



Remarkable effect of the incorporation of titanium on the catalytic activity and SO₂ poisoning resistance of magnetic Mn–Fe spinel for elemental mercury capture

Shijian Yang^a, Yongfu Guo^a, Naiqiang Yan^{a,*}, Daqing Wu^b,
Hongping He^b, Jiangkun Xie^a, Zan Qu^a, Jinping Jia^a

^a School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dong Chuan Road, Shanghai 200240, PR China

^b Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, 511 Kehua Street, Wushan, Tianhe District, Guangzhou 510640, PR China

ARTICLE INFO

Article history:

Received 9 July 2010

Received in revised form 2 November 2010

Accepted 5 November 2010

Available online 12 November 2010

Keywords:

Fe–Ti–Mn spinel
Elemental mercury
Capture capacity
Magnetic catalyst
SO₂ poisoning

ABSTRACT

Titanium (Ti) was incorporated into non-stoichiometric Mn–Fe spinel to improve its performance for elemental mercury capture. Although the number of Mn⁴⁺ cations on (Fe₂Ti_xMn_{1-x})_{1-δ}O₄ was less than that on the corresponding (Fe_{3-x}Mn_x)_{1-δ}O₄, the number of usable cation vacancies for elemental mercury oxidization obviously increased. As a result, elemental mercury capture by Mn–Fe spinel was generally promoted by the incorporation of Ti. Furthermore, SO₂ mainly reacted with ≡Fe^{III}–OH and few Mn⁴⁺ cations on the surface reacted with SO₂ at lower temperatures (100–150 °C), so SO₂ poisoning resistance improved at lower temperatures due to the incorporation of Ti. Especially, (Fe₂Ti_{0.5}Mn_{0.5})_{1-δ}O₄ showed an excellent capacity (4.2 mg g⁻¹) for elemental mercury capture in the presence of a high concentration of SO₂ at 150 °C. Meanwhile, (Fe₂Ti_{0.5}Mn_{0.5})_{1-δ}O₄ with the saturation magnetization of 30.6 emu g⁻¹ can be readily separated from the fly ash using magnetic separation, leaving the fly ash essentially free of catalyst and adsorbed HgO. Therefore, nanosized (Fe₂Ti_{0.5}Mn_{0.5})_{1-δ}O₄ may be a promising candidate catalyst for elemental mercury capture.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

Coal-fired utility boilers are currently the largest single-known source of anthropogenic mercury emissions. In China, approximately 38% of the emission of mercury comes from coal combustion [1]. In the United States, about one-third of the 150 tons of mercury emitted comes from coal-fired utility boilers [2]. In addition to particulate-bound mercury (Hg^p), elemental mercury (Hg⁰) and oxidized mercury (Hg²⁺) are also present as gaseous mercury in the flue gas from coal-fired utilities [3,4]. Particulate-bound mercury, which is associated with the fly ash, is effectively removed from the plant effluent by particulate control devices. Meanwhile, oxidized mercury is effectively removed from the flue gas by wet scrubbing or SO₂ control devices [3]. Because elemental mercury is not soluble in water, it is difficult to remove by currently available removal devices [5]. Therefore, elemental mercury is the major species emitted in the flue gas from coal-fired utilities [6]. In China, the total mercury concentrations in the flue gas from coal combustion

boilers were in the range of 1.92–27.15 μg m⁻³, with elemental mercury accounting for 66–94% of the total mercury and being the dominant species emitted to the atmosphere [7].

Many technologies have been investigated to remove elemental mercury from the flue gas, including sorbents, catalysts, and photochemical oxidations [8–21]. Catalysts for elemental mercury oxidization studied to date mainly fall into one of three groups: carbon-based catalysts (powdered activated carbon injection, PAC), selective catalytic reduction (SCR) catalysts, and metals and metal oxides [2]. The involved oxidants are mainly chlorine and oxygen. In China, the chlorine content in feed-coal varies from 63 to 318 mg kg⁻¹, which is much lower than the average value of US coals (628 mg kg⁻¹) [7], so catalytic oxidation of elemental mercury using gaseous oxygen in the flue gas as the oxidant is an economical method for elemental mercury control. Furthermore, the oxidized mercury formed (HgO or Hg₂O) is in a solid state at <300 °C, so it adsorbs on the catalyst and is then removed from the flue gas [22,23].

