



# The cooperation of Fe–Sn in a $\text{MnO}_x$ complex sorbent used for capturing elemental mercury



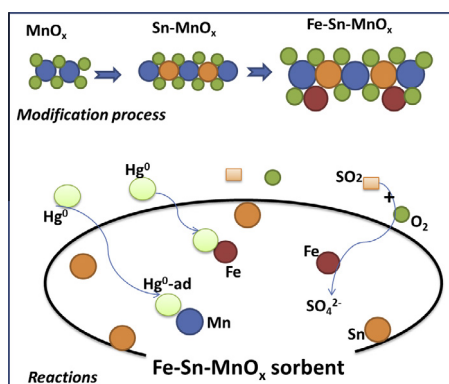
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## HIGHLIGHTS

- The Fe–Sn–Mn sorbent exhibited better performance on  $\text{Hg}^0$  removal than pure  $\text{MnO}_x$ .
- The Fe–Sn–Mn sorbent had a wide temperature window when used.
- Fe and Sn were helpful for enlarging the BET surface areas of pure  $\text{MnO}_x$ .
- Fe could protect manganese active sites from  $\text{SO}_2$  poison.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 23 April 2014

Received in revised form 14 August 2014

Accepted 1 October 2014

Available online 18 October 2014

### Keywords:

Manganese

Elemental mercury ( $\text{Hg}^0$ )

Fe–Sn modification

Sorbent

## ABSTRACT

Manganese oxide ( $\text{MnO}_x$ ) was an effective sorbent for capturing elemental mercury ( $\text{Hg}^0$ ) from coal-fired flue gas, but its usage was markedly limited by its lower porosity, lower temperature range, and sensitivity to sulfur dioxide ( $\text{SO}_2$ ). Tin (Sn) and iron (Fe) were tested for their ability to enhance  $\text{MnO}_x$  sorbent, and the Fe–Sn– $\text{MnO}_x$  complex exhibited excellent performance as a novel mercury sorbent.  $\text{SnO}_2$  appeared to be inert for  $\text{Hg}^0$  adsorption, but it could act as a suitable support to disperse  $\text{MnO}_x$ , which helps to produce more activated sites. The BET surface areas increased by approximately 10 times, and there was an increase of 3 times the  $\text{Hg}^0$  adsorption capacity. The available temperature range of the sorbent can be extended from 100 to 300 °C. Specifically, the presence of Fe can significantly improve the  $\text{SO}_2$  resistance of the sorbent. Furthermore, the mechanism of adsorption and  $\text{SO}_2$  tolerance at high temperatures was investigated by in situ Diffuse Reflectance Infrared Fourier Transform spectra (DRIFTS); Fe reacted with  $\text{SO}_2$  when  $\text{O}_2$  was present, which could protect manganese active sites from being poisoned by  $\text{SO}_2$ .

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## 1. Introduction

The Minamata Convention on Mercury was adopted in October of 2013, and it is an international treaty aimed at protecting

human health and the environment from anthropogenic mercury emissions. Mercury has long been known to be toxic to humans and other organisms. The famous Minamata disease was a large-scale public health crisis because of its toxic effects [1]. According to data calculated by Pirrone et al., approximately 2320 tons of mercury is emitted by human activities annually. Approximately 35% of the emissions result from fossil fuel combustion [2]. China

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is by far the largest consumer of coal in the world, and approximately 70% of China's electrical generation comes from coal-fired power plants. Chinese anthropogenic sources account for more than 25% of total global mercury emissions according to Feng et al. [3]. Researchers have estimated that mercury emissions from anthropogenic sources will increase in several years [4–6]. Therefore, preventing the release of mercury from coal-fired power plants will continue to be a challenge.

Mercury is released into exhaust gas as elemental mercury ( $\text{Hg}^0$ ), oxidized mercury ( $\text{Hg}^{2+}$ ) and particulate bound mercury ( $\text{Hg}^{\text{p}}$ ). At present,  $\text{Hg}^{2+}$  and  $\text{Hg}^{\text{p}}$  can generally be effectively removed by air pollution control devices (APCDs) [7–9]. However,  $\text{Hg}^0$  is the most difficult to capture because of its high volatility and low solubility in water. This type of mercury can circulate in the atmosphere for years, and its toxic effects have a global-scale impact [10]. Many efforts had been made to remove  $\text{Hg}^0$  from flue gas; there are two major methods for  $\text{Hg}^0$  capture [11–13] as follows: (1) Oxidation, which transforms  $\text{Hg}^0$  to  $\text{Hg}^{2+}$ . (2) Adsorption, transforms  $\text{Hg}^0$  to  $\text{Hg}^{\text{p}}$ . Through the oxidation method, soluble  $\text{Hg}^{2+}$  matters were carried into desulfurizing solution or desulfurization gypsum along with flue gas. A large gypsum product ( $8.5 \times 10^6 \text{ t a}^{-1}$ ) was derived from wet flue gas desulfurization (WFGD) systems. However, approximately 55% of the mercury was lost during manufacturing processes, which led to mercury secondary contamination in the atmosphere [14–16].  $\text{Hg}^{\text{p}}$  can be collected through the adsorption method by fabric filter (FF) or electrostatic precipitator (ESP). This mercury can be enriched by high temperature separation or magnetic separation technology. Thus, the adsorption method seems to be an effective and green technology.

