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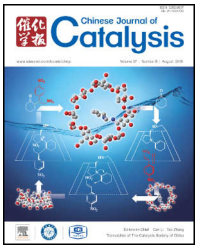

Article

Low temperature molten salt synthesis of porous $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \leq x \leq 0.6$) microspheres with high catalytic activity for CO oxidation

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ABSTRACT

A molten salt method was developed to prepare porous $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \leq x \leq 0.6$) microspheres using hierarchical porous δ-MnO_2 microspheres as a template in eutectic $NaNO_3$-KNO_3. X-ray diffraction patterns showed that single phase $LaMn_{0.8}Fe_{0.2}O_3$ with good crystallinity was synthesized at 450 °C after 4 h. Transmission electron microscope images exhibited that the $LaMn_{0.8}Fe_{0.2}O_3$ sample obtained at 450 °C after 4 h possessed a porous spherical morphology composed of aggregated nanocrystallites. Field emission scanning electron microscope images indicated that the growth of the porous $LaMn_{0.8}Fe_{0.2}O_3$ microspheres has two stages. SEM pictures showed that a higher calcination temperature than 450 °C had an adverse effect on the formation of a porous spherical structure. The $LaMn_{0.8}Fe_{0.2}O_3$ sample obtained at 450 °C after 4 h displayed a high BET surface area of 55.73 m^2/g with a pore size of 9.38 nm. Fourier transform infrared spectra suggested that Sr^{2+} ions entered the A sites and induced a decrease of the binding energy between Mn and O. The CO conversion with the $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \leq x \leq 0.6$) samples indicated that the $La_{0.4}Sr_{0.6}Mn_{0.8}Fe_{0.2}O_3$ sample had the best catalytic activity and stability. Further analysis by X-ray photoelectron spectroscopy demonstrated that Sr^{2+} doping altered the content of Mn^{4+} ions, oxygen vacancies and adsorbed oxygen species on the surface, which affected the catalytic performance for CO oxidation.

1. Introduction

Over the past several decades, catalytic oxidation of CO has attracted considerable attention due to its potential applications in many fields such as automobile exhaust, fuel cell technology, carbon dioxide laser and air purification in an enclosed atmosphere [1–3]. Among the catalysts suitable for this purpose, supported noble metals initially seemed to be good candidates. However, owing to high prices and low reserves of noble metals, nowadays, perovskite oxides such as the lanthanum manganites are potential substitutes for noble metal catalysts because of their unique properties such as their catalytic activity for CO oxidation [4].

In the $LaMnO_3$ perovskite oxide, Mn^{3+} ions are coordinated with six oxide ions and the MnO_6 units are connected in a corner-sharing manner making networks in which La^{3+} ions are located in the dodecahedral sites of the framework [5]. Due to its structural flexibility, the La^{3+} and/or Mn^{3+} ions in the lattice can be partially replaced by foreign cations (transition or rare metal ions) with no large change in the crystalline structure to produce substituted perovskites [6]. This property has frequently been exploited because the substitution usually pro-

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motes catalytic activity [7–10]. Substitution of La^{3+} ions with a divalent metal cation is accompanied by a change of the oxidation state of the manganese ions, thus leading to a modification in the catalytic activity for CH_4 combustion [7]. Ponce et al. [8] studied the partial substitution Sr^{2+} for La^{3+} ions in $La_{1-x}Sr_xMnO_3$ (x = 0–0.5) oxides and found that with the substitution amount increasing, to balance the total charge, the charge compensation was achieved by the oxidation of Mn^{3+} to Mn^{4+}. The presence of Mn^{4+} cations in $La_{1-x}Sr_xMnO_3$ oxide enhanced the catalytic activity by influencing the active oxygen near the Mn^{4+} that takes part in methane oxidation [9]. Nevertheless, the substitution of Mn^{3+} ions in $LaMnO_3$ oxide proved to be a far more effective method to optimize the catalytic activity than choosing different lanthanides to substitute for La^{3+} ions in A sites. Geng [10] revealed that compared with partial substitution of A sites in $La_{1-x}Sr_xMnO_3$ oxide with Sr^{2+} ions, the ignition temperature of $LaMn_{1-y}Cu_yO_3$ oxides with an equal substitution amount of B sites with Cu^{2+} ions was far lower in the catalytic oxidation of CO.

On account of the high catalytic activity of the substituted perovskite, many studies on the improvement of catalytic activity have been carried out. Among these, increasing the specific surface area was considered to be an effective strategy. Hence, different preparation routes and technical conditions such as a solid state reaction, sol-gel, hydrothermal treatment, spray-drying, freeze-drying, co-precipitation, chemical vapor deposition, microemulsion [11] and templates [12] have been used to prepare substituted perovskite catalysts with a high specific surface area to boost the catalytic performance for CO oxidiation.

