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Catalysis Communications 9 (2008) 55–59

www.elsevier.com/locate/catcom

Catalytic activity of nanometer $La_{1-x}Sr_xCoO_3$ ($x = 0, 0.2$) perovskites towards VOCs combustion

Haifeng Huang [a], Yaqin Liu [a], Wei Tang [a], Yinfei Chen [b,*]

[a] College of Biological and Environmental Engineering, Zhejiang University of Technology, Hangzhou 310032, PR China
[b] College of Chemical Engineering and Materials Science, Zhejiang University of Technology, Hangzhou 310032, PR China

Received 9 October 2006; received in revised form 27 April 2007; accepted 2 May 2007
Available online 10 May 2007

Abstract

Combustive oxidation of volatile organic compounds (VOCs), such as propyl alcohol, toluene and cyclohexane, were studied. The combustion was catalyzed by nanoparticles of $La_{1-x}Sr_xCoO_3$ ($x = 0, 0.2$) perovskites prepared by a co-precipitation method. The results showed high activities of the perovskite catalysts. Compared to $LaCoO_3$, in particular, $La_{0.8}Sr_{0.2}CoO_3$ was much higher in catalytic ability. The total oxidation of VOCs followed the increasing order: cyclohexane < toluene < propyl alcohol. The $T_{99\%}$ of cyclohexane was 40 °C lower than that of toluene, which appeared to be determined by the bond strengths of the weakest C–H and C–C bonds. The 100-h stability experiments showed that $La_{1-x}Sr_xCoO_3$ ($x = 0, 0.2$) perovskite was highly stable.

Keywords: Volatile organic compounds (VOCs); Catalytic combustion; Perovskite catalyst; Nanoparticle; $La_{1-x}Sr_xCoO_3$

1. Introduction

Volatile organic compounds (VOCs) are hazardous air pollutants due to their toxic and malodorous nature [1]. Automobiles and industrial processes are mostly responsible for VOCs emissions. VOCs such as hydrocarbons, alcohols, ketones, and aldehydes [2–5] are readily oxidizable. When the recovery of these compounds is not desired, they are usually destroyed via deep oxidation. Catalytic combustion is regarded as an effective and economic way for air pollution control [6]. Compared to thermal combustion, catalytic combustion is preferred, largely due to the lower temperature required for combustion initiation and to its higher selectivity. Performance of catalytic combustion would thus lead to a considerable saving of energy.

Previous studies have tested perovskites for VOCs combustion. Chang and Weng [7] found that $La_{0.8}Sr_{0.2}CoO_3$ was highly effective for deep oxidation of toluene and MEK. Lintz and Wittstock [8] studied the combustion of several VOCs on $LaMnO_3$. Arai et al. [9] found a very high activity for deep oxidation of methane with Sr-doped $LaMnO_3$. At conversion levels below 80%, Sr-doped $LaMnO_3$ was more active than Pt/Al_2O_3. High oxidation activities of $La_{0.75}Sr_{0.25}MnO_{3+x}$ and $La_{0.8}Sr_{0.2}MnO_3$ have also been reported by McCarty and Wise [10]. It was asserted that there exists a correlation between VOCs oxidation rate and the bond dissociation energy of the weakest C–H bond [11,12].

The perovskites have a general formula of $A_1A_2B_1B_2O_3$, in which A_1 is one of lanthanide elements (generally La, sometimes Ce, Pr, or Nd), and A_2 one of alkaline earth metals (Ca, Sr, or Ba); B_1 and B_2 are transition metals (Co, Mn, Fe, Cr, Cu, or V) or noble metals. A_2 and B_2 correspond to the partial substitution of the A_1 and B_1 ions, respectively. In particular, the partial replacement of La^{3+} by Sr^{2+} has often resulted in a considerable increase in combustion activity [13].

The main challenge in developing perovskite catalysts is to obtain their structures while preserving sufficiently

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[*] Corresponding author. Tel.: +86 571 8832 0622; fax: +86 571 8586 4008.
E-mail address: yfchen@zjut.edu.cn (Y. Chen).

1566-7367/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.catcom.2007.05.004

high surface areas. The preparation of a perovskite oxide involves a solid-state reaction of its precursor oxide to form the characteristic ABO_3 structure. This requires a significant exposure of the precursor oxide to high temperatures, thus leading to a low specific surface area of the catalyst. To circumvent this limitation, a number of alternative preparation methods have been tested, in an attempt to lower the firing temperature for perovskite synthesis.

In this paper, we studied the oxidation of selected VOCs (propyl alcohol, toluene and cyclohexane) by $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ catalysts prepared in the form of nanoparticles via co-precipitation with aqueous ammonia so as to enlarge their surface areas. The catalysts were characterized using X-ray diffraction (XRD), scanning electron micrographs (SEM) and other techniques to gain insight into the changes taking place on the surfaces of the catalysts and to relate these changes to the observed catalytic performance.

