



Elemental mercury (Hg^0) removal from containing SO_2/NO flue gas by magnetically separable $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4/\text{H}_2\text{O}_2$ advanced oxidation processes



Changsong Zhou^a, Lushi Sun^{a,*}, Anchao Zhang^b, Chuan Ma^a, Ben Wang^a, Jie Yu^a, Sheng Su^a, Song Hu^a, Jun Xiang^a

^a State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, 430074 Wuhan, Hubei, China

^b School of Mechanical and Power Engineering, Henan Polytechnic University, 454000 Jiaozuo, Henan, China

HIGHLIGHTS

- Magnetically separable catalyst $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4$ could improve $\cdot\text{OH}$ radicals yield.
- $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4/\text{H}_2\text{O}_2$ has high activity for mercury removal containing SO_2/NO .
- The stability of $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4$ catalyst showed some activity decay.
- Redox pairs of the catalyst play a dominant role for $\cdot\text{OH}$ production.

ARTICLE INFO

Article history:

Received 9 February 2015

Received in revised form 20 March 2015

Accepted 23 March 2015

Available online 30 March 2015

Keywords:

Elemental mercury

Removal

$\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4$

Advanced oxidation processes

Flue gas

ABSTRACT

Elemental mercury (Hg^0) removal from containing SO_2/NO simulated flue gas was systematically investigated, making use of $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4/\text{H}_2\text{O}_2$ advanced oxidation processes. The effectiveness follows from the hydroxyl radicals ($\cdot\text{OH}$) with the inherent character of non-selectivity and high activity, which can oxidize and remove Hg^0 under solvent free conditions. The magnetically separable $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4$ catalyst was prepared by chemical co-precipitation method, and characterized by the techniques of inductively coupled plasma-atomic emission spectrometry (ICP-AES), scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) surface area, vibrating sample magnetometer (VSM), and electron spin resonance (ESR). The performance of Hg^0 removal in $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4/\text{H}_2\text{O}_2$ solutions was carried out, and the effects of the most relevant operational parameters, such as solution pH values, catalyst dosage, and solution temperature, of the advanced oxidation processes were specifically studied. A high efficiency of Hg^0 removal was obtained under optimum operational parameters (about 96% with 0.5 M H_2O_2 at weak acid medium). The optimal pH value, catalyst dosage, and solution temperature are found at about 6, 0.6 g L⁻¹, and 50 °C, respectively. The presence of SO_2 in simulated flue gases has little effect on Hg^0 removal, while NO intensively promotes Hg^0 removal in advanced oxidation reactions. The activity of $\text{Fe}_{2.45}\text{Ti}_{0.55}\text{O}_4$ catalyst undergoes decay to some extent after three consecutive experiments have been conducted.

© 2015 Elsevier B.V. All rights reserved.

1. Introduction

The trace element mercury (Hg^0) has gradually become a leading concern due to its high toxicity, volatility and bioaccumulation. Mercury can be absorbed by the human body through diet and skin contact, and has severe damage to chromosomes and kidneys, as well as central nervous and respiratory systems. Coal-fired power

plants have been considered to be one of the major sources of anthropogenic mercury emission due to mercury enrichment in coal [1]. The US Environmental Protection Agency (EPA) proposed to permanently reduce mercury emission from coal-fired flue gases, and mercury emissions are expected to be reduced by 69% when this proposal is fully implemented.

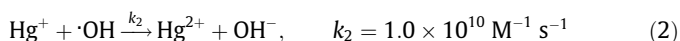
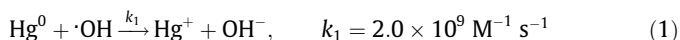
Studies have been conducted to develop efficient and low-cost treatments to solve Hg^0 pollution. Several methods, such as dry sorbent injection [2] and bamboo-activated carbon [3], have been extensively investigated to control Hg^0 emission. But most of them

* Corresponding author. Tel.: +86 27 87542417; fax: +86 27 87545526.

