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Hierarchically porous $LaFeO_3$ perovskite prepared from the pomelo peel bio-template for catalytic oxidation of NO

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ABSTRACT

In this paper, pomelo peel was used as biological template to obtain hierarchically porous $LaFeO_3$ perovskite for the catalytic oxidation of NO to NO_2. In addition, X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption–desorption analyses, X-ray photoelectron spectra (XPS), NO temperature-programmed desorption (NO-TPD), oxygen temperature-programmed desorption (O_2-TPD) and hydrogen temperature-programmed reduction (H_2-TPR) were used to investigate the micro-structure and the redox properties of the hierarchically porous $LaFeO_3$ perovskite prepared from pomelo peel biological template and the $LaFeO_3$ perovskite without the biological template. The results indicated that the hierarchically porous $LaFeO_3$ perovskite successfully replicated the porous structure of pomelo peel with high specific surface area. Compared to the $LaFeO_3$ perovskite prepared without the pomelo peel template, the hierarchically porous $LaFeO_3$ perovskite showed better catalytic oxidization of NO to NO_2 under the same conditions. The maximum NO conversions for $LaFeO_3$ prepared with and without template were 90% at 305 °C and 76% at 313 °C, respectively. This is mainly attributed to the higher ratio of Fe^{4+}/Fe^{3+}, the hierarchically porous structure with more adsorbed oxygen species and higher surface area for the hierarchically porous $LaFeO_3$ perovskite compared with the sample prepared without the pomelo peel template.

1. Introduction

With the rapid growth in the number of vehicles, the increasing amount of nitrogen oxides (NO_x) exhausted from the diesel engines inevitably causes environmental problems and harms human health [1]. Nowadays, the lean NO_x trap (LNT) and selective catalytic reduction (SCR) technologies are two of the most promising methods to solve the NO_x problem [2,3]. For the former technology, NO is oxidized to NO_2 firstly, then adsorbed on the catalysts as nitrates and finally reduced into N_2 and H_2O under lean conditions [4]. For the SCR technology, NO is converted into NO_2 partially and then reduced by NH_3 with the formation of N_2 [5]. In the two technologies, the oxidation of NO to NO_2 is a vital step for NO_x removal [6]. Nowadays, although noble metal-based catalysts are commonly used for NO oxidation, their application is limited due to the high cost and poor thermal durability. It is desirable to develop low-cost catalysts with good thermal stability and catalytic activity.

Recently, perovskite complex oxides have been reported as alternatives for noble metal catalysts in the catalytic oxidation of NO, due to their excellent thermal stability, low cost and flexible compositions [7]. The perovskite has a crystal structure in the form of ABO_3. The A site is usually a rare earth or alkaline earth cation, whereas the B site represents a transition metal cation [8]. For the catalytic NO oxidation reaction, considerable attention has been paid to Lanthanum-based perovskite oxides catalysts among which $LaMnO_3$ and $LaCoO_3$ showed better catalytic activity for NO oxidation than $LaFeO_3$ [9]. Compared to $LaMnO_3$ and $LaCoO_3$, $LaFeO_3$ is promising in the long term application at higher temperature due to its preferable thermal stability and lower phase formation temperature [10].

Usually, $LaFeO_3$ prepared by conventional method has low surface area and nonporous structure, which limits its catalytic performance. The template method is an effective way to get high surface area and exquisite porous structure. Among the numerous templates, biological templates have received significant interests owing to the low cost, large specific surface area, well-defined morphology and environmental friendly feature. For example, Li et al. [11] synthesized porous $LaFeO_3$

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through a sol–gel nanocasting method from a cotton cloth template, which displayed excellent catalytic performance for CO oxidation. Song and coworkers [12] have fabricated SnO_2 with porous structure using pollen grains as templates, which showed excellent gas sensing properties.

Pomelo peels, as agricultural by-products, are distributed widely in the world. Pomelo peels are thick, which can be divided into the outer exocarp, the middle mesocarp and the inner endocarp. The pore sizes increase from the exocarp to the endocarp. Considering the low cost, abundant resources, porous structure and good adsorption of metal ions, we have previously synthesized hierarchically porous $LaFeO_3$ from the pomelo peel template through citric acid method. It was found that pomelo-peel-templated $LaFeO_3$ could eliminate NO and CO efficiently [13].

In the present research, ethylene glycol is used as the solvent based on the previous researches [14,15]. Furthermore, we explored the application of pomelo peel templated $LaFeO_3$ in the catalytic oxidation of NO. The physicochemical properties of hierarchically porous $LaFeO_3$ were evaluated. The aim of the present study is to investigate the effect of pomelo peel template on the crystal structure, microstructure, oxidation states of ions on the surface, reducibility and catalytic performance for NO oxidation.

2. Materials, preparation and characterization

2.1. Catalyst preparation

Pomelo fruits (*Citrus maxima* (Burm.) Merr. cv. Guanxiyou) used in this work were purchased from a local market. Analytical grade chemicals ($Fe(NO_3)_3{\cdot}9H_2O$, $La(NO_3)_3{\cdot}nH_2O$(MW~324.92) and ethylene glycol) were purchased from Sinopharm Chemical Reagent Co., Ltd (China). $LaFeO_3$ with porous structure was prepared from pomelo peels templates with ethylene glycol as solvent. The mesocarp of fresh pomelo peels was pretreated as described in our pervious work [13]. In the following stage, 0.024 mol $La(NO_3)_3{\cdot}nH_2O$ and 0.024 mol $Fe(NO_3)_3{\cdot}9H_2O$ were dissolved in 54 mL distilled water under stirring until the nitrate salt dissolved completely. Then, 6 mL ethylene glycol was added to the solution. After stirring for 3 h at room temperature, pomelo peels were soaked in the above solution for 24 h. Finally, the precursor was fired at 600 °C for 3 h, followed by drying at 50 °C in the air. The sample was denoted as L1. The compared $LaFeO_3$ powder was prepared using the same method without adding template and this product was refered as L_{ref}.

