A Magnetically Recoverable Fe$_3$O$_4$–NH$_2$–Pd Sorbent for Capture of Mercury from Coal Derived Fuel Gas

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A sort of magnetical material named Fe$_3$O$_4$–NH$_2$–Pd was prepared by loading varying amounts of immobilizing Pd on the surface of the magnetic Fe$_3$O$_4$–NH$_2$ microspheres. This magnetical material was used firstly for capturing Hg° from coal derived fuel gas based on its recoverability. The experimental results showed that the loading Pd on the amine-functionalized magnetite nanoparticles can greatly improve the efficiency of removing Hg° at a high temperature range between 200 and 300 °C. The magnetic Fe$_3$O$_4$–NH$_2$–Pd sorbent with 5% Pd loaded exhibited significantly high activity and stability in capturing Hg°, affording over 93% capture efficiency at 200 °C for more than 8 hrs. Compared to the Fe$_3$O$_4$–NH$_2$ sorbent that converted the Hg° as HgS, this Fe$_3$O$_4$–NH$_2$–Pd sorbent can remove the Hg° by forming Pd–Hg amalgam and HgS. In addition, the experimental tests indicated that the as-synthesized Fe$_3$O$_4$–NH$_2$–Pd sorbent still showed stable magnetic properties after two regeneration cycles in removing Hg°, which provided the opportunity for preparing a recyclable sorbent which can be easily separated and recovered for Hg° removal.

Coal gasification is a promising technology for coal cleaning utilization$^1$. Some toxic gases, such as, H$_2$S, HCl and Hg, may form during coal gasification. The environmental friendly utilization of the coal derived fuel gas requires the removal of these toxic gases, or converting the toxic gases to less toxic substance by performing catalyzed chemical reactions. The highly toxic metallic substance, mercury, is considered as a global threat not only because it may cause a significantly negative effect on human beings, it also may result in irreversibly environmental damage relating to its nature such as volatility, persistence and bioaccumulation$^{2-4}$. Therefore, the control of mercury emissions from coal gasification arises a globally challenge. Overall, there are three types of mercury in the fuel gas generated from coal gasification. They are elemental mercury (Hg°), oxidized mercury (Hg$^{2+}$, Hg$^+$) and particle-bound-mercury (HgP)$^5$. Hg° is the predominant mercury that exists in the fuel gases because of the reducing environment during coal gasification$^6,7$. Hg° also is the most difficult substance to capture compared to others because it is highly vaporizable and nearly insoluble in water$^8$. Therefore, this work will focus on the removal of the Hg°.

Previously, a number of sorbents have been used for Hg° removing in the literature. It has been found that the activated carbon and fly ash$^9,10$, particularly the activated carbon impregnated with sulfur$^{11,12}$, chlorine$^{13,14}$, iodine$^{15}$ and bromine$^{16,17}$, showed a high efficiency in removing mercury. However, these previously studies also showed that the activated carbon and fly ash sorbents still suffer from practical utilization in separation and recycling besides the potential contamination caused by the converted products. Therefore, it has become crucial for preparing recyclable sorbents that could improve the efficiency in converting or removing mercury with the consideration of the economic and environmental impact. Recently, some work in the literature has showed that the magnetic nanoparticles (MNPs) were very promising as sorbent supports in promoting the mercury removal efficiency due to their large specific surface area and magnetic property$^{18,19}$. Granite et al. have reported that the supported noble metals, especially palladium, can be used for capturing mercury, arsenic, selenium and phosphorus from an experimental simulated fuel gases in an elevated temperatures range between 200 and 400 °C$^{20,21}$.
Because of its practical importance, this field has also attracted considerably theoretical interests. Sasmaz et al. studied the adsorption of Hg on Pd binary alloys and overlays using PW91 functionally. They found that Pd has the highest mercury binding energy in comparison to other noble metals. Lim et al. found that the number of vacancies surrounding the three-fold hollow site could affect the adsorption of Hg on Au surface. It has been found that the adsorption performance of the sorbents can be improved by doping second metal or adding promoter to the sorbents. It was found that the addition of small amounts of Au, Ag and Cu to the Pd could increase the overall mercury binding energy to the Pd surface. DFT calculations were also carried out to investigate the adsorption of mercury and its compounds on the V₂O₅-WO₃-TiO₂, it is found that the ternary systems (V₂O₅-WO₃-TiO₂) showed a higher reactivity compared with the binary systems (V₂O₅-TiO₂ or WO₃-TiO₂). Therefore, it is expected that the ideal mercury removal sorbents can be prepared by introducing the magnetic nanoparticles to the Pd sorbent to form a bimetallic or alloy sorbent.