E-mail address: sunlushi@hust.edu.cn (L. Sun).

are difficult to implement due to the complexity of sorbent preparation and low Hg⁰ removal efficiency. Some researchers focus on the oxidation of Hg⁰ to Hg²⁺ in a wet scrubber reactor. Renata et al. [4] investigated Hg⁰ removal in a limestone-based wet flue gas desulfurization (WFGD) scrubber and significant enhancement was obtained. Xu et al. [5] studied the aqueous phase oxidation of Hg⁰ by potassium persulfate catalyzed by Ag⁺ and Cu²⁺ in a glass bubble column reactor. Many other additives [6,7] have been investigated to enhance Hg⁰ oxidation. However, the use of these additives to oxidize Hg⁰ is limited by high costs and poor sustaining activity. Secondary pollution, such as the dissolved metal ions, should also be considered after Hg⁰ treatment.

Recently, many researchers found that the advanced oxidation processes have been widely studied to solve environmental pollution [8]. The effectiveness follows from the highly activity and non-selectivity of hydroxyl radicals ($\cdot\text{OH}$) production during these processes, which can oxidize and remove numerous pollutants. Sommar et al. [9] investigated the reactivity of $\cdot\text{OH}$ radicals toward Hg⁰ in gas phase and found that Hg⁰ oxidation by $\cdot\text{OH}$ could performed rapidly as shown in Eqs. (1) and (2).



Guo et al. [10] studied NO removal by FeSO₄/H₂O₂ reactions in a lab-scale bubbling reactor and found that NO can be oxidized and nitrate is detected in solution after oxidation occurs. Dennis et al. [11] added homogeneous additive to WFGD systems to study Hg⁰ oxidation and significant enhancement was obtained. However, the homogeneous catalysis has two significant disadvantages due to a certain concentration of Fe ions in the solution. Firstly, Fe ions accelerate the decomposition of H₂O₂ to H₂O and O₂ that do not go through the $\cdot\text{OH}$ radical producing pathway [12]. Secondly, it is difficult to recycle Fe ions at the end of oxidation reaction [13]. Thus far, many investigations have been conducted to develop heterogeneous catalysts of advanced oxidation processes, such as MnFeO₄ [14], Al₂O₃/SiO₂ [15], activated carbon [13], etc, to remove various pollutants in sewage treatment field, due to their extremely high specific surface area as well as quick and stable surface reaction.

It is known that magnetite is the only material that both contains Fe²⁺ and Fe³⁺ species in its structure to improve $\cdot\text{OH}$ radical production in advanced oxidation processes, and Fe³⁺ species can be easily reduced through electron transfer in semiconductor oxide from bulk or surface Fe²⁺ [16]. Furthermore, the introduction of a transition metal, such as Ti, Cr, or Ni, into magnetite structure to substitute iron species can strongly improve the activity of heterogeneous catalyst in Fenton-like reactions, particularly the use of Ti-doped magnetite [14,17]. However, it has been noticed that the synthesis of present heterogeneous catalysts are mainly concentrated on solving wastewater pollution, such as organic contaminants. Rarely studies focus on investigating Hg⁰ oxidation from coal-fired flue gas by heterogeneous catalyst, which can produce highly active $\cdot\text{OH}$ radicals. In our previous study, a series of Fe_{3-x}Ti_xO₄ (0 < x < 0.76) catalysts were prepared to facilitate Hg⁰ removal from non-acid flue gas [18]. The effect of H₂O₂ concentration and Ti-content in Fe_{3-x}Ti_xO₄ on Hg⁰ removal as well as the reaction kinetic model was preliminarily studied. But many factors affect Hg⁰ removal, the specific role of Ti species in catalyst structure during advanced oxidation processes remains unclear. The purpose of this further follow-on work is to systematically investigate the effect of other relevant operational parameters (such as SO₂/NO concentration, solution pH values, catalyst dosage, and reaction temperature) on Hg⁰ removal under the condition of H₂O₂ = 0.5 M and x = 0.55. Hg⁰ oxidation pathway by $\cdot\text{OH}$ radicals was confirmed through electron spin resonance (ESR) technique.