Activated carbon injection (ACI) technology is a simple and effective method for  $\text{Hg}^0$  capture. Unfortunately, this technology has been not widely used in Chinese coal-fired power plants because of its high cost [7,17–20]. Furthermore, the low chlorine concentration in coal limits the technology for being widely used, and the chlorine concentration has been suggested as a factor that clearly affects  $\text{Hg}^0$  removal efficiency from flue gas. Numerous studies have been performed to find an economic and efficacious sorbent as an alternative. Chemically modified active carbon, fly ash, Ca-based sorbents and metal oxide sorbents were often used in labs or in full scale research [19,21–24]. Because of its high removal efficiency and stability, metal oxide has attracted attention from investigators. Manganese oxide ( $\text{MnO}_x$ ) sorbent seems to be a very good candidate. This compound has been used for removing  $\text{Hg}^0$  from flue gas and as a selective catalytic reduction (SCR) catalyst in the past [25]. Yan et al. reported that an  $\text{MnO}_x$  support on inert alumina ( $\alpha\text{-Al}_2\text{O}_3$ ) could be used for  $\text{Hg}^0$  removal at lower temperatures (100–200 °C). However, the effects of sulfur dioxide ( $\text{SO}_2$ ) on  $\text{Hg}^0$  adsorption were remarkable [26]. Several metal elements were employed as dopants to modify the  $\text{MnO}_x$  sorbent and facilitate the removal efficiency of  $\text{Hg}^0$ . Wiatros-Motyka et al. reported that the  $\text{MnO}_x/\text{ZrO}_2$  sorbent adsorbs twice as much  $\text{Hg}^0$  as activated carbon, and the rate of  $\text{Hg}^0$  capture on the particle surface areas depends on the manganese content [27]. High surface area ceria-titania materials were used as supports for  $\text{MnO}_x$  for warm-gas  $\text{Hg}^0$  capture (175 °C), which also exhibited an excellent mercury capture capacity [28]. Experiments by Yang et al. showed that  $\text{Mn-Fe}_2\text{O}_3$  exhibited an excellent  $\text{Hg}^0$  removal capacity, and it had better performance for  $\text{SO}_2$  resistance than  $\text{MnO}_x$  [29]. Fe might be helpful for minimizing the infiltration of  $\text{SO}_2$  to the sorbent. However, the application of  $\text{MnO}_x$  was still markedly limited by this material's lower porosity, lower temperature range, and its sensitivity to  $\text{SO}_2$ .

Tin dioxide ( $\text{SnO}_2$ ) is usually regarded as an oxygen-deficient n-type semiconductor [30]. Our recent preliminary work indicated that Sn–Mn binary metal oxides could increase the BET surface areas. It can also be used within a broad temperature window

(100–300 °C). However,  $\text{SnO}_2$  had low  $\text{SO}_2$  resistance at high temperatures. The addition of Fe was used to enhance the  $\text{SO}_2$  resistance at high temperatures. With inspiration from these results and discussion, the objective of the present study is to investigate the cooperation of Sn and Fe modified  $\text{MnO}_x$  for  $\text{Hg}^0$  adsorption.

Herein, a series of Sn and Fe-doped  $\text{MnO}_x$  sorbents were prepared for  $\text{Hg}^0$  removal within a high temperature window (100–300 °C), and the  $\text{SO}_2$  impacts were also investigated in this study. The roles of Sn, Fe and  $\text{MnO}_x$  and the influence of  $\text{SO}_2$  were discussed, taking into account the results of BET, XRD, TEM and in situ Diffuse Reflectance Infrared Fourier Transform spectra (DRIFTS).

## 2. Experimental

### 2.1. Sorbent Preparation

The sorbents were prepared using a co-precipitation method. Suitable amounts of  $\text{Fe}(\text{NO}_3)_3$ ,  $\text{SnCl}_4$  and  $\text{Mn}(\text{NO}_3)_2$  were dissolved in distilled water. A stoichiometric amount of ammonia was added to the mixture as the precipitation agent under strong stirring for 2 h. For Fe–Sn– $\text{MnO}_x$  (Fe:Sn:Mn = 1:20:20), 20 mmol  $\text{SnCl}_4$ , 20 mmol  $\text{Mn}(\text{NO}_3)_2$  and 1 mmol  $\text{Fe}(\text{NO}_3)_3$  were dissolved in 100 ml of deionized water under stirring. Afterwards, 123 mmol of ammonia was added to the mixed solution under strong stirring for 2 h. The precipitate was then filtered and washed with deionized water three times to remove  $\text{Cl}^-$  from the water. Lastly, the precipitate was transferred to a muffle furnace and calcined at 500 °C for 5 h. All of the samples were ground to a 40–60 mesh size.

### 2.2. Sorbent characterization

Measurements of the BET surface areas were performed on a Quantachrome Nova 2200e Automated Gas Sorption system. All samples were degassed at 200 °C in a nitrogen flow prior to  $\text{N}_2$  physisorption at  $-196$  °C. The crystal structure was determined using powder X-ray Diffraction Patterns (XRD) (APLX-DUO, BRUKER, Germany), and the scanning range was from  $10^\circ$  to  $80^\circ$  with a scanning velocity of  $7^\circ \text{ min}^{-1}$  with Cu K radiation. The microstructure of the sorbent was analyzed by transmission electronic microscopy (TEM). The TEM image was created on a JEOLJEM-2010 TEM. The micrographs were obtained in bright-field imaging mode at an acceleration voltage of 200 kV. In situ DRIFT spectra were recorded on a Fourier transform infrared spectrometer (FTIR, Nicolet 6700) equipped with a smart collector and an MCT detector cooled by liquid  $\text{N}_2$ . Mass flow controllers and a sample temperature controller were used to simulate the real reaction conditions. Prior to each experiment, the sorbent was heated to the target temperature in  $\text{N}_2$ . And the component of flue gas ( $\text{O}_2$ ,  $\text{SO}_2$ ) was introduced in the simulate gas. The IR spectra were recorded by accumulating 100 scans at a resolution of  $4 \text{ cm}^{-1}$ .  $\text{H}_2$ -TPR experiment was performed on Chemisorp TPx 2920 instrument, the sorbents were degassed at 300 °C for 3 h under Ar atmosphere before  $\text{H}_2$ -TPR test, the reducing gas was 10% $\text{H}_2/\text{Ar}$ . Ion chromatography (EP-100) was used to detect  $\text{SO}_4^{2-}$  in the leachate, which was collected by washing the sorbent in ultrapure water after adsorption.