The objectives of this work are to develop a recyclable sorbent for Hg removal. To achieve the goals, the metallic Pd and a magnetic material were selected as the active metal and support to prepare these sorbents. The performance of these sorbents in removing Hg° from the simulated fuel gas was investigated using a laboratory-scale fixed-bed reactor. These include: (1) the effects of temperature on the removal of Hg° of the as-synthesized Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents; (2) the regeneration performance of the Fe₃O₄–NH₂–Pd sorbent. The fresh and used Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The mechanisms of Hg° removal over these sorbents were clarified based on the experimental results.

Results and Discussion
Effect of Pd loading content on Hg° removal over Fe₃O₄–NH₂–Pd sorbents. A comparison of the Hg° removal efficiencies over Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents at 200 °C according to our previous experimental results are shown in Fig. 1. For Fe₃O₄–NH₂, the Hg° removal only occurred within the first 30 minutes. Afterwards, the removal efficiencies sharply decreased and there was no Hg° removed after 60 min. With the addition of Pd onto the Fe₃O₄–NH₂, the Hg° removal ability was significantly enhanced. For example, the Fe₃O₄–NH₂–Pd with 1% Pd loaded on Fe₃O₄–NH₂ could remove approximately 45.7% of the Hg° after 8 h. A higher Hg° removal efficiency for the Fe₃O₄–NH₂–Pd sorbent was observed when 5 wt.% Pd was loaded. However, further increase of the Pd content, such as 10 wt.% Pd in the Fe₃O₄–NH₂–Pd, resulted in a slight decrease of the Hg° removal efficiency. Therefore, Fe₃O₄–NH₂–Pd sorbent containing 5 wt.% Pd were used in the following experiments to study the impact of temperature on Hg° removal and its regeneration performance.

Effect of temperature on Hg° removal over the magnetic sorbents. This section shows the effects of temperatures on removing Hg° for the sorbents of Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd with 5wt.% Pd loaded. The results are shown in Fig. 2. It was observed that the Hg° removal efficiency for the Fe₃O₄–NH₂ sorbent can remain above 80% for 500 min at 100 °C, as seen in Fig. 2a. When the temperature increased to 150 °C, the Hg° removal efficiency decreased from 80% to 73% within 500 min. At 200 °C, the Hg° removal efficiency for the Fe₃O₄–NH₂ sorbent sharply decreased from 96% to 0 within 60 min. These results implied that at low temperature, Fe₃O₄–NH₂ sorbent shows a good performance in removing Hg°.

Compared to the Fe₃O₄–NH₂ sorbent, when the Pd was loaded, the Fe₃O₄–NH₂–Pd sorbent showed a significantly increased capacity in capturing Hg° from the simulated coal derived fuel gas at a higher temperature, as seen in Fig. 2b. At 200 °C, the Fe₃O₄–NH₂–Pd sorbent can remove more than 90% of the Hg°, and the removal efficiency did not decrease within the tested time 500 min. With increasing temperature, the removal efficiency significantly decreased, such as 250 and 300 °C. However, the removal efficiency was still higher than that of the Fe₃O₄–NH₂ sorbent at 200 °C. Therefore, it can be concluded that the addition of Pd can dramatically improve the Hg° removal performance of the Fe₃O₄–NH₂ sorbent, and the Fe₃O₄–NH₂–Pd sorbent can be used at a higher temperature for capturing Hg°. On the basis of the different active temperatures for removing Hg°, it can thus be inferred that the Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents could remove Hg° at different paths.
Figure 3 summarizes the experimental tested mercury capacity (MC) and the theoretical mercury capacity (MCₜ) of the Fe₃O₄–NH₂–Pd sorbents. Clearly, it can be seen that the mercury capacities decreased with temperature. Compared to the theoretical mercury capacities, it can be seen that the MC obtained at three different temperatures were all lower than corresponding MCₜ. For instance, at 200 °C, the experimental mercury capacity was 30.1 μg/g, while the theoretical value is 35.0 μg/g. This is because the experimental mercury capacity (MC) was based on the measurements of the pyrolysis accessories of the mercury analyzer that can detect all the mercury species. By contrast, the theoretical mercury capacity (MCₜ) was calculated on the basis of the curve of the Hg° removal efficiency that was generated based on the detected Hg° by the online mercury analyzer. The online mercury analyzer can only detect the Hg° species in the gaseous phase because of its measurement limitation. Therefore, the difference between MC and MCₜ was considered the escaping oxidation state of mercury that were produced during removing Hg°. Such small difference, such as less than 5 μg/g, indicated that the amount of the escaping oxidation state of mercury was very limited and the majority of the mercury were absorbed as Hg° by the Fe₃O₄–NH₂–Pd sorbent.

