Hierarchical Ag-SiO$_2$@Fe$_3$O$_4$ magnetic composites for elemental mercury removal from non-ferrous metal smelting flue gas

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Abstract:
Hierarchical Ag-SiO$_2$@Fe$_3$O$_4$ magnetic composites were selected for elemental mercury (Hg$^0$) removal from non-ferrous metal smelting flue gas in this study. Results showed that the hierarchical Ag-SiO$_2$@Fe$_3$O$_4$ magnetic composites had favorable Hg$^0$ removal ability at low temperature. Moreover, the adsorption capacity of hierarchical magnetic composite is much larger than that of pure Fe$_3$O$_4$ and SiO$_2$@Fe$_3$O$_4$. The Hg$^0$ removal efficiency reached the highest value as approximately 92% under the reaction temperature of 150°C, while the removal efficiency sharply reduced in the absence of O$_2$. The characterization results indicated that Ag nanoparticles grew on the surface of SiO$_2$@Fe$_3$O$_4$ support. The large surface area of SiO$_2$ supplied efficient reaction room for Hg and Ag atoms. Ag–Hg amalgam is generated on the surface of the composites. In addition, this magnetic material could be easily separated from fly ashes when adopted for treating real flue gas, and the spent materials could be regenerated using a simple thermal-desorption method.

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Introduction

Mercury (Hg), a hazardous and global environmental contaminant with high volatility, bioaccumulation and persistence in the environment, has drawn increasing attention worldwide in recent years (Liu et al., 2017a, 2017c; Zhang et al., 2015). It was reported that approximately 2320 tons of mercury was emitted annually from anthropogenic activities (Ma et al., 2015). Moreover, China was regarded as the largest contributor to global anthropogenic atmospheric mercury emission. It was calculated that that China accounted 27% of the total emission (Pacyna et al., 2010; Pirrone et al., 2010). Among all the emission sources in China, non-ferrous metal smelting industries contributed to approximately 40% (Liu et al., 2017b; Zhang et al., 2015). Especially, the lead, zinc and copper smelting accounted for 86% of the mercury emissions from non-ferrous smelting processes (Zhang et al., 2012). Global atmospheric mercury emissions from non-ferrous metal smelters reached 310 tons in 2007, among which more than 65% were emitted from China (Streets et al., 2005; Wu et al., 2012). The Minamata Convention on Mercury, a new worldwide treaty aimed to reduce anthropogenic mercury
emission to environment and protect human health, was signed on October 10, 2013, and came into force from August 6, 2017 (Selin, 2014a, 2014b). Hence, it is urgent to control mercury emission from non-ferrous metal smelting industries.

Compared with the coal-fired flue gas, the mercury concentration was high and fluctuate widely during the production process in non-ferrous metal smelting flue gas, which also contained high concentration of SO2 (Wang et al., 2010b). However, most of the previous studies focused on the mercury removal from coal-fired flue gas but paid little attention to the non-ferrous metal smelting flue gas (Louie, 2005; Ma et al., 2015). Traditional mercury purification technologies in non-ferrous smelters contained wet adsorption and adsorption methods (Wang et al., 2010a). Considering the high concentration of Hg0 in non-ferrous smelting flue gas, the most feasible method is the adsorption process which enables the capture and reclamation of Hg0.

The adsorption methods highly dependent on the efficient adsorbents such as carbon-based materials (Liu et al., 2017b), metal oxides (Xiao et al., 2008), functionalized mesoporous materials (Cao et al., 2017), magnetic adsorbents and noble metal adsorbents (Dong et al., 2017). However, most of these adsorbents are limited in large-scale application for non-ferrous smelting flue gas due to their low capacity, unrecyclable performance and high cost (Liu et al., 1998; Yang et al., 2011a). Usually, carbon-based materials take activated carbon (AC) as an example, can convert gaseous elemental mercury (Hg0) and oxidized mercury (Hg2+) to particle bound mercury (Hg0). Then Hg0 can be removed by particulate control devices (e.g., Electrostatics precipitator or Fabric filter). However, the cost of AC is high, which limited its wide utilization. Some transition metal oxides were recognized as potential adsorbents (Yang et al., 2011c). Mn-based materials were indicated to have large Hg0 adsorption capacities. The high valence of Mn in Mn-based oxides result in a prominent catalytic oxidation of Hg0 to Hg2+ over Mn-based oxides (Xu et al., 2015b). However, Mn-based oxides are easily poisoned to deactivity by SO2 in the flue gas.