Mercury-catalyst materials are currently extremely restricted in their applications for at least four reasons: catalyst recovery, removal of toxin from industrial waste, interference of the chemical composition in the flue gas, and cost of operation [24]. First, the spent catalyst for this particular application is generally collected as a mixture with greater than 99% of ultrafine fly ash particles by

* Corresponding author. Tel.: +86 21 54745591; fax: +86 21 54745591.
E-mail addresses: yangshijiangsq@163.com (S. Yang), nqyan@sjtu.edu.cn (N. Yan).

particulate control devices such as fabric filters or electrostatic precipitators (ESPs) [25]. It will be extremely difficult and impractical to reclaim the spent catalyst from the fly ash mixture for regeneration. Second, if the spent catalyst is not effectively removed from the fly ash mixture, the fly ash will be contaminated by mercury-loaded catalyst. If the contaminated fly ash is used as a cement additive, the toxin may be released in the cement plant during the calcination process. Third, the chemical composition in the flue gas (for example SO₂ and H₂O) may significantly affect elemental mercury oxidization by catalysts [17,18,26–29]. SO₂ gas molecules may compete with gaseous elemental mercury for the activity sites. The concentration of SO₂ in the real flue gas is about 10⁴–10⁵ times that of elemental mercury (v/v) [27,29]. Furthermore, SO₂ can react with metals and metal oxides to form a surface sulfate species [30,31], which may make them inefficient for elemental mercury oxidization. Fourth and mostly importantly, the catalyst must be cheap and easy to use.

The separation of catalyst from the fly ash can be solved by the magnetic property of catalyst material [24]. A magnetic sorbent MagZ-Ag⁰ was once investigated for elemental mercury capture [25,32], but it was too expensive to apply in the larger coal-fired power plants. Previous researches have reported that maghemite (γ-Fe₂O₃) had some ability for elemental mercury oxidization [2,22]. γ-Fe₂O₃ is one of the simplest spinel ferrites. Spinel ferrites are of great fundamental and technological importance due to their structural, electronic, magnetic and catalytic properties [33]. Furthermore, an interesting feature of spinel ferrites is the possibility to replace iron cations by other metal cations while maintaining the spinel structure [34]. The physicochemical properties of spinel ferrites are strongly dependent on the site, nature and amount of metal incorporated into the structure. Ti⁴⁺ in the γ-Fe₂O₃ structure can strongly improve the ability for elemental mercury oxidization, but the presence of a high concentration of SO₂ can result in a severe interference. Furthermore, the incorporation of Mn⁴⁺ into the γ-Fe₂O₃ structure to form non-stoichiometric Mn–Fe spinel can promote elemental mercury oxidization, but a high concentration of SO₂ still shows a moderate negative effect.

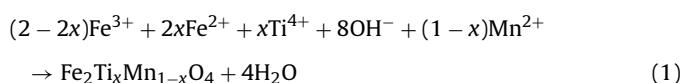
Previous researches demonstrated that Fe–Ti–Mn mixed oxides showed a promising application in environmental catalysis [35–39]. Here, titanium was incorporated into the structure of non-stoichiometric Mn–Fe spinel to improve its catalytic ability for elemental mercury oxidization and to suppress the interference of a high concentration of SO₂. A series of (Fe₂Ti_xMn_{1-x})_{1-δ}O₄ were synthesized using a co-precipitation method and characterized using X-ray diffraction (XRD), N₂ adsorption/desorption isotherms, transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and magnetization measurement. Then, a packed-bed reactor system was used to preliminarily evaluate their performance for elemental mercury capture.

2. Experimental

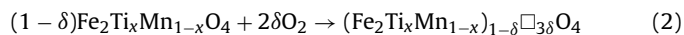
2.1. Sample preparation

Nanosized Fe₂Ti_xMn_{1-x}O₄ was prepared using a co-precipitation method. Suitable amounts of titanium tetrachloride, ferrous sulfate, ferric trichloride, and manganous sulfate were dissolved in distilled water (cation concentrations ≈ 0.3 mol L⁻¹).

