

# A novel multi-functional magnetic Fe–Ti–V spinel catalyst for elemental mercury capture and callback from flue gas†

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**A novel magnetic Fe–Ti–V spinel catalyst showed an excellent performance for elemental mercury capture at 100 °C, and the formed HgO can be catalytically decomposed by the catalyst at 300 °C to reclaim elemental mercury and regenerate the catalyst.**

Mercury is a major pollutant because of its toxicity, mobility and bioaccumulation in the ecosystem and food chain. The emission of mercury from anthropogenic activities is a serious concern in both developed and developing countries.<sup>1</sup> Coal-fired utility boilers are currently the largest single-known source of anthropogenic mercury emissions. Elemental mercury is the major mercury species emitted in the flue gas from coal-fired utilities.<sup>2</sup> Many technologies have been investigated to remove elemental mercury from the flue gas. Catalysts for elemental mercury oxidization studied to date mainly fall into one of the three groups: carbon-based sorbents, selective catalytic reduction catalysts, and metals and metal oxides.<sup>3</sup> The involved oxidants are mainly chlorine and oxygen. 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 formed HgO is in a solid state, so it adsorbs on the catalyst and is then removed from the flue gas.<sup>4</sup>

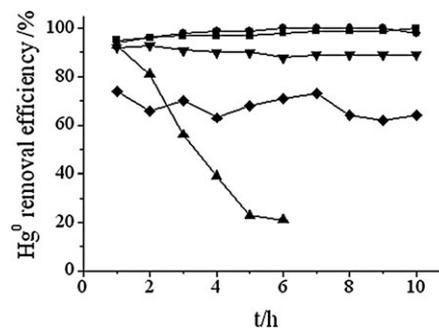
Now, the mercury-sorbent materials are extremely restricted in the application for at least four reasons: sorbent recovery, removal of toxin from industrial waste,<sup>5</sup> interference of the chemical composition in the flue gas and cost of operation. First, the spent sorbent for this particular application is generally collected as a mixture with greater than 99% of ultrafine fly ash particles by particulate control devices.<sup>5</sup> It will be extremely difficult and impractical to reclaim the spent sorbent from the fly ash mixture for regeneration. Second, if the spent sorbent is not effectively removed from the fly ash mixture, the fly ash will be contaminated by mercury-loaded sorbent. 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 (especially SO<sub>2</sub>) significantly affects mercury adsorption by sorbents. SO<sub>2</sub> gas molecules may compete with gaseous elemental mercury for the activity sites. The concentration of

SO<sub>2</sub> in the real flue gas is about 10<sup>4</sup>–10<sup>5</sup> times that of elemental mercury (v/v). Furthermore, SO<sub>2</sub> can react with metals and metal oxides to form a surface sulfate species,<sup>6</sup> which may make them inefficient for elemental mercury capture. Fourth and mostly importantly, the sorbent must be cheap and easy to operate.

The separation of the sorbent and adsorbed oxidized mercury from the fly ash can be achieved by the magnetic property of sorbent material.<sup>5,7</sup> A magnetic sorbent MagZ–Ag<sup>0</sup> was once investigated for elemental mercury capture,<sup>5,7</sup> but it was expensive. In our previous researches, magnetic nanoparticles (Fe<sub>3–x</sub>Ti<sub>x</sub>)<sub>1–δ</sub>O<sub>4</sub>, (Fe<sub>3–x</sub>Mn<sub>x</sub>)<sub>1–δ</sub>O<sub>4</sub> and (Fe<sub>2</sub>Ti<sub>x</sub>Mn<sub>1–x</sub>)<sub>1–δ</sub>O<sub>4</sub> were developed to capture elemental mercury from the flue gas. (Fe<sub>2</sub>Ti<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>1–δ</sub>O<sub>4</sub> showed an excellent capacity for elemental mercury capture and the presence of a high concentration of SO<sub>2</sub> resulted in an insignificant effect. However, the adsorbed HgO was difficult to be removed from (Fe<sub>2</sub>Ti<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>1–δ</sub>O<sub>4</sub> at <500 °C. During the thermal treatment at 500 °C under air, the phase transition of (Fe<sub>2</sub>Ti<sub>0.5</sub>Mn<sub>0.5</sub>)<sub>1–δ</sub>O<sub>4</sub> would happen and the magnetic property would disappear.