However, there have been few reports of perovskite-type oxides with specific morphologies prepared by the metal salt method. Liu et al. [13] reported that perovskite-type $ACeO_3$ (A = Sr, Ba) was synthesized by the metal salt method at low temperatures in eutectic NaCl-KCl. Chen et al. [14] revealed that the perovskite single crystalline $LaMnO_3$ nanocubes have been fabricated by a facile salt-assisted solution combustion process. Wang et al. [15] studied a morphology-controlled molten salt route developed to synthesize porous spherical $LaMnO_3$ and cubic $LaMnO_3$ nanoparticles using the as-prepared porous Mn_2O_3 spheres as a template.

In this work, first, hierarchical porous δ-MnO_2 microspheres were synthesized by a hydrothermal reaction at 80 °C. Then, in order to decide the optimal calcination temperature, the $LaMn_{0.8}Fe_{0.2}O_3$ catalysts were synthesized at different temperatures (450, 550 and 650 °C) using the synthesized δ-MnO_2 microspheres as a template in eutectic $NaNO_3$-KNO_3. Finally, $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \le x \le 0.6$) catalysts obtained at the optimal calcination temperature were used to investigate the effect of Sr^{2+} doping on the catalytic activity for CO oxidiation.

2. Experimental

2.1. Material preparation

All the chemical reagents were analytical purity and used without any further purification. Distilled water was used in the synthesis and treatment processes.

Hierarchical porous δ-MnO_2 microspheres were synthesized by a hydrothermal reaction. In a typical procedure [16], first, 0.9 g of $KMnO_4$ and 2 ml of 37 wt% HCl were dissolved into 80 mL of distilled water at room temperature. After continuous magnetic stirring for 30 min, the homogeneous purple solution was sealed in a 100 mL Teflon-lined autoclave and maintained at 80 °C for 10 h in an oven. After cooling down to room temperature, the products were separated by filtration, washed with distilled water and absolute ethanol several times, and then dried in an oven at 60 °C for 12 h. The product was denoted as S80.

The spherical porous $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \le x \le 0.6$) catalysts, referred to as LSMF (X) ($0 \le X \le 0.6$), were prepared by the molten salt method, using the synthesized hierarchical porous δ-MnO_2 microspheres as a template. A mixture of $NaNO_3$ and KNO_3 with a molar ratio of 1.5:1 was adopted as the molten salt. Stoichiometric amounts of $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$, as-synthesized MnO_2 and $Fe(NO_3)_3 \cdot 9H_2O$ were well mixed and ground in an agate mortar for 20 min. The nitrate and as-synthesized MnO_2 to molten salt molar ratio was of 1:15. Then, in order to decide the optimal calcination temperature, the $LaMn_{0.8}Fe_{0.2}O_3$ samples were heated at different temperatures (450, 550 and 650 °C) with a heating rate of 5 °C/min for 4 h, respectively denoted as S450, S550 and S650. After cooling to room temperature in air, the products were immersed into deionized water in a beaker to transfer the product into an aqueous solution for the subsequent separation and purification. The remnant molten salts were removed from the products by washing with hot deionized water several times until there was no white precipitate on the surface. The synthesized products were finally dried at 80 °C for 12 h. The $La_{1-x}Sr_xMn_{0.8}Fe_{0.2}O_3$ ($0 \le x \le 0.6$) catalysts were synthesized at the optimal calcination temperature to investigate the effect of Sr^{2+} doping on the catalytic activity for CO oxidiation.

2.2. Material characterization

Powder X-ray diffraction (XRD) patterns were obtained using a D/max-RB type X-ray diffractometer with a step size of 0.02° and Cu K_α radiation (λ = 0.15418 nm). The 2θ scan range was 10°–80°. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded on a Nicolet 6700 spectrometer (Thermo, USA) using KBr pellets in the wavenumber range of 4000–400 cm^{-1}. Scanning electron microscope (SEM) images were obtained on a JSM-IT300 electron microscope (JEOL, Japan). Field emission SEM (FESEM) and transmission electron microscope (TEM) analysis as well as the corresponding selected area electron diffraction (SAED) patterns were conducted on a Zeiss Ultra Plus-43-13 (German) and JEM-2100F electron microscope (JEOL, Japan), respectively. The specific surface area (A_{BET}) and porosity were determined by nitrogen adsorption isotherms at –196 °C using a Micromeritics ASAP 2020 M sorption analyzer (USA). The Brumauer-Emmett-Teller (BET) model was applied for specific surface area determination and the Barrett-Joyner-Halanda (BJH) model was used for porosity characterization using the adsorption branches of the