Functionalized mesoporous materials also have excellent adsorption performances (Tomer et al., 2014). Mesoporous silica was applied to pollution control in a previous study (Cao et al., 2017). The large specific surface area of mesoporous silica provides sufficient space for reactions (Cao et al., 2017). Another advantage of using silica as support is its diffusion ability, which avoids the agglomeration of the supported metal nanoparticles (Zhang et al., 2011). In addition, silica is a non-toxic material with the cross-linking structure (Du et al., 2006). However, most of adsorbents used for Hg0 removal from flue gas mix into fly ash could not be separated, resulted in adsorbent loss and mercury secondary pollution (Huang et al., 2008). To resolve these problems, magnetically separable adsorbents are proposed in recent years because of their superparamagnetic, strong adsorption ability and magnetic segregation properties (Du et al., 2017; Liang et al., 2017).

Noble metal-based adsorbents such as platinum (Pt), gold (Au) and silver (Ag)-based adsorbents, were indicated to have Hg0 removal performances with the amalgamation mechanism. Silver-based sorbents, such as Ag-graphene (Xu et al., 2015a), Ag-MagZ (Dong et al., 2017), were proved to have excellent Hg0 adsorption efficiencies. When silver-based sorbents used for mercury removal, it exhibited a possibility for Hg2+ removal and Ag-Hg amalgams were generated. Then, mercury from the amalgamation could be recycled through thermal treatment at a high temperature. In this paper, a hierarchical Ag-SiO2@Fe3O4 magnetic composite was synthesized and employed for Hg0 removal from simulated non-ferrous smelting flue gas. SiO2 was designated as the coating of Fe3O4 to prepare SiO2@Fe3O4 composites, which formed a protective film against instability of it. Also, the mechanism of the interaction between Hg0 and Ag nanoparticles was discussed.

1. Experimental section

1.1. Materials

FeCl3·6H2O (99.0%, AR grade, Sigma–Aldrich Co., Ltd.), ethylene glycol (AR grade, Sigma–Aldrich Co., Ltd.), PEG 20000 (Chemical pure grade, Sigma–Aldrich Co., Ltd.), anhydrous sodium acetate (99.0%, AR grade, Kermel), ethyl alcohol (99.7%, AR grade, Sigma–Aldrich Co., Ltd.), tetraethyl orthosilicate (Reagent grade, 98.0%, Aladdin), AgNO3 (AR grade, 99.8%, Aladdin), polyvinyl pyrrolidone (AR grade, Aladdin) were used directly without further purification. The SO2 (5%, Dalian Date Gas Co., Ltd.) and O2 (99.9%, Dalian Date Gas Co., Ltd.) were stored in cylinders.

1.2. Preparation of Fe3O4, SiO2@Fe3O4 and Ag-SiO2@Fe3O4

Fe3O4 was synthesized using a typical method and SiO2 was coated on the surface of Fe3O4. Ag nanoparticles were loaded on the surface of SiO2@Fe3O4 microspheres using an ion exchange method. The detailed synthesis process was conducted as follows: (1) Synthesis of monodisperse Fe3O4 microspheres. 1.35 g of FeCl3·6H2O was absolutely dissolved in 40 mL of ethylene glycol, then 1.0 g of PEG 20000 was added into the above solution. Afterwards, 2.2 g of anhydrous sodium acetate was added and the solution was kept stirring for several minutes. When the mixture was totally dissolved, the solution was poured into a reactor with a Teflon inner container. The products were collected after heating at 200°C for 8 hr, and then washed with ethanol for several times, finally dried at 60°C for 6 hr in a vacuum oven. (2) Synthesis of magnetic Fe3O4@SiO2 microspheres. Typically, 0.2 g of above-prepared Fe3O4 microspheres was ultrasonically dispersed in a mixture of 20 mL of ethyl alcohol and 4 mL of deionized water to form a homogeneous solution. Then 0.8 mL of tetraethyl orthosilicate was added into the solution under continuous mechanical stirring, followed by adding 1 mL of ammonium hydroxide. After 3 hr of continuous mechanical stirring at 25°C, magnetic separation was carried out for the Fe3O4@SiO2 products and then dried at 60°C for 3 hr. (3) Synthesis of monodisperse Ag-coated Fe3O4@SiO2 composite microspheres. 0.173 g of AgNO3 was dispersed in deionized water to form a clear solution. Then, 0.173 g of polyvinyl pyrrolidone (PVP) was added into the homogeneous solution and ultrasonically treated for 10 min. As a result, the mass ratio of AgNO3:PVP was 1:1. Then, 1.0 g of magnetic Fe3O4@SiO2
microspheres synthesized in process (2) was added to the homogeneous solution and ultrasonically treated for 10 min. After that, the products were transferred into a conical flask equipped with the rotary evaporators. The solution was concentrated at a temperature of 50°C until it got thicken. Then, the above products were dried at 100°C for 5 hr until the surface water was completely evaporated. Finally, the materials were transferred into a muffle furnace for calcining 2 hr at 350°C.