### 2.3. Elemental mercury capture

The process flow of the  $\text{Hg}^0$  capacity assessment system is depicted in Fig. A1. The experimental facility consisted of an  $\text{Hg}^0$  permeation tube, a fixed-bed reactor with a parallel blank tube, a cold vapor atomic absorption spectrometer (CVAAS) and an online data acquisition system. The  $\text{Hg}^0$  removal capacity of the sorbents (40–60 mesh) was measured in the fixed-bed quartz reactor under the following reaction conditions: 30 mg sorbent, 4%  $\text{O}_2$ , and 1.25

(±0.05) mg/m<sup>3</sup> of Hg<sup>0</sup>, all of which was balanced in N<sub>2</sub> with a total gas flow rate of 200 ml/min. To test the impact of the temperature on the Hg<sup>0</sup> adsorption performance, the experiments were performed within a temperature range from 100 to 300 °C. To test the influence of SO<sub>2</sub>, 500–1000 ppm of SO<sub>2</sub> were introduced into the gaseous influent through a mass flow controller, and the total flow rate was also balanced with N<sub>2</sub>. The Hg<sup>0</sup> concentrations of gaseous influent and effluent were continuously measured by a CVAAS (SG 921, Jiang fen Ltd., China), which was calibrated by a Lumex RA 915 + mercury analyzer.

To investigate the effects of the temperature and SO<sub>2</sub> concentration in the flue gas, the breakthrough curve areas for Hg<sup>0</sup> on Fe–Sn–MnO<sub>x</sub> sorbents during the test time (10 h or 20 h) was integrated and the adsorption capacities of Hg<sup>0</sup> were calculated according to Eq. (1).

$$Q = \frac{1}{m} \int_{t_2}^{t_1} (Hg_{in}^0 - Hg_{out}^0) \times f \times dt \quad (1)$$

where *Q* is the Hg<sup>0</sup> adsorption capacity, *m* is the mass of the sorbent in the fixed-bed, *f* denotes the flow rate of the influent, and *t*<sub>0</sub> and *t*<sub>1</sub> represent the initial and ending test time of the breakthrough curves.

### 3. Results and discussion

#### 3.1. Elemental mercury capture performance

In this work, prepared pure metal oxides and complex metal oxide sorbents for Hg<sup>0</sup> adsorption were tested using a fixed-bed experimental facility. Fig. 1 shows the Hg<sup>0</sup> adsorption capacity at different temperatures. Pure SnO<sub>2</sub> sorbent showed nearly no activity for Hg<sup>0</sup> capture at 100–300 °C. Pure FeO<sub>x</sub> also exhibited a low capacity. By contrast, pure MnO<sub>x</sub> had a higher adsorption capacity, and the Hg<sup>0</sup> capacity could reach approximately 2 mg/g at 100 °C. However, this capacity clearly decreased with the increasing temperature, and the capacity at 300 °C was only a quarter of the capacity at 100 °C.

To improve the Hg<sup>0</sup> capture performance of the MnO<sub>x</sub> sorbent, Fe and Sn were used for modification on the MnO<sub>x</sub> sorbent. The performances of Fe–MnO<sub>x</sub>, Fe–SnO<sub>2</sub>, Sn–MnO<sub>x</sub> and Fe–Sn–MnO<sub>x</sub> complex metal oxide sorbents are shown in Fig. 1. The molar ratio of Fe:Sn:Mn was 1:20:20 in each sorbent. With the Fe–MnO<sub>x</sub> sorbent, the doped Fe can increase the adsorption capacity, with an increase by approximately 50% at 100 °C. However, the Hg<sup>0</sup> adsorption capacity of Fe–MnO<sub>x</sub> still markedly decreased with the temperature

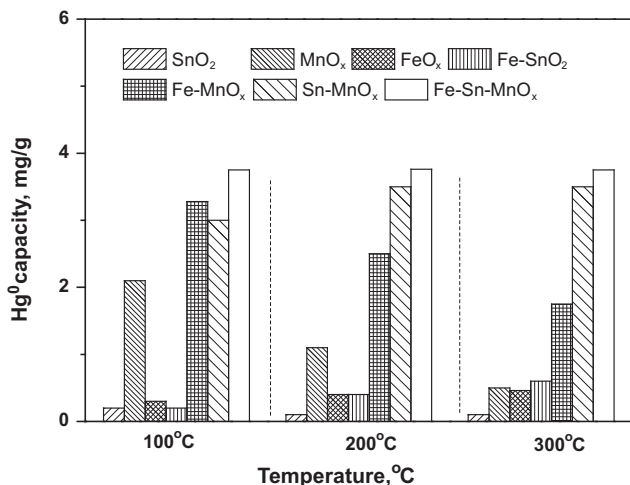


Fig. 1. Temperature impact on the Hg<sup>0</sup> adsorption capacity (10 h) of the prepared sorbents.

