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Short communication

A dual-functional $MnO_2/La_{0.6}Sr_{0.4}MnO_3$ composite catalyst: high-efficiency for elemental mercury oxidation in flue gas

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ABSTRACT

A dual-functional $MnO_2/La_{0.6}Sr_{0.4}MnO_3$ composite catalyst was prepared and tested for the oxidation of elemental mercury (Hg^0) present in the coal-derived flue gas. The thus derived Hg^{2+} can then be removed from the flue gas via current pollution control devices. The MnO_2 appears as the active component for the oxidation of elemental mercury, whereas the superior magnetic property of $La_{0.6}Sr_{0.4}MnO_3$ catalytic component makes the catalyst recoverable from the fly-ash mixture. The Hg^0 oxidation efficiency was found larger than 80% in the temperature range of 150–300 °C and at a GHSV of 120,000 mL/ (g h), whereas the catalytic efficiency could be further increased to > 95% in the presence of 5 ppm HCl in the flue gas.

1. Introduction

Mercury is highly toxic heavy metal that causes serious human health problems even at low concentrations due to its bioaccumulation and low boiling point [1–3]. Among the anthropogenic sources of mercury emissions, coal burning is the most significant one [4,5]. There exist three forms of mercury in the coal-derived flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particle-bound mercury (Hg^P) [6,7]. Hg^0 is the major mercury species formed and the most difficult to be controlled because of its high volatility and low solubility in water [8,9]. Many technologies have been developed so far to remove Hg^0 from the flue gas, such as catalytic oxidation, sorbent injection and others [10–14]. Adsorption technology is limited for wide applications owing to the high cost, poor capacity, narrow operation temperature range, and slow regeneration rates [12]. Conversely, Hg^{2+} (oxidized by Hg^0) is facile to be removed through currently available pollution control devices. Therefore, catalytic oxidation could be more feasible to some practical applications [11].

During the process of Hg^0 oxidation, the catalytic activity suffers from the fly ash, which commonly exists in the coal-derived flue gas. The surface of the catalyst is easily covered by fly ash, restricting the contact between Hg^0 and the catalyst, thus reducing the activity of the catalyst for Hg^0 oxidation. One of the solutions is to prepare composite materials with high catalytic activity and magnetic properties. The used catalyst can then be recovered from the fly ash by applying a magnetic separation process. In recent years, more and more researches are focused on the development of such magnetic catalysts [15–19]. Zhao et al. [15] prepared a composite catalyst by loading cobalt oxides on magnetospheres. This Co-MF catalyst attained approximately 95% Hg^0 removal efficiency at 150 °C and could be recycled. Yan et al. [16–18] introduced magnetic iron oxides to a series of transition metal oxides (TiO_2, V_2O_5 and MnO_2). The obtained catalysts expressed excellent Hg^0 removal performance and magnetic properties. Xu and co-workers synthesized magnetic zeolite with supported silver nanoparticles, which showed outstanding Hg^0 oxidation activity and recyclability [19]. Accordingly, the combination of a high-efficiency catalytic material and magnetic component appears as a potential method for Hg^0 oxidation and its removal from industrial flue gas streams. However, the preparation procedures of the active component and magnetic material need to be performed separately, which is visibly complicated and rather expensive. Hence it is necessary and important to develop a facile method to prepare such composite catalytic materials.

$La_xSr_{1-x}MnO_3$ perovskite is not a good catalyst in Hg^0 oxidation given the fact that its surface is preferentially occupied by La and Sr elements, which are not considered as catalytically active components [20]. However, $La_xSr_{1-x}MnO_3$ is a superior magnetic material at room temperature, when $0.3 \le x \le 0.6$ [21]. If the surface La and Sr cations could be selectively removed, exposing highly active Mn species, the obtained catalyst may exhibit both good Hg^0 oxidation activity and magnetic properties.

Herein, a facile route to prepare $MnO_2/La_{0.6}Sr_{0.4}MnO_3$ (MnO_2/LSMO) composite catalyst by an acid treatment method is reported

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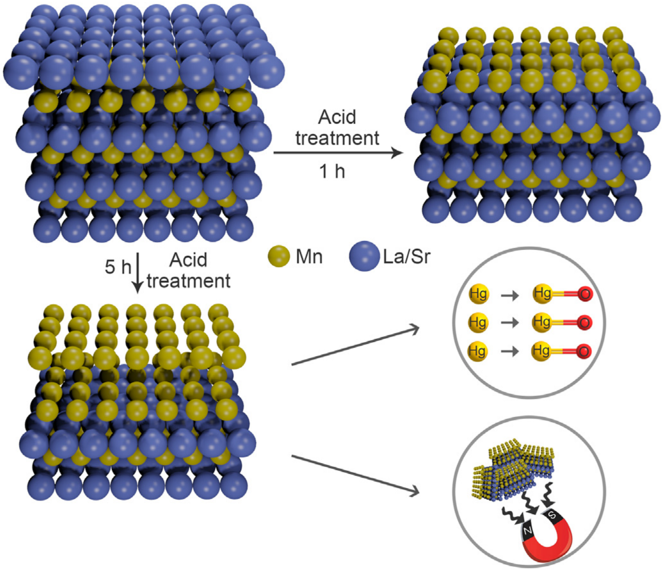

Scheme 1. Synthesis route of the composite MnO_2/LSMO catalyst.