1.3. Characterization of Fe3O4, SiO2@Fe3O4 and Ag-SiO2@Fe3O4

The microstructures of the materials were characterized by field emission scanning electron microscopy (FESEM, JSM-7001F) and transmission electron microscopy (TEM, JEM-2100). And the micrographs were obtained in the bright-field imaging mode at an acceleration voltage of 200 kV. Powder X-ray diffraction (PXRD) was obtained to detect the crystal structure of the prepared material, and the result was recorded on an X-ray diffractometer (DS, Advanced, Germany) with Cu Kα radiation. The scanning scale was in the 2θ range from 10° to 80° with a scanning velocity of 10°/min. The surface element analysis of the material was performed by X-ray photoelectron spectroscopy (XPS), and the results were recorded by ESCALAB 250 Xi XPS instrument (Thermo Fisher Scientific, USA) with the excitation source of Al Kα. Before each processing of data, the C 1s line at 284.6 eV was calibrated for the binding energy of the detected element. The hysteresis loops of the hierarchical magnetic particles were measured by a Quantum Design MPMS-XL-7 magnetometer at magnetic field intensity from −15,000 to 15,000 Oe. In addition, the surface functional groups were characterized by FT-IR spectroscopy, and the 633 nm line of Ar+ laser was used for the excitation source.

1.4. Hg0 removal experiments

The bench-scale experimental equipments for Hg0 removal performance consists of four parts: a gas distributing system, a reaction system of tubular furnace, an online detection system and a tail gas treatment system, which was depicted in our previous study (Ma et al., 2017). A detection system and a tail gas treatment system, which was equipped with the rotary evaporators. The solution was collected and recorded by a data transition and acquisition device (N2000, Zhida Ltd., China). A bottle contained 5% KMnO4 solution and another bottle filled with active carbon were used for the off-gas cleaning in the tail-end equipment.

During each experiment, the mercury inlet gas bypassed the adsorbent bed and passed into the side road until the curve of inlet mercury concentration approached to flat. 20 mg of As-prepared adsorbents were added into the quartz tube with amounts of silica wool for immobilizing at a certain position. The temperature of the reaction was set by a temperature controller in the tubular furnace. To investigate the effect of temperature on the adsorption performance, the temperature during the experiment was varied from 50 to 200°C. Moreover, the reaction time of 120 min was permitted for this experiment. And pure N2, 5%, 10% of O2 and 100, 200, 500 ppm of SO2 were chosen to investigate the effects of various gas components. The Hg0 removal efficiency was calculated as Eq. (1):

$$\text{Removal efficiency} = \frac{C_0 - C}{C_0} \times 100\%$$

where the $C_0$ is the inlet concentration of Hg0, and C is the outlet concentration of Hg0.

In addition, the mercury temperature programmed desorption (Hg-TPD) experiment was also conducted after the Hg0 removal experiment under the condition of simulated flue gas. In advance of each test, the adsorbent was treated via the mixture of N2 + O2 accompanied with mercury vapor for 30 min at 150°C to make it had a certain Hg0 concentration. Only pure N2 was the carrier gas for the Hg-TPD experiment. The temperature of tubular furnace in this system was set from 150 to 500°C with a speed of 5°C/min. The Hg-TPD could be accelerated at higher temperature, but the morphology of the Ag-SiO2@Fe3O4 might also be negatively impacted. During the test process, the flow rate was kept at 350 mL/min, and the mercury concentration was calculated by a CVAAS mercury detector.

