Three-dimensionally ordered macroporous SrFeO$_{3-\delta}$ with high surface area: Active catalysts for the complete oxidation of toluene

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** Abstract **

Three-dimensionally ordered macroporous (3DOM) cubic perovskite-type oxides SrFeO$_{3-\delta}$ were prepared using the citrate acid-assisted poly(methyl methacrylate)-templating method in the presence of ethylene glycol, sucrose or $\gamma$-lysine (denoted as SFO-0, SFO-Sucrose, and SFO-Lysine, respectively). It is found that the SrFeO$_{3-\delta}$ samples possessed a 3DOM architecture and were high in surface area (34–61 m$^2$/g). The porous SrFeO$_{3-\delta}$ catalysts performed well in toluene combustion, with the SFO-0 sample exhibiting the highest catalytic activity ($T_{90\%} = 292$ C and $T_{99\%} = 340$ C at 20,000 mL/(g.h)). The catalytic activity of the samples showed a good relationship with surface area, oxygen adspecies concentration, and low-temperature reducibility, all decrease in the order of SFO-0 > SFO-Lysine > SFO-Sucrose > SFO-bulk. It is deduced that the good catalytic performance of the porous SrFeO$_{3-\delta}$ materials is due to the good low-temperature reducibility, large surface area, and high oxygen adspecies concentration.

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1. Introduction

With interesting electronic, magnetic, transport, and redox properties, oxygen-deficient perovskite-type oxides SrFeO$_{3-\delta}$ ($0 < \delta < 0.5$) have been investigated extensively. The crystal structure of SrFeO$_{3-\delta}$ is dependent on the oxygen vacancy density ($\delta$). It was reported that SrFeO$_{3-\delta}$ is cubic at $\delta = 0–0.12$ [1,2], tetragonal at $\delta = 0.16–0.24$ [1,3], orthorhombic at $\delta = 0.25$ [1,3,4], and brownmillerite at $\delta = 0.50$ [2]. The flexible accommodation of highly mobile oxygen vacancies renders SrFeO$_{3-\delta}$ to be useful in catalysis. Although a number of heterogeneous catalytic [5,6] and photocatalytic [7,8] applications of SrFeO$_{3-\delta}$ can be found in the literature, reports on the catalytic combustion of toluene over such materials are rare. It is well known that factors such as surface area, crystal structure, oxygen nonstoichiometry, particle morphology or even crystal type (single- or polycrystal) influence the physicochemical properties of perovskite-type oxides. Unfortunately, the SrFeO$_{3-\delta}$ materials prepared using the traditional methods (e.g., sol–gel [5], citrate [6], solid-state [9], and coprecipitation [10] methods) are nonporous and low in surface area ($<10$ m$^2$/g), unfavorable for the enhancement of catalytic performance. It is hence highly desirable to develop an efficient strategy for controlled preparation of porous SrFeO$_{3-\delta}$ that are high in surface area.

With high surface areas and highly developed porous structures, three-dimensionally ordered macroporous (3DOM) perovskite-type oxides are promising catalysts for the oxidation of volatile organic compounds (VOCs). In the past years, 3DOM perovskite-type oxides (e.g., LaMnO$_3$ [11], LaFeO$_3$ and La$_{1-x}$SrFeO$_3$ [12], La$_{0.7}$Ca$_{0.3}$MnO$_3$ [13], Au/LaFeO$_3$ [14], and LaCo$_x$Fe$_{1-x}$O$_3$ ($x = 0–0.5$) [15]) have been prepared via the templating routes using poly(methyl methacrylate) (PMMA) or polystyrene (PS) colloidal crystal microspheres as the template. To the best of our knowledge, the fabrication of 3DOM SrFeO$_{3-\delta}$ and their application in catalyzing the combustion of toluene have never been reported before.

Previously, our group generated a number of 3DOM-structured materials with high surface areas by surfactant-assisted PMMA-templating approaches (e.g., $\gamma$-Al$_2$O$_3$ and Ce$_{1-x}$Zr$_x$O$_2$ [16], CeO$_2$ [17], Fe$_2$O$_3$ [18], LaMnO$_3$ [19], and La$_2$CuO$_4$ [20]), and observed that some of the 3DOM materials showed excellent catalytic performance in the combustion of toluene and methane [18–20]. In this paper, we report the oxidative removal of toluene over 3DOM-structured SrFeO$_{3-\delta}$ prepared by the citric acid-assisted PMMA-templating method.

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