2.2. Catalyst characterization

The crystal structure of samples was characterized using a Bruker D8 Focus X-Ray Diffractometer (Bruker Corporation, Germany) with Cu K_α radiation from 10 to 90°. The average crystallite sizes were calculated using the Scherrer formula: $D = 0.89\lambda/\beta\cos\theta$. High-purity silicon powder was used to measure the instrumental broadening and the Cauchy correction was used to remove the instrument broadening to obtain the true crystal broadening. Cu kα_2 lines were corrected by the Rachinger correction method, which assumes the intensity of the Cu kα_2 as half as that of Cu kα_1. K was a shape factor, which was used for the calculation via the Scherrer function. The integral line width was used in the Scherrer formula to calculate d_{XRD} of the peak. Scanning electron microscope (Hitachi SU-70) measurement was used to characterize the morphologies of samples. The specific surface areas and pore structures of the two samples were measured using a Micromeritics ASAP 2020 instrument. X-ray photoelectron spectra (XPS) were performed on the Thermo Fisher Scientific ESCALAB 250Xi instrument with a monochromatic Al Kα X-ray source (Energy 1486.6eV). Hydrogen temperature-programmed reduction (H_2-TPR) was carried out in a quartz tube reactor equipped with a thermal conductivity detector (TCD). Prior to the TPR, 100 mg samples were pretreated at 550 °C for 1 h under a flow (50 mL/min) of 8% O_2/Ar. After cooling to room temperature, the samples were heated up to 900 °C at a rate of 10 °C/min under 5%H_2/Ar. Oxygen temperature-programmed desorption (O_2-TPD) was carried out on Micromeritics Autochem II 2920. The catalyst (100 mg) was pretreated in an 8% O_2/He (50 mL/min) stream at 550 °C for 1 h. After cooling to room temperature, a He flow was introduced for 1 h. Then the samples were heated from room temperature to 900 °C at a rate of 10 °C/min. FT-IR spectra was conducted by Nicolet 6700 spectrometer in the range of 400–4000 cm^{-1}.

2.3. Catalytic test

The catalytic activities of the samples (0.3 g diluted with 1.5 mL quartz sands, 40–60 mesh) for NO oxidation were performed in the fixed-bed reactor (i.d. = 9 mm) of a catalyst evaluation device (Tianjin Xianquan Company WFSM-3060) at atomspheric pressure. The reactant mixture of 400 ppm NO/8% O_2 with balanced N_2 was fed into the catalysts. The total flow rate was 450 mL/min, corresponding to a gas hourly space velocity (GHSV) of about 12,000 h^{-1}. The catalysts were pretreated in the air (250 mL/min) at 550 °C for 1 h before test and then cooled down to room temperature. The temperature increased from room temperature to 480 °C at a rate of 2 °C/min. The outlet gas stream was analyzed by an on-line infrared flue gas analyzer (Gasboard-3000, Quartet Optical Technology Co., Ltd., Wuhan, China). The NO conversion was calculated by the following equation:

$$XNO(\%) = 100 \times \frac{[NO]_{in} - [NO]_{out}}{[NO]_{in}}$$

where $[NO]_{in}$ and $[NO]_{out}$ were the conversions of the NO inlet gas and outlet gas, respectively. The stability test was performed under the same conditions as the above test at 300 °C for 72 h.

3. Results and discussion

3.1. Crystal structure

The crystal structure and phase information of the two samples are shown in Fig. 1. The diffraction peaks of two samples were in good agreement with JCPDS card No. 37-1493, which was attributed to $LaFeO_3$ perovskite phase with orthorhombic structure. No other phases such as lanthanum oxide or ferric oxide were observed in the XRD patterns. The average crystallite sizes of L_{ref} and L1 were estimated from the three major peaks of 32.2°, 46.1° and 57.4° using the Scherrer formula: $D = 0.89\lambda/\beta\cos\theta$ [16]. The calculated average crystallite sizes of L_{ref} and

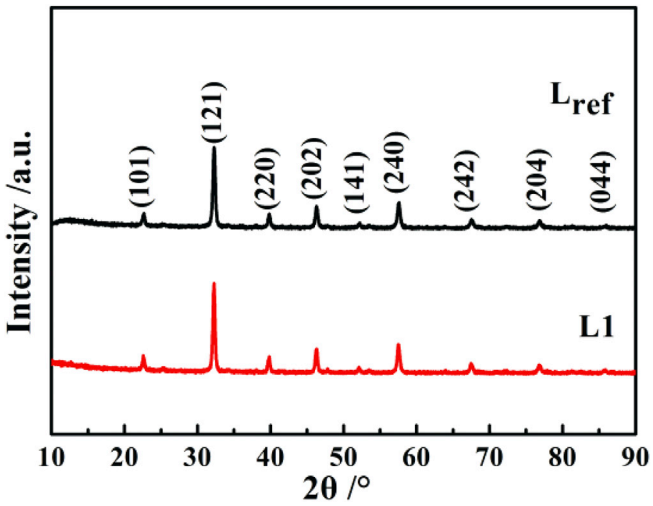

Fig. 1. The XRD patterns of the L1 and L_{ref}.