increase. In addition, the Fe–SnO<sub>2</sub> metal oxide sorbent displayed far less Hg<sup>0</sup> capture capacity in comparison with Fe–MnO<sub>x</sub>, but its capacity increased slightly as the temperature went up. The Sn–MnO<sub>x</sub> sorbent had a higher Hg<sup>0</sup> capacity compared with Fe–SnO<sub>2</sub> and Fe–MnO<sub>x</sub> sorbents, and it could reach approximately 3 mg/g at 100 °C. Moreover, the adsorption capacity of Hg<sup>0</sup> also increased slightly as the temperature rose. The Sn–MnO<sub>x</sub> sorbent displayed a wide temperature window for Hg<sup>0</sup> adsorption. Additionally, the Fe doped to Sn–MnO<sub>x</sub> further enhanced the Hg<sup>0</sup> adsorption capacity, and the Hg<sup>0</sup> adsorption capacity for Fe–Sn–MnO<sub>x</sub> increased by approximately 20–30% in comparison with Sn–MnO<sub>x</sub>. Fe–Sn–MnO<sub>x</sub> also had a wide temperature window for Hg<sup>0</sup> adsorption. Obviously, Sn played an important role in enhancing the high temperature activity. H<sub>2</sub>-TPR technology was employed to collect the reducing information during the temperature-programmed process. The results were shown in Fig. A2. Sn–Mn binary metal oxides appeared at 200–600 °C and the peaks turned to high temperature along with the increasing of Sn. The reducing peak of SnO<sub>2</sub> emerged at higher than 600 °C. It could indicate that adding Sn into MnO<sub>x</sub> expands the temperature window of MnO<sub>x</sub> sorbent.

Sorbents with different Fe contents were prepared and evaluated to investigate the Fe effect in Fe–Sn–MnO<sub>x</sub>. As shown in Fig. 2, the Hg<sup>0</sup> adsorption capacity (20 h) slightly decreases with the increased Fe concentration. An Fe molar percentage of 2–5% in the sorbent appeared to be enough for the modification (the molar ratio of Fe:Sn:Mn was 1:20:20 in the following section). Therefore, Mn was the primary active site for Hg<sup>0</sup> adsorption, Fe also had a capacity for Hg<sup>0</sup> to some extent, and Sn could improve the high temperature activity for Hg<sup>0</sup> capture.

#### 3.2. The physiochemical characterization of Fe and Sn modified MnO<sub>x</sub>

BET, XRD and TEM were employed for structural analysis to reveal the cooperative effects of Sn and Fe on MnO<sub>x</sub>. Table 1 summarizes the BET surface areas. The results show that the BET

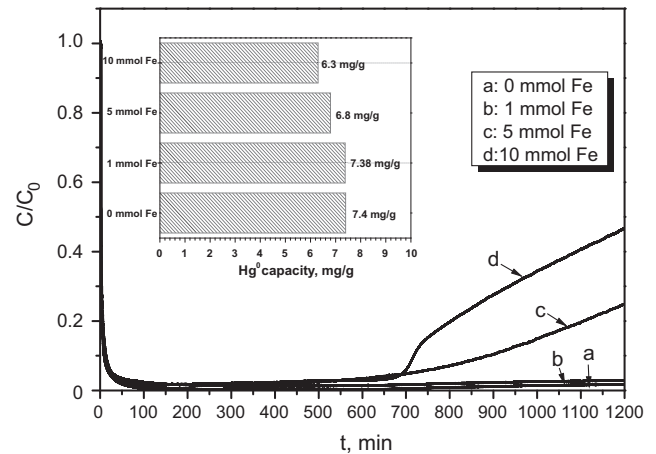
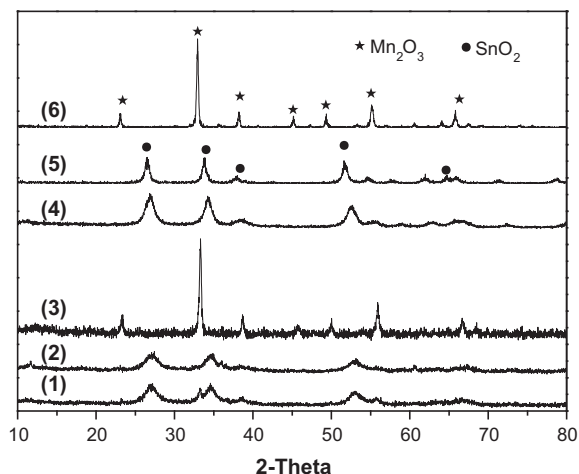


Fig. 2. The impact of different Fe concentrations on the Fe–Sn–MnO<sub>x</sub> sorbent for Hg<sup>0</sup> removal.

Table 1  
BET surface areas of prepared sorbents.

Sorbents	BET surface areas (m <sup>2</sup> /g)
SnO <sub>2</sub>	25.5
MnO <sub>x</sub>	5.3
FeO <sub>x</sub>	18.7
Sn–MnO <sub>x</sub>	53.9
Fe–SnO <sub>2</sub>	64.3
Fe–MnO <sub>x</sub>	21.9
Fe–Sn–MnO <sub>x</sub>	74.5

surface areas of pure  $\text{SnO}_2$ ,  $\text{MnO}_x$  and  $\text{FeO}_x$  were 25.2, 5.3 and 18.7  $\text{m}^2/\text{g}$ , respectively. With the addition of Sn to the  $\text{MnO}_x$ , the BET surface areas of Sn– $\text{MnO}_x$  were approximately two times larger than pure  $\text{MnO}_x$ , and they expanded to 53.9  $\text{m}^2/\text{g}$ . Upon adding approximately 2.5% Fe to Sn– $\text{MnO}_x$ , Fe–Sn– $\text{MnO}_x$  exhibited the largest BET surface areas among the prepared sorbents, reaching up to 74.5  $\text{m}^2/\text{g}$ . Such large surface areas could provide more active sites on  $\text{MnO}_x$  sorbents, which was beneficial for the adsorption. The BET surface areas of Fe– $\text{SnO}_2$  also reached as high as