2. Results and discussion

2.1. Characterization of As-prepared materials

2.1.1. XRD

Powder XRD was employed to measure the crystal structures of As-prepared materials. The results are shown in Fig. 1. As shown in Fig. 1 (a), all the diffraction peaks were in accordance with the standard Fe3O4 reflections (JCPDS card No. 75-1609), where these diffraction peaks are Fe3O4 (111), Fe3O4 (220), Fe3O4 (311), Fe3O4 (400), Fe3O4 (511) and Fe3O4 (440), respectively. As shown in Fig. 1 (b), the broad band ranging from 2θ = 10° to 32° was the characteristic peak of SBA-15 amorphous silica matrix (Cao et al., 2017). As silver coated on the surface of SiO2@Fe3O4, in the pattern of Ag-SiO2@Fe3O4 composites, another three diffraction peaks were marked to Ag (111), Ag (200) and Ag (220), comparing to the standard silver diffraction peaks (JCPDS No. 4-0783).
2.1.2. TEM

The nanostructures of Fe₃O₄, SiO₂@Fe₃O₄ and Ag-SiO₂@Fe₃O₄ were exhibited via TEM images, and the results are shown in Fig. 2. Fe₃O₄ images were displayed in Fig. 2 (a) and (b), from which a spherical morphology with a diameter of 200 ± 10 nm could be clearly seen. Furthermore, the agglomeration phenomenon was not observed in the Fe₃O₄ micro-particles, and the distance between the interplanar spacing was approximately 0.245 nm, corresponding to the (111) crystal phase of Fe₃O₄. As shown in Fig. 2 (c) and (d), the SiO₂ shell was successfully coated on the surface of Fe₃O₄ micro-particles. Moreover, the thickness of SiO₂ shell was about 20 ± 5 nm, which indicated the successful synthesis of SiO₂@Fe₃O₄ core-shell structure. The Ag-SiO₂@Fe₃O₄ images were exhibited in Fig. 2 (e), (f) and (g). The uniform spherical morphologies of Ag-SiO₂@Fe₃O₄ were exhibited with a diameter of about 260 ± 10 nm. Therefore, hierarchical Ag-SiO₂@Fe₃O₄ magnetic composites were successfully synthesized based on TEM and XRD results.

2.1.3. FT-IR

The surface functional groups of the adsorbents were also detected by FT-IR spectra and the results are shown in Fig. 4. As shown in the spectra, the peaks centered at 3425 and 1634 cm⁻¹, reflecting the stretching and bending vibration peaks of hydroxyl group appeared, respectively (Xu et al., 2015b). The Fe–O characteristic absorption peak at centered at 586.4 cm⁻¹. The peaks at 1091.1, 950 and 806.7 cm⁻¹ were the symmetric stretching and bending absorption peaks of O–Si–O, revealing that the presence of element Si in the SiO₂@Fe₃O₄ and Ag-SiO₂@Fe₃O₄ nano-composites (Xu et al., 2015b). Moreover, Ag–O peak was not detected in the FT-IR spectra of Ag-SiO₂@Fe₃O₄ magnetic particles. Therefore, it was speculated that AgNO₃ was converted to elemental Ag on the surface of the particles.

2.1.4. Magnetization

To investigate the magnetic characteristic of the prepared adsorbents, the hysteresis loops of the adsorbents were detected via vibrating sample magnetometer (VSM). The results are shown in Fig. 5. The adsorbents exhibited soft magnetic characterization, and the saturation magnetization of Fe₃O₄, SiO₂@Fe₃O₄ and Ag-SiO₂@Fe₃O₄ were 70.6, 30.4 and 28.5 emu /g, respectively. The reduction of saturation magnetization of SiO₂@Fe₃O₄ and Ag-SiO₂@Fe₃O₄ was mainly due...
Fig. 3 – SEM patterns of (a) and (b) Fe$_3$O$_4$, (c) SiO$_2$@Fe$_3$O$_4$ and (d) Ag-SiO$_2$@Fe$_3$O$_4$.

Fig. 4 – FT-IR spectra of Fe$_3$O$_4$, SiO$_2$@Fe$_3$O$_4$ and Ag-SiO$_2$@Fe$_3$O$_4$.