Furthermore, the magnetic property, stability, and recyclability of Fe_{2.45}Ti_{0.55}O₄ in advanced oxidation processes were also studied.

2. Experiments

2.1. Catalysts synthesis

All materials were analytical grade and were used as outlined in our previous work [18]. Deionized water was ultrasonic treatment for 30 min before used in order to remove oxygen. Iron sulfate heptahydrate and titanium chloride were dissolved in diluted hydrochloric acid solution, make sure the pH value of the mixed solution was less than 1.0 to prevent any Fe²⁺ or Ti⁴⁺ hydroxide precipitation. The total concentration of Fe²⁺ and Ti⁴⁺ was 0.8 M. Then 1 ml of hydrazine hydrate was dropped into the solution to prevent the oxidation of Fe²⁺. Adequate amount of sodium hydroxide and sodium nitrate were dissolved in deionized water. Predetermined volume of the alkaline solution was poured into a three-neck flask after filling with N₂ for 15 min, at the same time, the alkaline solution in the three-neck flask was heated. When the temperature of the alkaline solution went up to 65 °C, a stoichiometric volume of metal ion solution was added into the three-neck flask while vigorous stirring at a rate of 500 rpm. After dropping the metal ions solution, the precipitate was kept at 65 °C for 2 h. During the procedure, N₂ was passed through the flask to prevent the oxidation of Fe²⁺ in the solution. The magnetic particles were cooled at room temperature and separated by centrifugation at 3000 rpm for 3 min followed by washed at least 5 times with deionized water and ethanol. Finally, the particles were dried in vacuum oven at 80 °C for 24 h.

2.2. Characterization

Fe and Ti contents in Fe_{2.45}Ti_{0.55}O₄ catalyst were determined by a highly efficient inductively coupled plasma-atomic emission spectrometry (ICP-AES) with a detection limit of 0.1–1.0 ppb. Fe_{2.45}Ti_{0.55}O₄ morphology was observed through scanning electron microscopy (SEM) with a VEQA-3SOU scanning electron microscope. BET surface areas of the catalyst were determined using a nitrogen (N₂) adsorption apparatus (ASAP-2020, Micromeritics). Fe_{2.59}Ti_{0.41}O₄ magnetic property was studied using a Lakeshore 7404 vibrating sample magnetometer (VSM) at room temperature, and the hysteresis loop was obtained by varying magnetic field between ± 15 kOe. Radical signals were confirmed using a Bruker X-Band A-200 (Germany) electron spin resonance (ESR) spectrometer.

2.3. Experimental apparatus and methods

Fig. 1 shows the schematic arrangement of experimental apparatus. The device consists of simulated flue gas cylinders (N₂, CO₂, O₂, SO₂, NO), mass flowmeters, mercury vapor generator, absorptive reactor, and mercury vapor analyzer. The total flow was adjusted to 0.8 L min⁻¹. Mercury permeation tube (VICI Metronics, US) was placed in a sealed U shaped quartz tube immersed in a temperature controlled water bath. Hg⁰ concentration was controlled by adjusting the temperature of water bath and N₂ flow rate passing through the mercury permeation tube. A semi-continuous VM3000 vapor-phase mercury analyzer (Mercury Instruments GmbH, Germany) was used to detect the inlet and outlet Hg⁰ concentration. Before each test was conducted, the mixed gases were diverted to blank reactor without H₂O₂ reagent, meanwhile the VM3000 was used to determine the baseline of Hg⁰ concentration. The inlet Hg⁰ concentration C₀ was kept at 30 μg m⁻³, 45 μg m⁻³, 60 μg m⁻³, and 75 μg m⁻³ (fluctuated

Download English Version:

<https://daneshyari.com/en/article/6584884>

Download Persian Version:

<https://daneshyari.com/article/6584884>

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