Chinese Journal of Catalysis 34 (2013) 1811–1815

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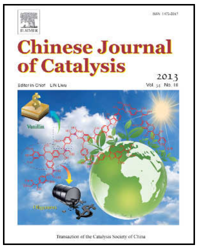

Communication

Perovskite hollow nanospheres for the catalytic wet air oxidation of lignin

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ARTICLE INFO

Article history:
Received 10 July 2013
Accepted 16 August 2013
Published 20 October 2013

Keywords:
Perovskite-type oxide
Lignin
Catalytic wet air oxidation
High catalytic activity
Low leaching

ABSTRACT

A urea-assisted solvothermal-calcination method was used to prepare $LaFe_xMn_{1-x}O_3$ and $La_{0.9}Sr_{0.1}MnO_3$ hollow nanospheres, and their crystal phase, morphology, and specific surface area properties were analyzed by X-ray diffraction, transmission electron microscopy, and nitrogen adsorption-desorption isotherms. These materials were then evaluated as catalysts for the catalytic wet air oxidation (CWAO) of lignin, and showed much better catalytic performance than perovskite prepared by the traditional sol-gel method. The structure of the hollow nanospheres has been suggested as the reason of this higher catalytic activity. For the CWAO reaction at 120 °C and 0.2 MPa O_2, the conversion of lignin was greater than 80% after 1 h. Analysis of the ions leaching from the material following the completion of the reaction showed that the catalysts were very stable under the reaction conditions because of their perovskite phase structure.

Fossil fuels have been used by humans for thousands of years. With an increasing sense of sustainability, it has been realized that non-renewable resources, such as coal and oil, will be completely exhausted at some point in the future, and that the development of alternative energy sources is therefore urgently required. As a renewable and abundant recourse that can be used to produce energy and fuels, biomass has thus become the focus of intense research activity in recent years [1–3]. Lignin is an important component of biomass and has a natural reserve ranking that is second only to cellulose. Globally, plants produce about 50 billion tons of lignin a year by photosynthesis. The main industrial source of lignin is the effluent from paper manufacturing, which provides about 50 million tons of lignin every year. To date, however, only a limited amount of lignin has been efficiently used with only 5% of the lignin potentially available being used in commercial applications of low value, such as concrete additive [4] or low-grade fuel [5]. In most developing countries, lignin is still a wasted resource, which is directly discharged or even burnt. From the perspectives of environment concern and energy efficiency, the effective conversion of lignin is of great significance.

Lignin is a natural polymer composed predominantly of three primary units, including 4-propyl-phenol, 2-methoxy-4-propyl-phenol, and 2,6-dimethoxy-4-propyl-phenol. These three so-called “monolignols” are also known as p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively. These three units can be converted to the three aromatic aldehydes vanillin, syringaldehyde and *p*-hydroxybenzaldehyde, respectively, which are widely used to manufacture food additives, deodorants, air fresheners, herbicides, and pharmaceuticals [6–8]. Researchers working with lignin generally consider catalytic wet air oxidation (CWAO) to be a good method for the oxidation decomposition of lignin. This method has several advantages, including mild conditions, good selectivity, and

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This work was supported by the National Natural Science Foundation of China (21003121 and 21076211).
DOI: 10.1016/S1872-2067(12)60691-3 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 34, No. 10, October 2013

short reaction times [9,10]. The products of lignin CWAO can either be categorized as gases, liquids, or solids. The gas products generally consist of CO, CO_2, and a variety of different hydrocarbons, whereas the solid product is mainly char adhering to the surface of the catalyst. In contrast, the liquid products generally consist of small organic molecules (e.g., formic acid, acetic acid, formaldehyde, and acetaldehyde), monomeric aromatic aldehydes, and oligomers. Among the latter two, aromatic aldehydes are considered to be high value-added chemicals, while oligomers also possess considerable economic value as fuel additives [11,12].

Among the catalysts for CWAO reactions, noble metal and transition metal-based catalysts have been the most widely studied. Deng et al. [13–15] recently prepared perovskite-type oxides (with the chemical formula ABO_3) using the citric acid sol-gel method and suggested that these ABO_3 materials could potentially be used as catalysts for the CWAO of lignin. Compared with the high cost of noble metals and collateral contaminations caused by transition metal ions, the affordability and stability properties of perovskites have placed them in a promising position in terms of their potential application for the conversion of lignin. This particular type marterials, however, are usually prepared via processes that involve high-temperature crystallization stages, which can lead to a significant reduction in the specific surface area. In our previous work [16], a urea-assisted solvothermal method was developed to synthesize perovskite-type hollow nanospheres. These materials with relatively high specific areas and excellent mass transfer properties are highly effective for the CWAO of phenol. In this study, we prepared a series of $LaFe_{1-x}Mn_xO_3$ (nominally, x = 0, 0.25, 0.5, 0.75, 1.0) and $La_{0.9}Sr_{0.1}MnO_3$ hollow nanospheres using a similar method. The resulting materials were evaluated as catalysts for the CWAO of lignin, and the results showed that both types of material provided high catalytic performances and stability.