Herein, a novel regenerable magnetic sorbent (non-stoichiometric Fe–Ti–V spinel) was developed for elemental mercury capture and callback. The stoichiometric nanosized Fe–Ti–V spinel was prepared using a co-precipitation method. Then the non-stoichiometric Fe–Ti–V spinel was derived from the calcination of the stoichiometric nanosized Fe–Ti–V spinel at 400 °C under air for 3 h. Meanwhile, some cation vacancies (□) were incorporated to compensate for the oxidization of V<sup>4+</sup> and Fe<sup>2+</sup> cations. The BET surface area of synthesized non-stoichiometric Fe–Ti–V spinel was about 58.5 m<sup>2</sup> g<sup>–1</sup>.

Elemental mercury capture by the non-stoichiometric Fe–Ti–V spinel is shown in Fig. 1. Clearly, a high elemental mercury removal efficiency (>95%) was achieved

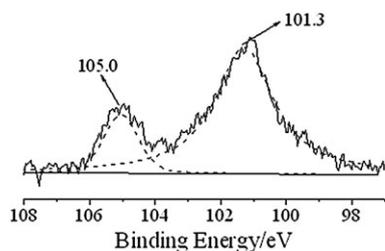


**Fig. 1** Elemental mercury removal efficiency at ■, 100 °C under air; ●, 150 °C under air; ▲, 200 °C under air; ▼, 100 °C in the presence of SO<sub>2</sub>; ◆, 150 °C in the presence of SO<sub>2</sub>.

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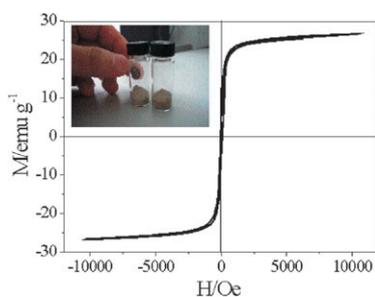


**Fig. 2** XPS spectra of Fe–Ti–V spinel after the adsorption at 100 °C in the presence of SO<sub>2</sub> over Hg 4f spectral region.

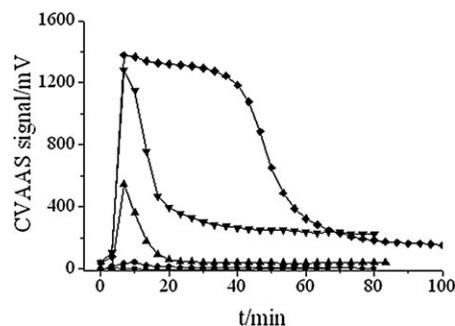
at 100–150 °C under air. The presence of 1000 ppm of SO<sub>2</sub> resulted in a slight effect on elemental mercury capture at 100 °C and the removal efficiency was about 90%. But 1000 ppm of SO<sub>2</sub> showed an obvious effect at 150 °C. The capacity of the non-stoichiometric Fe–Ti–V spinel for elemental mercury capture was about 1.0 mg g<sup>-1</sup> at 100 °C in the presence of 1000 ppm of SO<sub>2</sub> with more than 85% of removal efficiency. This performance was better than those of V<sub>2</sub>O<sub>5</sub>–TiO<sub>2</sub>,<sup>1</sup> Z–Ag<sup>0</sup>,<sup>8</sup> MagZ–Ag<sup>0</sup>,<sup>5,7</sup> and so on. Taking account of the binding energies of Hg 4f 7/2 at 101.3 eV and Hg 4f 5/2 at 105.0 eV, the oxidized mercury formed was mercuric oxide (HgO) (shown in Fig. 2).

The saturation magnetization of synthesized non-stoichiometric Fe–Ti–V spinel was about 26.0 emu g<sup>-1</sup>, which made it possible to separate the Fe–Ti–V spinel from the fly ash mixture (shown in the insert of Fig. 3). Furthermore, the Fe–Ti–V spinel showed the super-paramagnetism with a minimized coercivity and a negligible magnetization hysteresis (shown in Fig. 3). The magnetization characteristic ensures that the magnetic sorbent does not become permanently magnetized after being exposed to an external magnetic field, so the sorbent particles can be re-dispersed without aggregation when the magnetic field is removed.<sup>5</sup>