Performance of the regenerated Hg° sorbent. In practice, the utilization of this mercury sorbent could be improved if it can be recycled by regeneration. Therefore, the performance of the multi-regenerated sorbent was included in this work. It has been found that the used magnetic materials can be easily regenerated by the external magnetic force. The used sorbent had been regenerated at 300 °C under N₂ for 2 hrs before it was used for the second Hg° removal test. The results are shown in Fig. 4. It can be seen that, for the first regenerated sorbent, the Hg° removal efficiency dropped from 96% to only 72% after 250 min. By contrast, it dropped linearly to 56% for the second regenerated sorbent with the same period of time. The unknown strategy of how to improve the performance of the regenerated Fe₃O₄–NH₂–Pd sorbent will be an angle for the future work.

Recoverability of the as-synthesized Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents. The recoverabilities of the as-synthesized Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd magnetic nanocomposite were also investigated. It can be seen from Fig. 5a and c that the Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd magnetic nanoparticles can disperse in water to form a black suspension solution. They can be pulled to the sidewall from the solution by applying a magnet.
besides the vial (Fig. 5b and d). Figures 5e and f show that Fe₃O₄–NH₂–Pd sorbent had excellent magnetic properties even after two regeneration cycles of removal of Hg⁰, which was convenient for separation and recovery.

**Stabilization of the Hg in the sorbent phase.** The stabilization of the Hg in the sorbent was tested based on the following experiments. Firstly, the Hg content of the used Fe₃O₄–NH₂–Pd sorbent after two days washing by water is 30.3 μg/g, corresponding to the data of 30.1 μg/g in Fig. 3. Also, the Hg content in the sorbents after being stored for more than one year at normal pressure and temperature is 29.7 μg/g, therefore, the Hg in the adsorbed phase can be considered to be stable.

**Characterization of Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents.** Analysis of FTIR. The existence of the amine functionalization was proved by the Fourier transform infrared (FTIR) spectra of the Fe₃O₄–NH₂ and
Fe₃O₄-NH₂–Pd sorbents before and after the Hg° removal measurements. Figure 6 indicates that a strong peak at 583 cm⁻¹ was assigned to the vibration of Fe–O bonds, which demonstrated the existence of the iron oxides. The peaks at 1070 cm⁻¹, 1624 cm⁻¹ and 3440 cm⁻¹ correspond to C–N stretching vibration, N–H deformation vibration and N–H stretching vibration, indicating the existence of the -NH₂ group on the Fe₃O₄-NH₂ sorbent. Therefore, it can be confirmed that the magnetic nanocrystals had been functionalized with amino groups in the synthetic process. There was no distinct variation after immobilization of palladium on the Fe₃O₄-NH₂ surface except that the peak intensity became slightly weak. The FTIR spectrum of the used Fe₃O₄-NH₂ (line c) and Fe₃O₄-NH₂–Pd (line d) sorbents were shown. It was found that the signals (curves) did not show significantly change after the Hg° removal except for the peak intensity. The weak peak intensity of the Fe₃O₄-NH₂–Pd after two regenerations (line e) indicated that the structure of Fe₃O₄-NH₂–Pd changed partly. This is considered one of the reasons of the lower Hg removal efficiencies for the regenerated sorbent.