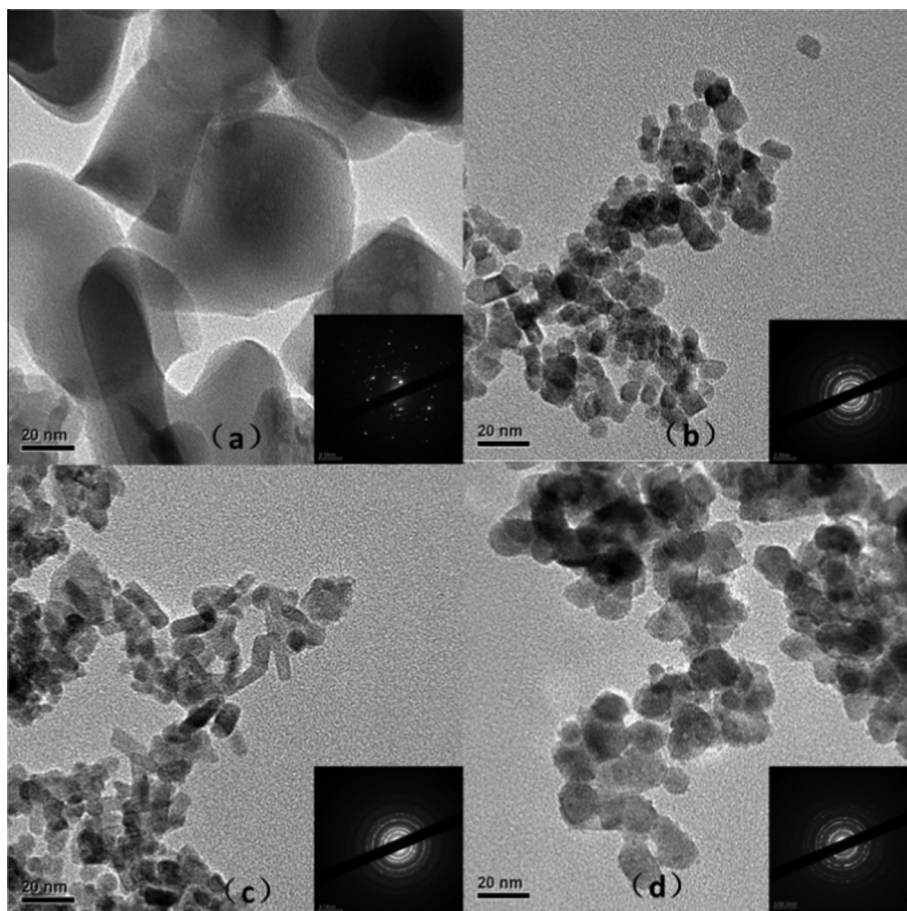


**Fig. 3.** The XRD patterns of the prepared sorbents. (1) Fe–Sn– $\text{MnO}_x$ ; (2) Sn– $\text{MnO}_x$ ; (3) Fe– $\text{MnO}_x$ ; (4) Fe– $\text{SnO}_2$ ; (5)  $\text{SnO}_2$ ; and (6)  $\text{MnO}_x$ .