This mixture was added to an ammonium hydroxide solution leading to an instantaneous precipitation according to the following reaction:



During the reaction, the system was continuously stirred at 800 rpm. According to Ti, Mn and Fe solubility constants, the precipitate composition was the same as it in the liquid phase. The particles were then separated by centrifugation at 4500 rpm for 5 min and washed with distilled water. After 3 washings, the particles were collected and dried in a vacuum oven at 105 °C for 12 h. After the thermal treatment at 400 °C under air for 3 h, (Fe₂Ti_xMn_{1-x})_{1-δ}O₄ was obtained according to the following reaction:



(Fe₂Ti_xMn_{1-x})_{1-δ}O₄ had a structure similar to that of Fe₂Ti_xMn_{1-x}O₄. It differed from Fe₂Ti_xMn_{1-x}O₄ in that all of the Fe cations were in the trivalent state and most of the Mn cations were in the trivalent/tetravalent state. Meanwhile, cation vacancies (□) were incorporated to compensate for the oxidation of Fe²⁺ and Mn²⁺ [34]. With the increase of Ti content (i.e. x) in Fe₂Ti_xMn_{1-x}O₄, the amount of Fe²⁺ obviously increased and the amount of Mn²⁺ decreased (shown in Reaction (1)). As a result, the cation vacancies in (Fe₂Ti_xMn_{1-x})_{1-δ}O₄ resulting from the oxidation of Fe²⁺ obviously increased with the increase of Ti content.

Furthermore, Ni was incorporated into the structure of Mn–Fe spinel as a comparison.

2.2. Sample characterization

Crystal structure was determined using an X-ray diffraction-meter (BRUKER-AXS) between 20° and 70° at a step of 2° min⁻¹ operating at 35 kV and 30 mA using Cu Kα radiation. BET surface area was determined using a nitrogen adsorption apparatus (Micromeritics ASAP 2010 M+C). The sample was outgassed at 200 °C before BET measurement. Saturation magnetization was determined using a vibrating sample magnetometer (VSM, Model JDM-13) at room temperature. TEM image was performed on a JEOL JEM-2010 TEM. The micrographs were obtained in the bright-field imaging mode at an acceleration voltage of 200 kV. XPS (Thermo ESCALAB 250) was used to determine the binding energies of Fe 2p, Mn 2p, Ti 2p, S 2p, O 1s and Hg 4f with Al Kα (hν = 1486.6 eV) as the excitation source. The C 1s line at 284.6 eV was taken as a reference for the binding energy calibration.

2.3. Elemental mercury capture

The assembly used for elemental mercury capture consisted of an elemental mercury permeation tube, a packed-bed reactor, a cold vapor atomic absorption spectrometer (CVAAS) and an online data acquisition system (shown in Fig. 1). A flow of air passed through the permeation tube and yielded a stable concentration of elemental mercury. A temperature control device was employed to keep the reactor at the desired temperatures. The gas containing elemental mercury first passed through the empty tube, and then entered the CVAAS to determine the baseline. When the concentration of elemental mercury had fluctuated within ±10% for more than 30 min, the gas was diverted to the catalyst bed for the test. An exact amount of catalyst was inserted in the middle of the column reactor and then packed with quartz wool to support the catalyst layer and avoid its loss. It was demonstrated that quartz wool has no ability for elemental mercury capture.

To preliminarily estimate the performance for elemental mercury capture, (Fe₂Ti_xMn_{1-x})_{1-δ}O₄ was first tested under air. The inlet gas contained about 1.30 mg Nm⁻³ (±20%) of elemental mercury and 20–30 g Nm⁻³ of H₂O (uncontrolled) with a feed of 12 L h⁻¹. For each test, the time was about 10 h, the catalyst mass was 30.0 mg (the gas space velocity was about 1.2 × 10⁶ h⁻¹) and the reaction temperatures varied from 100 to 400 °C.

Download English Version:

<https://daneshyari.com/en/article/6502779>

Download Persian Version:

<https://daneshyari.com/article/6502779>

[Daneshyari.com](https://daneshyari.com)