(Scheme 1). The LSMO cubic crystal was synthesized by the hydrothermal method. After 1 h acid treatment, the surface La and Sr elements were partially removed, leaving behind plenty of Mn cations on the surface of the LSMO sample. When the treating time increased to 5 h, more La and Sr elements on the surface as well as inside of LSMO crystal were removed and MnO_2/LSMO structure formed. This composite catalyst possesses dual-functional characteristics, shows outstanding Hg^0 oxidation activity and could be separated from fly ash mixture after applying a magnetic separation process.

2. Experimental

2.1. Chemicals and materials

The chemicals used for the catalysts preparation were all of A.R. grade. Lanthanum nitrate hydrate ($La(NO_3)_3$ $6H_2O$), strontium nitrate ($Sr(NO_3)_2$), potassium permanganate ($KMnO_4$) and nitric acid (HNO_3) were purchased from Sinopharm Chemical Reagent Co., Ltd. Manganese chloride tetrahydrate ($MnCl_2$ $4H_2O$) were obtained from Alfa Aesar. All chemicals were used without further purification.

2.2. Catalyst preparation

$La_{0.6}Sr_{0.4}MnO_3$ sample (denoted as LSMO) was synthesized by a traditional hydrothermal method [22]. $La(NO_3)_3$ (0.40 M), $Sr(NO_3)_2$ (0.40 M), $KMnO_4$ (0.36 M) and $MnCl_2$ (0.56 M) aqueous solutions were first prepared. Next, 21 mL of $La(NO_3)_3$, 14 mL of $Sr(NO_3)_2$ and 9 mL of $KMnO_4$ were mixed together under stirring. Then 40 g of KOH solid were added into the mixture slowly to avoid vigorous reaction. Next, 18.3 mL of $MnCl_2$ were added drop wise under continuous stirring. The obtained mixture solution was then transferred into a stainless steel lined Teflon vessel, sealed and heated at 260 °C for 48 h. After cooled to room temperature, the solid was washed with abundant deionized water and dried at 60 °C. In order to account for structural stability issues of the catalyst, the latter was calcined at 450 °C for 3 h before all the characterization and catalytic activity tests. The final product is coded LSMO.

The LSMO powder was subsequently immersed in dilute HNO_3 solution. The treating time was either 1 h or 5 h. The solid was then filtered and washed by deionized water until the pH became neutral. At last, the samples were dried at 60 °C overnight. All the catalysts samples were calcined at 450 °C for 3 h before all the characterization and catalytic activity tests. The corresponding products are denoted LSMO-1 h and LSMO-5 h, respectively.

2.3. Catalyst characterization studies

The crystal structure of the three samples was characterized by powder X-ray diffraction (XRD). The morphology and the elemental composition of each catalyst were obtained by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS). The surface atom-% composition and oxidation state of elements on the surface of the solids were determined by X-ray photoelectron spectroscopy (XPS). The BET surface area was acquired via N_2 adsorption at -196 °C. Hydrogen temperature-programmed reduction (H_2-TPR) and oxygen temperature-programmed desorption (O_2-TPD) experiments, and saturation magnetization measurements were also conducted according to specific procedures and apparatus described in the Supporting Information.

2.4. Catalytic activity studies

The Hg^0 oxidation activity of the catalysts was investigated in a fixed-bed quartz microreactor (i.d. = 6 mm). The vapor phase Hg^0 was generated by passing a N_2 gas-flow through a permeation tube holding liquid Hg. The total gas flow was 200 mL/min, containing 120 μg/m^3 of Hg^0, 20% of O_2, 5 ppm of HCl (when needed), and N_2 (balance gas). The catalyst mass used was 0.1 g (40–60 mesh) providing a GHSV of 120,000 mL/ (g h). The concentration of Hg^0 was measured by an RA-915 M cold vapor atomic absorption spectroscopy mercury analyzer (Lumex Co., Ltd., Russia). Further details are described in the Supporting Information.

3. Results and discussion

3.1. Powder XRD - crystal structure

Powder XRD patterns of the three samples in the 2θ range of 20–80° are shown in Fig. S1 (Supporting Information). By comparing with the XRD patterns of the standard LSMO sample (JCPDS PDF# 51–0118), it can be found that the LSMO and LSMO-1 h samples are of high crystallization and exhibit the characteristic diffraction peaks (22.9°, 32.7°, 40.3°, 46.9°, 52.9°, 58.3°, 68.7°, 73.3° and 78.1°) of typical perovskite phase [23]. For the LSMO-5 h sample, the intensity of the diffraction peaks appears slightly weaker, suggesting that the crystallinity of the sample was slightly lower after the acid treatment for 5 h. Furthermore, some new peaks at 37.2° and 42.6° appear, which might be assigned to the characteristic peaks of γ-MnO_2 (JCPDS PDF # 14-0644) [24–26]. This result indicates that a MnO_2/LSMO composite structure was formed after 5 h of acid treatment. The change of the crystal structure could be envisioned by the schematic structures presented in Scheme 1. When the treating time was 1 h, the crystal structure of LSMO-1 h sample did not change. Since the treating time was short, only a small amount of La and Sr elements on the surface of the solid catalyst were removed. As a result, the XRD pattern of the solid still expressed the characteristic peaks of LSMO. When the treating time increased to 5 h, some new XRD peaks assigned to MnO_2 phase were observed (LSMO-5 h sample). The reason is that more La and Sr elements on the surface as well as inside of the LSMO crystal were removed with increasing treating time in HNO_3. The remaining structural elements were able to generate stable MnO_2 crystals, in agreement also with our previous work [24].

3.2. Morphology, chemical composition, and BET area

SEM and EDS measurements were conducted to elucidate morphology and chemical composition changes after the acid treatment of the LSMO solid. The results are shown in Fig. S2 (Supporting