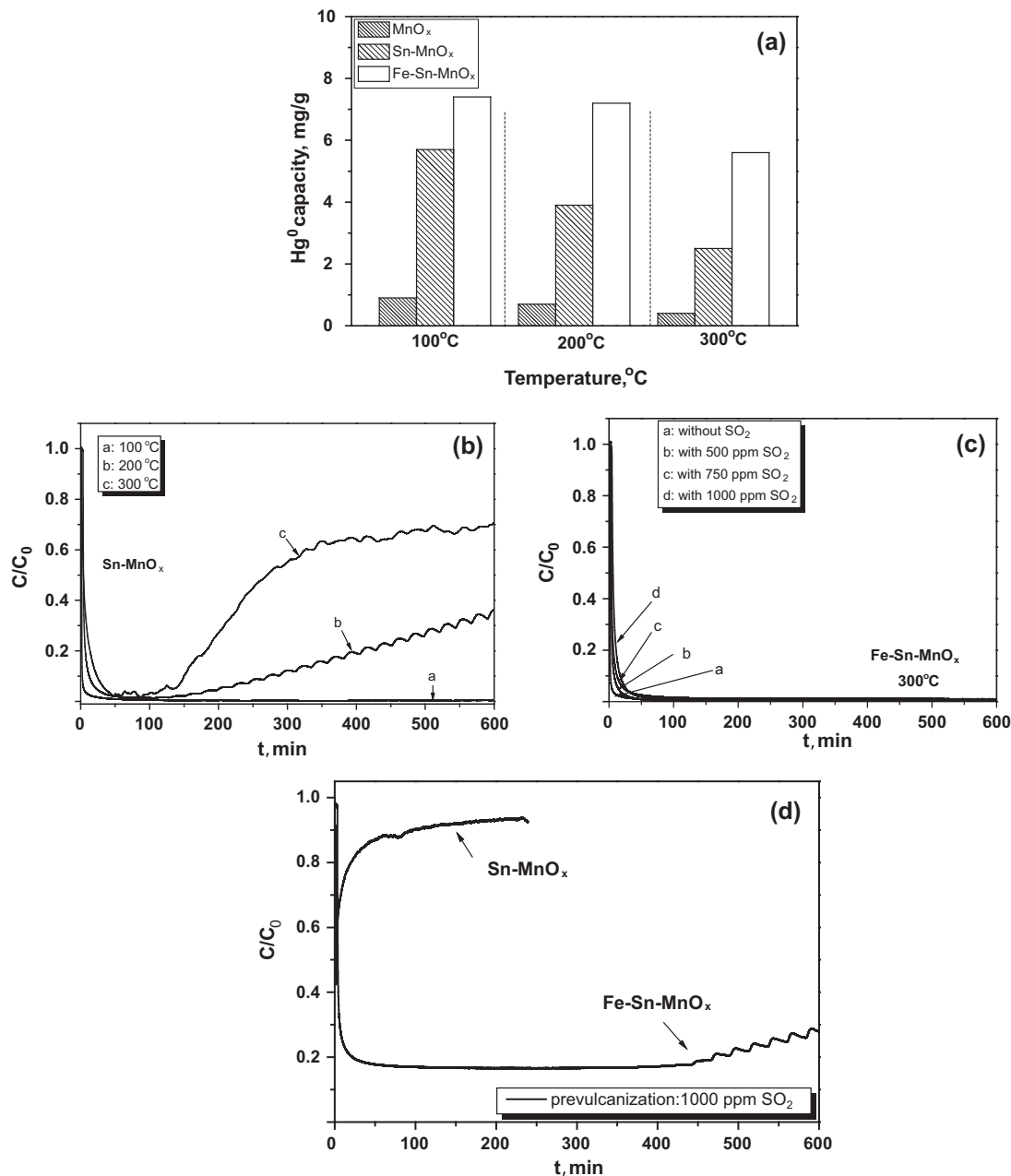
64.3  $\text{m}^2/\text{g}$ . This finding indicated that the existence state of  $\text{SnO}_2$  was greatly changed by adding Fe. However, the BET surface areas of the Fe– $\text{MnO}_x$  sorbents were only 21.9  $\text{m}^2/\text{g}$ . Therefore,  $\text{SnO}_2$  appeared to be an excellent support for dispersing Fe or Mn atoms, which would dramatically increase the BET surface areas for the sorbents.

Fig. 3 illustrates the XRD patterns of Fe–Sn– $\text{MnO}_x$ , Sn– $\text{MnO}_x$ , Fe– $\text{MnO}_x$ , Fe– $\text{SnO}_2$ , pure  $\text{SnO}_2$  and pure  $\text{MnO}_x$  metal oxides. The peaks at 23°, 33°, 38°, 50°, 56° and 67° for pure  $\text{MnO}_x$  were attributed to the  $\text{Mn}_2\text{O}_3$  structure (PDF#31-0825). The XRD pattern of Fe– $\text{MnO}_x$  had almost the same peaks. Fe–Sn– $\text{MnO}_x$ , Sn– $\text{MnO}_x$ , and Fe– $\text{SnO}_2$  all had the same peak at  $2\theta = 27^\circ$ ,  $34^\circ$ ,  $53^\circ$ , and  $67^\circ$ , respectively. The same peaks were also found in pure  $\text{SnO}_2$  patterns. This finding could definitely be attributed to the same crystal structure of  $\text{SnO}_2$  (PDF#41-1445). Therefore, most of the Mn atoms were doped into the crystal lattice of  $\text{SnO}_2$  and changed the lattice parameter, and employing such a small amount of Fe did not clearly affect the crystal structure of complex oxides [31]. Furthermore, the diffraction peaks of Fe–Sn– $\text{MnO}_x$ , Sn– $\text{MnO}_x$  and Fe– $\text{SnO}_2$  became broader in comparison with pure  $\text{SnO}_2$  peaks, so smaller particle sizes tended to form. The results were consistent with the BET data.

TEM was also employed to further study the morphology of the prepared sorbents. As shown in Fig. 4, the Fe– $\text{MnO}_x$  particles were much larger than the other sorbents. The size of the Fe– $\text{SnO}_2$ , Sn– $\text{MnO}_x$  and Fe–Sn– $\text{MnO}_x$  particles were all approximately 10–20 nm. In comparison with Sn– $\text{MnO}_x$  particles, evenly spherical particles could be observed for Fe–Sn– $\text{MnO}_x$ . This shape can provide more chances to form Mn active sites on these particles. Thus, in synthesizing the above results,  $\text{SnO}_2$  could serve as an



**Fig. 4.** TEM images of the prepared sorbents. (a) Fe– $\text{MnO}_x$ ; (b) Fe– $\text{SnO}_2$ ; (c) Sn– $\text{MnO}_x$ ; and (d) Fe–Sn– $\text{MnO}_x$ .



**Fig. 5.** The impact of SO<sub>2</sub> on the Hg<sup>0</sup> adsorption of the sorbents. (a) Hg<sup>0</sup> capacity in 20 h; (b) Sn-MnO<sub>x</sub>, SO<sub>2</sub> concentration: 500 ppm; (c) Fe-Sn-MnO<sub>x</sub>, temperature: 300 °C; and (d) pre-vulcanization with 1000 ppm SO<sub>2</sub> (10 h).

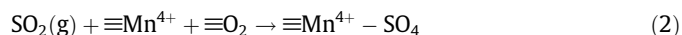
excellent support to disperse Mn. Mn atoms could enter into the crystal lattice of SnO<sub>2</sub> [32]. The presence of Fe in the sorbent can improve the dispersion of Mn in the sorbent. With the addition of the Sn and Fe atoms, the BET surface areas of MnO<sub>x</sub> increased sharply. These characteristics of the prepared sorbent will provide the potential ability for Hg<sup>0</sup> adsorption on the sorbent surface.