Fig. 5 – Hysteresis loops of Fe$_3$O$_4$, SiO$_2$@Fe$_3$O$_4$ and Ag-SiO$_2$@Fe$_3$O$_4$ nanoparticles.
to the blocking effect by amorphous silica shell. As it was expected, the adsorbents possessed the superparamagnetic characterization due to the minimized coercive force (tend to zero) and a negligible magnetization hysteresis. Therefore, the superparamagnetic adsorbents could be separated from fly ashes when used in real flue gas.

2.1.5. XPS

The XPS spectra (Fig. 6) were detected to further explore the surface composition of the magnetic particles. As illustrated in Fig. 6 (f), peaks with binding energy of 284.8, 532.7, 712.4, 103.4 and 368.2 eV were attributed to C 1s, O 1s, Fe 2p, Si 2p, and Ag 3d, respectively (Yang et al., 2011c). It indicated that the elements

Fig. 6 – Survey XPS spectra (f) of the prepared Ag-SiO2@Fe3O4 and enlarged areas corresponding to the C1s (a), O1s (b), Fe 2p (c), Si 2p (d) and Ag 3d (e) peaks of hierarchical Ag-SiO2@Fe3O4 magnetic particles.
dropped to about 30%. However, the Hg\textsuperscript{0} removal efficiency of 45% in the initial few minutes and finally got to the maximum Hg\textsuperscript{0} removal efficiency at 200°C was only 58%. At 50°C, the adsorbent had a remarkable performance, with the removal efficiency as about 90% in the initial few minutes and then got to the maximum efficiency of 92% after 30 min reaction. However, after reaction for 80 min, the Hg\textsuperscript{0} removal efficiency dropped to lower than 80%. At 150°C, the Hg\textsuperscript{0} removal efficiency was approach to 92%, and kept higher than 85% even 100 min reaction. Obviously, Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} adsorbent has the best Hg\textsuperscript{0} removal efficiency among all the As-prepared materials at 150°C.

To investigate the effects of different gas components on Hg\textsuperscript{0} removal over Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}, O\textsubscript{2} and SO\textsubscript{2} were selected as primary gas components, and the results are shown in Fig. 9. The reaction temperature was set at 150°C, and the reaction time was 120 min. As illustrated in Fig. 8, under the condition of N\textsubscript{2} and 10% O\textsubscript{2}, the Hg\textsuperscript{0} removal efficiency was approximately 84% during the 120 min. When the adsorbents reacted under pure N\textsubscript{2}, the Hg\textsuperscript{0} removal efficiency sharply decreased to 32%. Combining with Hg\textsuperscript{0}, the atomic oxygen generated by catalysis of Fe\textsubscript{3}O\textsubscript{4} formed the HgO on the surface of adsorbent. This indicated that oxygen was beneficial for the Hg\textsuperscript{0} removal reaction, which may be attributed to the atomic oxygen generated by catalysis of Fe\textsubscript{3}O\textsubscript{4} and Ag, and then active O combined with Hg\textsuperscript{0} were transformed to HgO on the surface of Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} particles. The literature reported the Reaction (2) which could illustrate the catalysis of Fe\textsubscript{3}O\textsubscript{4} for O\textsubscript{2} to form O (Yang et al., 2011a). According to the literatures, surface chemisorbed atomic oxygen was easily formed on the Ag nanoparticles. The initial inlet Hg\textsuperscript{0} concentration was 100 \( \mu g/\) \( m^3 \) in flue gas, and the adsorption capacity was calculated in 120 min reaction. The Hg\textsuperscript{0} adsorption capacities of Fe\textsubscript{3}O\textsubscript{4}, SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}, Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} were 30.97, 40.53, 116 \( \mu g/g \) in 120 min at 150°C, respectively. It indicated that adsorption capacity of hierarchical magnetic composites was much higher than that of pure Fe\textsubscript{3}O\textsubscript{4} and SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4}.