2. Experimental

2.1. Synthesis of catalysts

Perovskites, $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$, were prepared via co-precipitation using aqueous ammonia. Briefly, nitrate salts (La, Mn, Co, or Sr) were initially dissolved in deionized water. Following titration, the solutions were mixed in desired proportions to prepare concentrated solutions. Aqueous ammonia was subsequently added dropwise into the solutions at the temperature of 40 °C with constant agitation to obtain the catalyst suspensions until pH reached 12.0. The suspensions were kept at the same temperature for 24 h, filtered, and then washed with deionized water. The solids were dried at 80 °C for 2 h and calcinated in the air at 600 °C for 6 h. After grinding and sieving, $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ were obtained.

2.2. Characterization of catalysts

The phases of the synthesized catalysts were characterized by X-ray diffraction (XRD) using an ARL SCINTAG X'TRA X-ray powder diffractometer equipped with a position-sensitive detector, allowing all angles between 20° and 80° to be read simultaneously, at a scan rate of $4° \min^{-1}$. Monochromated CuKα was used as the radiation source. BET surface areas (SA_{BET}) of the catalysts were measured by nitrogen (N_2) adsorption, recorded at liquid nitrogen temperature on an ASAP2010 surface area analyzer (Micromeritics, USA). The mean crystallite sizes were estimated using the Scherrer equation [14], $d = k\lambda/(\beta\cos\theta)$, where $k = 0.89$, $\lambda = 0.15418$ nm (Cu), β is the half peak width of the X-ray reflection and θ is the diffraction angle. The scanning electron microscopy (SEM) was performed on an S-4700 Scanning Electron Microscope (Hitachi Corp., Japan).

2.3. Catalytic activities

The activities of the catalysts were tested for the combustion of propyl alcohol, toluene and cyclohexane in a continuous fixed bed working at the atmospheric pressure. A catalyst of 4 g was used in VOCs combustion tests. The concentration of VOCs in the feed gas was 0.1% ($\mathrm{mol\,mol^{-1}}$), the hourly gas flow space velocity (GHSV) was $7200\ \mathrm{h^{-1}}$, and the reaction temperature ranged from 160 °C to 360 °C. The reaction temperature was measured inside the catalytic bed using a K-type thermocouple. The aging effect of $La_{0.8}Sr_{0.2}CoO_3$ was also studied under the same conditions except that the reaction temperature was 300 °C.

Reactants and products were analyzed by gas chromatography (FULI, GC-9790), equipped with a flame ionization detector (FID). The conversion rate was obtained by calculating the concentrations of reactants (inlet and outlet) at different temperatures.

3. Results and discussion

3.1. Characterization of catalysts

The scanning electron micrographs (SEM) of $LaCoO_3$and $La_{0.8}Sr_{0.2}CoO_3$ are shown in Fig. 1. It can be seen that the particles of the two perovskites were small ($\leqslant$100 nm) and similar in size. The XRD patterns of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ (before and after the 100-h combustion tests) are shown in Fig. 2. Intensive peaks at 2θ of 23.1°, 32.7°, 47.0° and 58.9° indicate main features of perovskite materials (in comparison with the standard patterns of perovskites). $La_{0.8}Sr_{0.2}CoO_3$ had stronger peaks than $LaCoO_3$. According to the peaks and Scherrer formula, the diameters of the crystalline particles of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ were calculated as 50 nm and 64 nm with 2θ of 23.1°, respectively. The particles of both catalysts were thus in the nanometer range ($\leqslant$100 nm). The XRD patterns of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ showed that they were single-phase pervoskite oxides with primitive rhombohedral cell in the R3m space group. There were no obvious changes in peak positions and intensity before and after the combustion tests for toluene. The crystal structures were apparently stable and the activities remained high. The BET surface areas of $LaCoO_3$ ($16.53\ \mathrm{m^2\,g^{-1}}$) and $La_{0.8}Sr_{0.2}CoO_3$ ($15.36\ \mathrm{m^2\,g^{-1}}$) were similar.

3.2. Catalytic activities for a single VOC

Toluene was chosen as the model molecule to investigate the catalytic activities of perovskites for single VOC. Control test without catalysts was performed under the following conditions: air flow rate, $120\ \mathrm{mL\,min^{-1}}$; inlet concentration of toluene, 0.1% ($\mathrm{mol\,mol^{-1}}$); GHSV, $7200\ \mathrm{h^{-1}}$; and reaction temperature, 160–360 °C. The activities of $LaCoO_3$ and $La_{0.8}Sr_{0.2}CoO_3$ in the oxidation