Ce(CH_3COO)_3\cdot 6H_2O$ was subsequently mixed into the liquid precursor. The total metal (La + Mn) concentration of the liquid precursor was 0.2 M when preparing the $La_{1-x}Ce_xMnO_3$ perovskites (where x represents the nominal mole fraction of Ce incorporated into the perovskite structure, $x = 0$, 2.5%, 5.0%, 7.5%, and 10.0%).

Perovskite-structure catalysts were synthesized by FSP, using a process described elsewhere in detail (Liu, Yue, et al., 2013). In brief, the liquid precursor was supplied by a peristaltic pump and sprayed through a nozzle in a stream of oxygen. The precursor supply rate and the dispersion oxygen flow rate were set to 10.27 mL/min and 4.0 L/min, respectively. The sprayed precursor was ignited by a support flame derived from a combination of oxygen and methane with flow rates of 4.0 and 2.4 L/min, respectively. The resulting particles were collected on a glass fiber filter with the aid of a vacuum pump. On average, approximately 6.6 g of powder was collected on the filter per hour during operation of the lab-scale FSP apparatus. During FSP, a yellow-green flame was observed for all the samples, whereas the as-prepared powders exhibited a black coloration.

Catalyst characterization

Data concerning the phases of the $La_{1-x}Ce_xMnO_3$ perovskites were obtained by X-ray diffractometer (XRD, X'Pert Pro), applying scans from 5° to 90° (2θ) with Cu Kα ($\lambda = 1.54$ Å) radiation. Phases were identified by comparison with JCPD 51-1516 (lanthanum manganese oxide). The average crystallite sizes and cell parameters were calculated using the Scherrer equation. Specific surface areas were determined by employing the BET method, using data from an Autosorb-1-C-TCD (Quantachrome Instruments). Prior to measurements, powder samples (ca. 200 mg) were pretreated at 300 °C for 3 h to remove moisture. A JSM-6700F field emission scanning electron microscope (FESEM) and a JEM 2100F electron microscope (JEOL, Japan) combined with X-ray energy dispersive spectroscopy (EDX) were used to characterize the morphology of the $La_{1-x}Ce_xMnO_3$ perovskites. XPS data were obtained with an ESCALab220i-XL electron spectrometer (VG Scientific, UK) using 300 W Al Kα radiation. The base pressure during these measurements was approximately 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. H_2-TPR was performed on a Micromeritics Chemisorb 2720 pulse chemisorption system (Micromeritics, USA) equipped with a TPx system and a thermal conductivity detector (TCD). Samples of approximately 30 mg were heated from ambient temperature to 850 °C at 10 °C/min and a mixture of H_2 (10 vol%) and Ar was employed as a reducing atmosphere at a flow rate of 25 mL/min.