The Hg\textsuperscript{0} removal efficiencies of the prepared hierarchical Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles were tested at different temperatures under the gas condition of N\textsubscript{2} + 10% O\textsubscript{2}, and the results are displayed in Fig. 8. As expected, the prepared adsorbents have an excellent removal performance at low temperature (lower than that at 150°C), while the Hg\textsuperscript{0} removal efficiency at 200°C was only 58%. At 50°C, the adsorbent had a remarkable performance, with the removal efficiency as about 90% in the initial few minutes and then got to the maximum efficiency of 92% after 30 min reaction. However, after reaction for 80 min, the Hg\textsuperscript{0} removal efficiency dropped to lower than 80%. At 150°C, the Hg\textsuperscript{0} removal efficiency was approach to 92%, and kept higher than 85% even 100 min reaction. Obviously, Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} adsorbent has the best Hg\textsuperscript{0} removal efficiency among all the As-prepared materials at 150°C.
nanomaterials (Yang et al., 2011b; Ma et al., 2014; Kaichev et al., 2003). The synergistic interaction might exist between Ag and Fe3O4 for generating atomic oxygen, which then contributed to the Hg0 removal.

\[
\text{Fe}^{2+} + \frac{1}{4} \text{O}_2 \rightarrow \text{Fe}^{3+} + \frac{1}{2} \cdot \text{O}
\]  

Although amalgam was the primary adsorption mechanism for Hg0 adsorption, such process was also beneficial for enlarging the mercury adsorption capacities.

When 100 ppm SO2 was added into the simulated flue gas, the Hg0 removal efficiency declined to 35%. It indicated that SO2 has a poison effect on mercury surface uptake. The SO2 reacted with silver atoms to form Ag2S on the surface of Ag-SiO2@Fe3O4 magnetic nanoparticles, which may interfere with the chemical adsorption of Hg0 from flue gas. However, the Hg0 removal efficiency was improved when the SO2 concentration reached 500 ppm in flue gas, the Hg0 removal efficiency increased to 60%. Previous studies postulated a mechanism for the heterogeneous uptake and oxidization of SO2 on iron oxides (Yang et al., 2011b; Fu et al., 2007), and the reactions can be described as Eqs. (3) and (4):

\[
\text{Fe}^{3+} + \text{OH}^{-} + \text{SO}_2(g) \rightarrow \text{Fe}^{3+} \cdot \text{OSO}_2^{-} + \text{H}^+ 
\]  

\[
\text{Fe}^{2+} + \text{SO}_2 \rightarrow \text{Fe}^{3+} + \text{SO}_3^-
\]  

HgO + SO3• → HgSO4

HgSO4 + Hg0 → Hg2SO4

As shown in Eqs. (3) and (4), the uptake of SO2 on iron oxides may involve hydroxyl groups on the surface. In absence of hydroxyl groups, the uptake of SO2 on iron oxides was negligible (Yang et al., 2011b; Fu et al., 2007). Then HgO on the surface of Ag-SiO2@Fe3O4 may transform to HgSO4 and Hg3O4 in the presence of SO3•− formed in Reactions (5) and (6). Furthermore, mercurous sulfate was previously observed as a mercury product in a photochemical oxidation process for elemental mercury oxidation and capture (McLarnon et al., 2005; Granite and Pennline, 2002). Therefore, elemental mercury capture by Ag-SiO2@Fe3O4 was obviously interfered by the high concentration of SO2.

2.3. Hg0 removal mechanism over Ag-SiO2@Fe3O4

As a result, the presence of the high concentration of SO2 performed positive effect on elemental mercury capture by Ag-SiO2@Fe3O4 at 150°C.

Hg-temperature programmed desorption (Hg-TPD) was carried out at the lab-scale fixed-bed adsorption system under the gas condition of N2, and the results are shown in Fig. 10. The initial temperature of the TPD system was 150°C, and then the temperature increased with a heating rate of 5°C/min. When the temperature reached 500°C, it maintained for a period of time until the adsorbed Hg0 desorbed completely. As shown in Fig. 10, the peak at the time of 75 min was the desorption peak of Ag-Hg amalgam, while another one at the time of 85 min was the desorption peak of Hg-0 on the Fe3O4 particles. In the process of Hg0 adsorption under O2 condition, atomic oxygen was generated by catalysis of Fe3O4, and the atomic oxygen combing with Hg0 formed the HgO on the surface of Fe3O4 particles. After desorption for about 2 hr, the desorption profile became flat, indicating that the adsorbed mercury was mostly released from the adsorption materials.