### 3.3. SO<sub>2</sub> effects

#### 3.3.1. Hg<sup>0</sup> capture performance

In general, the SO<sub>2</sub> concentration is hundreds of times higher than that of Hg<sup>0</sup> [33]. Therefore, the effect of SO<sub>2</sub> on Hg<sup>0</sup> adsorption should be taken into account. Fig. 5(a) shows the Hg<sup>0</sup> adsorption capacity for 20 h of pure MnO<sub>x</sub>, Sn-MnO<sub>x</sub> and Fe-Sn-MnO<sub>x</sub> sorbents. Notably, the pure MnO<sub>x</sub> and Sn-MnO<sub>x</sub> sorbent capacity for Hg<sup>0</sup> decreased along with the temperature increase when SO<sub>2</sub>

was present. These compounds had a weak SO<sub>2</sub> tolerance at high temperatures. Therefore, the Mn active component may not have higher temperature-tolerant activity in the presence of SO<sub>2</sub> [34]. The higher temperature could degrade this component's performance in Hg<sup>0</sup> capture when SO<sub>2</sub> is present. SO<sub>2</sub> may compete with gaseous Hg<sup>0</sup> for the activity sites. Thus, the sorbents were poisoned by SO<sub>2</sub> during the adsorption process, which could be explained by the follow reaction [35]:



According to the above reaction, the Mn active sites were occupied by sulfate. For the Fe-Sn-MnO<sub>x</sub> sorbent, there was a better performance at 300 °C than that of pure MnO<sub>x</sub> and Sn-MnO<sub>x</sub> when SO<sub>2</sub> was present. The Hg<sup>0</sup> capacity could reach 2 times greater than that of Sn-MnO<sub>x</sub>. Fig. 5(b) indicated that the Hg<sup>0</sup> capacity of Sn-MnO<sub>x</sub> decreased with the temperature increase when SO<sub>2</sub>

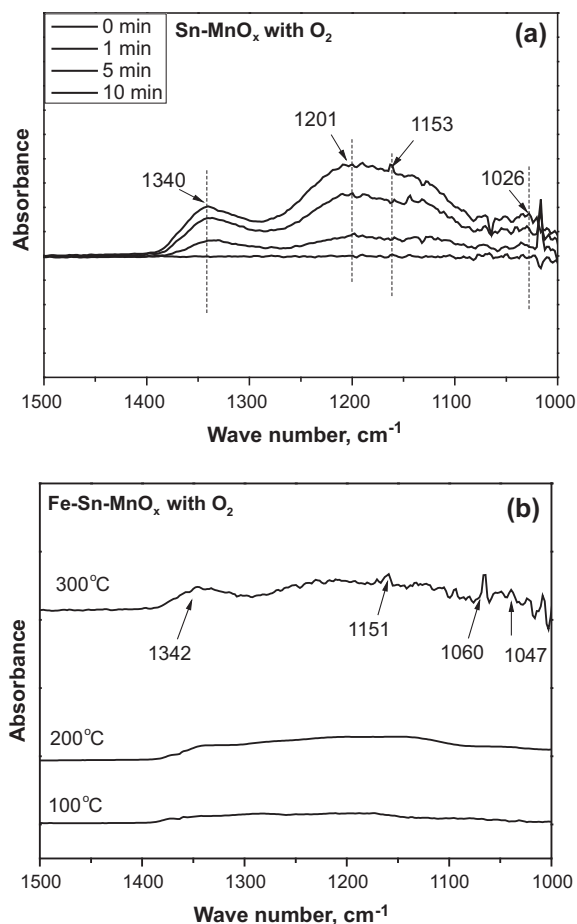


Fig. 6. (a) DRIFT spectra taken at 300 °C upon passing O<sub>2</sub> over Sn–MnO<sub>x</sub>; (b) DRIFT spectra taken at 100–300 °C upon passing O<sub>2</sub> over Fe–Sn–MnO<sub>x</sub> (10 min).

was present. The results in Fig. 5(c) exhibited excellent SO<sub>2</sub> tolerance at various SO<sub>2</sub> concentrations of Fe–Sn–MnO<sub>x</sub> sorbent at 300 °C. The Fe in the Fe–Sn–MnO<sub>x</sub> sorbent was excellent at resisting SO<sub>2</sub> at high temperatures. To verify this phenomenon, an additional experiment was performed by pre-vulcanizing the sorbents in the gas with 1000 ppm SO<sub>2</sub> for 10 h, and the results are shown in Fig. 5(d). Sn–MnO<sub>x</sub> lost nearly all its capacity for Hg<sup>0</sup> capture, but the Fe–Sn–MnO<sub>x</sub> sorbent remained at more than 80% of the Hg<sup>0</sup> capture efficiency within 10 h at 300 °C. Apparently, Fe plays an important role in SO<sub>2</sub> tolerance, and its mechanism will be discussed in the following section.