Analysis of SEM and TEM. The morphology and crystallography of the as-synthesized sorbents were characterized by SEM, and the structure was clearly revealed by TEM images. Figure 7a and b indicate the Fe₃O₄-NH₂ and Fe₃O₄–NH₂–Pd particles were regular sphere and the diameters of those spheres were less than 100 nm. There was no Pd nanoparticles identified according to the SEM images, which provides a clear evidence that the Pd nanoparticles had successfully loaded onto the surface of the Fe₃O₄-NH₂ nanoparticles. The TEM image in Fig. 7c shows that the synthesized Fe₃O₄-NH₂ nanoparticles were nearly monodisperse with an average diameter of 90 nm. Figure 7d shows that the Fe₃O₄–NH₂–Pd showed the uniform TEM micrographs. The small Pd nanoparticles were highly dispersed around the surface of the magnetite. The overall morphology and the size of these particles did not vary obviously after the palladium was attached onto the surface of the magnetic nanoparticles. Besides, it can also be concluded that the particle size distribution of the Pd was centered within 7 nm. Figure 7e showed that the morphologies of the Fe₃O₄–NH₂–Pd after two regenerations cycles varied significantly compared to the fresh sorbent. It can be seen that the looser and larger aggregate structures were formed after two regeneration for the Fe₃O₄–NH₂–Pd sorbents. Some Fe₃O₄ particles were crushed and the Pd particles were partly aggregated, this may be the second reason that leads to the low Hg° removal efficiency for the Fe₃O₄–NH₂–Pd sorbents after two regenerations.

Analysis of XRD. The crystalline structures of the Fe₃O₄–NH₂ and the Fe₃O₄–NH₂–Pd were determined by the powder X-ray diffraction (XRD). As presented in Fig. 8, six characteristic diffraction peaks (2θ = 30.1, 35.5, 43.1, 53.5, 57.0 and 62.5°) can be clearly observed for Fe₃O₄–NH₂ particles. The positions and relative intensities of all diffraction peaks matched well with those from the JCPDS card (75–1610) for magnetite. These peaks were sharp and strong, indicating the products were well crystallized. However, no diffraction peaks for the Pd species were found from the XRD patterns of the fresh Fe₃O₄–NH₂–Pd sorbent, indicating that Pd species highly dispersed on the surface of Fe₃O₄–NH₂–Pd nanoparticles after the reduction with KBH₄, which was coincident with the results of TEM in Fig. 7d. The characteristic diffraction peaks of Fe₃O₄–NH₂–Pd after two regeneration cycles were slightly weak compared to those of the fresh counterpart.

Analysis of XPS. XPS spectra of both survey and high-resolution scans for the key elements on Fe₃O₄–NH₂–Pd surface were used to determine element valence of the sorbents before and after the Hg° removal, as seen in...
Figure 8. XRD patterns of (a) fresh Fe₃O₄-NH₂, (b) fresh Fe₃O₄–NH₂–Pd and (c) Fe₃O₄–NH₂–Pd after two regeneration cycles.

Figure 9. XPS spectra of Fe₃O₄–NH₂–Pd sorbents: (a) survey scan and high-resolution scan of (b) Pd3d, (c) Fe2p, (d) S2p and (e) Hg4f.
react with H₂S to form PdS. Pd²⁺/Pd₃₆ and HgS₃₇ can be assigned to PdS₃₆ and HgS₃₇, respectively. The binding energy of 164.0 eV can be assigned to Pd-Hg amalgam formed during the Hg⁰ removal can be found in the used sample. The binding energy of 337.4 eV, 336.9 eV (Pd 3d₃/₂) and 342.7 eV, 342.2 eV (Pd 3d₅/₂) could assign to Pd²⁺. The Pd 3d₃/₂ peaks also shifted to higher values due to the presence of ammonium groups. Pd²⁺ species in the fresh sorbent could be assigned to PdO that were from the oxidation of the Pd²⁺ by the lattice oxygen of Fe₂O₃. PdO can react with H₂S to form PdS. Pd²⁺ on the surface of the used and the regenerated sorbents may be assigned to PdS²⁺.