Furthermore, the reusability tests of Ag-SiO2@Fe3O4 were investigated, and the results were shown in Fig. S2. The adsorbed Hg0 could be released from the surface of Ag-SiO2@Fe3O4 composite through TPD method. As shown in Appendix A Fig. S2, six cycles of Hg0 adsorption and desorption tests were carried out. The Hg0 removal efficiency was almost the same as 90% in the first three cycles, and had a slight decrease after the fourth cycle. The results indicated that the synthesized Ag-SiO2@Fe3O4 adsorbents were promising adsorbents for Hg0 removal due to its excellent reusability.

2.3. Hg0 removal mechanism over Ag-SiO2@Fe3O4

On the basis of Hg0 removal performances and characterization results of Ag-SiO2@Fe3O4, it could be concluded that the magnetic particles Ag-SiO2@Fe3O4 performed the best adsorption performance at the temperature of 150°C. In the synthesis process of Ag-SiO2@Fe3O4, atomic silver was successfully loaded on the material surface. Ag nanoparticles which supplied active sites for generating Ag-Hg amalgam played an important role in Hg0 adsorption. Moreover,
dispersive Fe\textsubscript{3}O\textsubscript{4} micro-particles avoided the agglomeration of Ag nanoparticles. In addition, mesoporous silica provided sufficient active room for reactants due to its large specific surface area. The diffusion ability of silica core-shell made the Ag nanoparticles diffusion rather than agglomeration, which ensured sufficient Ag active sites for Hg\textsuperscript{0} removal.

It was observed that Hg\textsuperscript{0} was adsorbed from flue gas without SO\textsubscript{2} by Ag to form the silver amalgam at low temperature range (about 50–150°C). Moreover, atomic oxygen was generated by catalysis of Fe\textsubscript{3}O\textsubscript{4}, and then formed the HgO on the surface of Fe\textsubscript{3}O\textsubscript{4} particles combining with Hg\textsuperscript{0}. When SO\textsubscript{2} was in flue gas, low concentration of SO\textsubscript{2} competed the silver active sites with Hg\textsuperscript{0} and formed Ag\textsubscript{2}S on the surface of Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles, leading to the reduction of Hg\textsuperscript{0} removal efficiency. However, the high concentration of SO\textsubscript{2} in flue gas could be oxidized by iron oxides to SO\textsubscript{3}•, and then the HgO on the surface of Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} may transform to Hg\textsubscript{2}SO\textsubscript{4} and HgSO\textsubscript{4} in the presence of SO\textsubscript{3}•, which was beneficial for the conversion and adsorption of Hg\textsuperscript{0}.

3. Conclusion

In this study, hierarchical Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} magnetic particles were synthesized for Hg\textsuperscript{0} removal from simulated non-ferrous smelting flue gas. The characterizations results showed that SiO\textsubscript{2} was coated on the surface of Fe\textsubscript{3}O\textsubscript{4} micro-particles and formed SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} core-shell structure. Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} was homogeneous spherical morphology with the diameter of 260 ± 10 nm. The hysteresis loops of the adsorbents revealed high magnetization, indicating the separation performance from fly ash.

The hierarchical Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} magnetic particles exhibited prominent Hg\textsuperscript{0} removal efficiency as approximately 92% at 150°C. For Hg\textsuperscript{0} removal process, it was ascribed to a chemical-adsorption process. Hg\textsuperscript{0} was adsorbed by atomic Ag to form the silver amalgam, and atomic oxygen generated by catalysis of Fe\textsubscript{3}O\textsubscript{4} was transformed to HgO on the surface of Fe\textsubscript{3}O\textsubscript{4} particles combining with Hg\textsuperscript{0}. With SO\textsubscript{2} in flue gas, SO\textsubscript{2} could occupy the silver active sites and form Ag\textsubscript{2}S on the surface of Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} magnetic nanoparticles, leading to the reduction of Hg\textsuperscript{0} removal efficiency. However, the high concentration of SO\textsubscript{2} in flue gas could be oxidized by iron oxides to SO\textsubscript{3}•, and then the HgO on the surface of Ag-SiO\textsubscript{2}@Fe\textsubscript{3}O\textsubscript{4} may transform to Hg\textsubscript{2}SO\textsubscript{4} and HgSO\textsubscript{4} in the presence of SO\textsubscript{3}•, which was beneficial for the conversion and adsorption of Hg\textsuperscript{0}.

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Appendix A. Supplementary data

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