The decomposition temperature of HgO under air is about 500 °C. Fig. 4 shows the decomposition of the formed HgO on the non-stoichiometric Fe–Ti–V spinel at 100–300 °C. At the beginning (<20 min), the reaction temperature may be higher than the desired temperature. As a result, a peak for elemental mercury release appeared at the beginning. Elemental mercury in the outlet gas can hardly be detected at <150 °C. It indicates that the formed HgO was very stable at <150 °C. With the increase of reaction temperature, the formed HgO began to be catalytically decomposed by the non-stoichiometric Fe–Ti–V spinel. 17.9 μg of elemental mercury was once obtained after the thermal treatment of the used Fe–Ti–V spinel at 300 °C for 90 min, and only 2.75 μg of



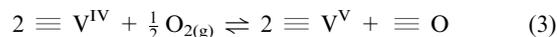
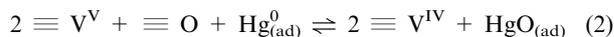
**Fig. 3** Magnetization characteristics of synthesized Fe–Ti–V spinel.



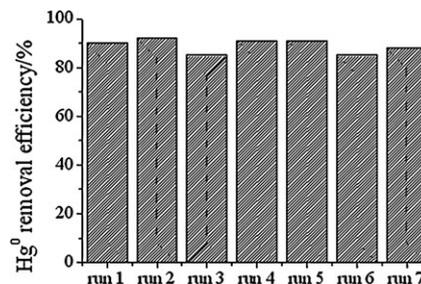
**Fig. 4** Catalytic decomposition of the formed HgO by the Fe–Ti–V spinel under air at ■, 100 °C; ●, 150 °C; ▲, 200 °C; ▼, 250 °C; ◆, 300 °C.

elemental mercury was obtained after further thermal treatment at 400 °C for 90 min. It indicates that most of the formed HgO can be decomposed at 300 °C within 90 min. The concentration of elemental mercury in the exhaust of catalyst regeneration was much higher than that in the flue gas, so it may be collected as liquid mercury at room temperature. Fig. 5 shows the removal efficiencies of elemental mercury at 10 h during the 7 circulations of the adsorption (at 100 °C in the presence of 1000 ppm of SO<sub>2</sub>)–desorption (at 300 °C under air for 60 min). It shows that the removal efficiency of elemental mercury did not decrease, and still achieved about 90% at each 10 h.

Elemental mercury capture by metal oxides is generally attributed to the Mars–Maessen mechanism.<sup>3,4</sup> The reactions, which happened during elemental mercury capture by the non-stoichiometric Fe–Ti–V spinel, were described as follows:



Reaction (1) was the collision of elemental mercury with the surface, resulting in a “physical” adsorption on the active sites. It was an exothermic reaction, so the concentration of elemental mercury adsorbed on the surface would decrease with the increase of reaction temperature. Reaction (2) was the oxidation of adsorbed elemental mercury by V<sup>5+</sup> cations on the surface. Reaction (3) was the re-oxidation of formed V<sup>4+</sup> cations. Reactions (1)–(3) were all reversible reactions. At <200 °C, the positive reaction would predominate over reaction (2) due to the higher concentration of elemental mercury adsorbed on the surface. Some of the adsorbed



**Fig. 5** Stability test of elemental mercury capture by the non-stoichiometric Fe–Ti–V spinel.

elemental mercury would desorb from the surface with the increase of reaction temperature, so the concentration of elemental mercury adsorbed on the surface was very little at  $>250\text{ }^{\circ}\text{C}$ . It was demonstrated by the  $\text{NH}_3$ -TPD analysis. Furthermore, the reverse reaction of reaction (3) may happen at a higher temperature to sustain the spinel structure<sup>9</sup> due to the stabilization effect of Ti on the spinel structure,<sup>10</sup> which was demonstrated by the XPS analysis. As a result, the reverse reaction predominated over reaction (2) at  $>250\text{ }^{\circ}\text{C}$ .

In summary, a novel magnetic Fe–Ti–V spinel catalyst was developed to capture elemental mercury from the flue gas. At  $100\text{ }^{\circ}\text{C}$ , it showed an excellent performance for elemental mercury capture and the presence of a high concentration of  $\text{SO}_2$  resulted in an insignificant effect. After being separated from the fly ash mixture using magnetic separation, the formed HgO can be catalytically decomposed by the catalyst at  $300\text{ }^{\circ}\text{C}$  to reclaim elemental mercury and regenerate the catalyst. It had been recycled multiple times without performance degeneration.

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