All of the reagents used were purchased as the analytical reagent grade. The method used to synthesize the hollow nanospheres was described in our previous publication [16]. Briefly, ethanol (2 mL), H_2O (2 mL), and ethylene glycol (8 mL) were mixed to form a ternary solvent system, and then citric acid ($C_6H_8O_7{\cdot}H_2O$, 10 mmol), urea (45 mmol), and P123 (1.0 g) were added, followed by $La(NO_3)_3{\cdot}6H_2O$ (LN), $Fe(NO_3)_3{\cdot}9H_2O$ (FN), $Sr(NO_3)_2$ (SN), and 50 wt% $Mn(NO_3)_2$ solution (MN) as listed in Table 1. The resulting mixture was then stirred for 5 h at room temperature before being transferred into a 70 mL autoclave and heated at 100 °C for 48 h. The precursors obtained were subsequently washed sequentially with deionized water and absolute ethanol before being centrifuged at 12000 ×*g* for 10 min and then dried in an oven at 60 °C. The resulting dried precursors were then grounded and calcined at 600 °C for 4 h, with a temperature ramp of 0.5 °C/min to produce the perovskite hollow nanospheres (denoted as PHSs hereafter). For comparison, we also used a traditional citric acid method to prepare $LaMnO_3$ (CALM) material.

Table 1
Nominal formulas and abbreviations of the PHSs materials and the corresponding amounts of the nitrate reactants.

Nominal formula	Abbreviation	Amounts of nitrate reactants (g)			
		LN	SN	FN	MN
$LaFeO_3$	LFHS	1.08	0	1.01	0
$LaFe_{0.75}Mn_{0.25}O_3$	LFMHS-1	1.08	0	0.75	0.56
$LaFe_{0.5}Mn_{0.5}O_3$	LFMHS-2	1.08	0	0.50	1.12
$LaFe_{0.25}Mn_{0.75}O_3$	LFMHS-3	1.08	0	0.25	1.68
$LaMnO_3$	LMHS	1.08	0	0	2.28
$La_{0.9}Sr_{0.1}MnO_3$	LSMHS	0.97	0.05	0	2.28

A Tecnai G2 Spirit electron microscope (FEI, USA) was used to record transmission electron microscope (TEM) images of the materials. A PANalytical X'Pert PRO powder X-ray diffractometer (the Netherlands) was used to record the powder X-ray diffraction (XRD) patterns of the materials using Cu K_α radiation. A Micromeritics ASAP 2010 apparatus (USA) was used to obtain the N_2 adsorption-desorption isotherms of the materials, and the Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface areas. An inductively coupled plasma optical emission spectrometer (ICP-OES, IRIS Intrepid II XSP, Thermo, USA) was used to determine the La/Fe/Mn/Sr ratios of the materials synthesized. Thermogravimetric (TG) analyses were conducted on a SETSYS 16/18 thermal analyzer (SETARAM, France).

Lignin samples were obtained by the alkali extraction of the solid residue derived from the hydrochloric acid catalyzed hydrolysis of corn stalks [17]. Prior to the oxidation reaction, lignin was dissolved in NaOH solution (2 mol/L) at a concentration of 10 g/L. A portion (20 mL) of the resulting lignin solution was then loaded into a 70-mL stainless steel autoclave together with 0.02 g of the catalysts (1 g/L). The autoclave was then purged before being filled with O_2 to an initial pressure of 0.2 MPa. Under a fixed stirring rate, the reactor was heated to 100 °C within 30 min and then heated to 120 °C within 30 min. The temperature was then held at 120 °C for 1 or 2 h.

Upon completion of the CWAO reactions, the product solutions were centrifuged at 12000 ×*g* for 10 min to separate the catalysts, which were used for TG analysis to determine the yield of char. The pH values of the solutions were then adjusted using concentrated HCl to pH 1–2. The solutions were then extracted with chloroform to extract the products (aromatic aldehydes), until the chloroform layer became colorless. The solutions were then centrifuged again, and the resulting liquid supernatants were analyzed by ICP-OES to investigate the extent of any leaching from the hollow nanospheres, before being evaporated to dryness to allow for the dry weight of the oligomers to be determined. The combined extracts were treated with $NaHCO_3$ and dried with anhydrous Na_2SO_4 before being diluted with chloroform to 50 mL. An Agilent Varian 320-MS TQ mass spectrometer (USA) was used to analyze the products. An Agilent 6890N Network Gc System gas chromatography system (USA) equipped with a HP-5 column (30 m × 0.32 mm × 0.25 μm) was used to determine the quantity of vanillin, c_{vanillin} (g/L). Given that c_{lignin} = 10 g/L, the yield of vanillin can be calculated as follows:

$$\text{Yield}_{\text{vanillin}} = (c_{\text{vanillin}} \times 50\ \text{ml} / c_{\text{lignin}} \times 20\ \text{mL}) \times 100\%$$
$$= 0.25c_{\text{vanillin}} \times 100\%$$

A total organic carbon (TOC) analyzer (Elementar) was used to determine the other catalytic parameters. Thus, on the basis