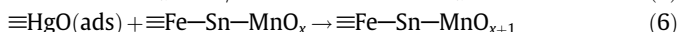
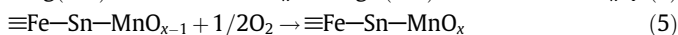
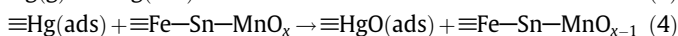
### 3.3.2. DRIFTS study for the mechanism of SO<sub>2</sub> on the surface of the sorbents

As mentioned above, both Sn–MnO<sub>x</sub> and Fe–Sn–MnO<sub>x</sub> sorbents exhibited good performance in terms of the Hg<sup>0</sup> capacity within a wide temperature window. However, Sn/MnO<sub>x</sub> seems to be impacted by SO<sub>2</sub> at high temperatures. SO<sub>2</sub> showed comparatively less inhibition to Fe–Sn–MnO<sub>x</sub> for Hg<sup>0</sup> adsorption at different temperature ranges. DRIFTS were employed to collect in-situ spectra data for investigating the mechanism of SO<sub>2</sub> impact at high temperatures in these two sorbents. As shown in Fig. 6(a), several peaks at 1340, 1201, 1153 and 1026 cm<sup>-1</sup> emerged, and the intensity increased with the exposure time. The peak at 1340 cm<sup>-1</sup> could be attributed to the ν(S=O) vibration of the surface sulfate species with only one S=O band [36]. Peaks at 1201, 1153 and 1026 cm<sup>-1</sup> could be assigned to the stretching motion of adsorbed bisulfate or sulfate on the surface of the sorbent [36]. Moreover, the higher the temperature was, the more sulfate species could

be found. It was speculated that SO<sub>2</sub> reacts with manganese at high temperatures, and the sulfate species formed on the surface of the sorbent, which would inhibit the Hg<sup>0</sup> adsorptive property. In Fig. 6(b), only small peaks could be found in the spectra when 4% O<sub>2</sub> was added to the simulated flue gas. These broad absorbance bands between 1000 and 1300 cm<sup>-1</sup> were assigned to the stretching mode of adsorbed bisulfate, HSO<sub>4</sub><sup>-</sup>, and/or sulfate, SO<sub>4</sub><sup>2-</sup>, on the surface of the sorbent [37]. Ion chromatography was used to determine the sulfate formed on the surface of the sorbent. The sulfate was detected and the results are shown in Fig. A3. Therefore, the mechanism for Fe–Sn–MnO<sub>x</sub> tolerance of SO<sub>2</sub> may be that Fe can preferentially react with SO<sub>2</sub> when O<sub>2</sub> was present, which can prevent MnO<sub>x</sub> from combining with SO<sub>2</sub>.

### 3.4. The Hg<sup>0</sup> capture mechanism on Fe–Sn–MnO<sub>x</sub> sorbents

In combining the results and characterization, the mechanism of Hg<sup>0</sup> adsorbed on the surface can be illustrated as follows. MnO<sub>x</sub> was the primary active component for Hg<sup>0</sup> capture. Fe oxide also had Hg<sup>0</sup> capacity to some extent [29]. The binary Sn–Mn metal oxide sorbent had a higher adsorption capacity compared with the MnO<sub>x</sub> sorbent, and it can be used within a wide temperature window. The resulting Fe–Sn–MnO<sub>x</sub> complex sorbent had the highest capacity among the sorbents, which could also be used within a wide temperature interval. The role of Sn and Fe clearly improved the performance of MnO<sub>x</sub>. The Hg<sup>0</sup> captured by metal oxide sorbents may be attributed to the Mars–Maessen mechanism [8,11,19]. The possible reactions for Hg<sup>0</sup> on the surface of the Fe–Sn–Mn–O<sub>x</sub> sorbent are as follows:



Sn enlarged the BET surface areas of MnO<sub>x</sub> when Mn entered the lattice of the SnO<sub>2</sub> metal oxide. Fe further influenced the enlarging surface areas of Sn–Mn binary metal oxides. SnO<sub>2</sub> provided excellent support for Mn and Fe in the Fe–Sn–MnO<sub>x</sub> complex sorbent according to the physiochemical characterization results. Sn plays another role in enhancing the activity at high temperatures for MnO<sub>x</sub>. The doped Fe could further enhance the dispersibility of Mn in the Fe–Sn–Mn complex oxides. Fe also exhibits excellent performance at high temperatures. The doped Fe solved another problem in that the Sn–Mn binary lost its Hg<sup>0</sup> capacity to some extent when SO<sub>2</sub> was present at high temperatures. The synthesized Fe–Sn–MnO<sub>x</sub> had excellent performance in terms of Hg<sup>0</sup> capture and SO<sub>2</sub> tolerance within a wide temperature window.

## 4. Conclusions

Fe–Sn–Mn complex oxide sorbents were synthesized and evaluated for their effective removal of Hg<sup>0</sup> from simulated flue gas. BET results showed that Fe–Sn–MnO<sub>x</sub> had the largest BET surface areas among the prepared sorbents. The adsorption capacity of Hg<sup>0</sup> could reach as high as 3.75 mg/g in 10 h. It can also be used within a wide temperature range with SO<sub>2</sub>. The physiochemical characterization shows that Sn and Fe play important roles in enlarging the BET surface areas, which provide the possibility for more Mn active sites. Moreover, Fe could protect the Mn active sites at high temperatures from SO<sub>2</sub> poisoning.

## Acknowledgments

This study was supported by the Major State Basic Research Development Program of China (973 Program, No. 2013CB430005),

the National Natural Science Foundation of China (No. 50908145, No. 21277088) and the National High-Tech R&D Program (863) of China (No. 2011AA060801, No. 2013AA065403). Ms. Xiaofang Hu is acknowledged for the assistance in DRIFT analysis.

## Appendix A. Supplementary material

The Hg<sup>0</sup> capacity assessment system, H<sub>2</sub>-TPR and ion chromatography are in the Appendices. Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.fuel.2014.10.004>.

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