The intensity of the XPS spectra peak reflects the content of the surface atom. Table 1 showed the key elements on the surface for the fresh and used Fe₃O₄–NH₂–Pd sorbents based on the results of the XPS spectra. The ratio of Pd²⁺/Pd on the surface of the fresh Fe₃O₄–NH₂–Pd was 71.17%, indicating that the elemental Pd was the main composition of the fresh sorbent. It was deduced from the Pd²⁺/Pd ratio on the surface of the used Fe₃O₄–NH₂–Pd sorbents (79.08%) that the Pd²⁺ species was the main compositions after the removal of Hg⁰. The Pd²⁺/Pd on the surface of the used fresh Fe₃O₄–NH₂–Pd decreased to 20.92%, accordingly. It indicated that the elemental Pd on the surface of the fresh sorbent was greatly oxidized to Pd²⁺ species such as PdO or PdS during the Hg⁰ removal. It was found in Fig. 9b that only Pd²⁺ of Pd existed in Fe₃O₄–NH₂–Pd after three regeneration cycles while the Hg⁰ removal efficiency sharply decreased for the Fe₃O₄–NH₂–Pd after two regeneration cycles (showed in Fig. 4c), it also demonstrated that Pd²⁺ was the main active component. Some variations of the relative abundance between Fe²⁺ and Fe³⁺ species before and after removing of Hg⁰ were elucidated by Fe 2p XPS spectra in Fig. 9c. The Fe 2p peak consisted of octahedral Fe²⁺ (710 eV), octahedral Fe³⁺ (714 eV) and tetrahedral Fe³⁺ (712 eV) peaks. These values were very close to those of magnetite (Fe₃O₄) reported in the literature. The ratio of Fe²⁺/Fe³⁺ on the surface of Fe₃O₄–NH₂–Pd sorbent before and after removing Hg⁰ decreased from 4.36 to 3.99 (shown in Table 1). Our previous study showed that Fe₂O₃ can react with H₂S to form FeS and Sₐd (3H₂S + Fe₂O₃ → 2FeS + Sₐd + 3H₂O). This result suggested that Fe³⁺ could be reduced to Fe²⁺ by H₂S. However, the magnetism of Fe₃O₄–NH₂–Pd sorbent did not change obviously based on the results of recoverabilities of the used Fe₃O₄–NH₂–Pd sorbents.

Figure 9d shows the XPS spectra of S 2p on the surface of the used Fe₃O₄–NH₂–Pd sorbent. The binding energy of 161.6 eV and 162.9 eV can be assigned to PdS³⁶ and HgS³⁷, respectively. The binding energy of 164.0 eV belonged to elemental S. This result proved that H₂S could react with lattice oxygen and Fe²⁺ in Fe₂O₃ to form FeS, elemental S and H₂O. Afterwards, the S can react with Hg to form HgS which is considered the Hg removal reaction. However, the active temperature range of the reactions to produce HgS was very limited, being efficient only in the range of 60–140 °C since elemental S was volatized with the increasing temperature. This can explain the high efficiency in Hg⁰ removal over Fe₃O₄–NH₂–Pd sorbent at 100 °C and low efficiency at 150 °C and 200 °C. However, for Fe₃O₄–NH₂–Pd sorbent, the active temperature range of the Hg⁰ removal was enlarged because of the loading of Pd. Pd and Hg can react to generate Pd-Hg amalgam (shown in Fig. 9b), resulting in the removal of Hg⁰. The content of sulfur on the surface of the used Fe₃O₄–NH₂–Pd sorbent was 0.58%, indicating that there are abundant sulfur species such as elemental S, HgS, PdS and FeS after of the Hg⁰ removal. The binding energy of 161.6 eV and 162.9 eV can be assigned to PdS and HgS, respectively. The unreacted Pd° and Pd-Hg amalgam formed during the Hg⁰ removal was higher because that Pd and Hg can react to generate Pd-Hg amalgam. The active temperature range of the Hg⁰ removal was enlarged because of the presence of the surrounding positively charged ammonium groups. It implied the existing of –NH₂ group can stable Pd on the surface of the Fe₃O₄–NH₂ nanoparticles. The binding energy of 161.6 eV and 162.9 eV can be assigned to PdS₃₆ and HgS₃₇, respectively. The binding energy of 164.0 eV can be assigned to Pd-Hg amalgam formed during the Hg⁰ removal can be found in the used sample. The binding energy of 337.4 eV, 336.9 eV (Pd 3d₃/₂) and 342.7 eV, 342.2 eV (Pd 3d₅/₂) could assign to Pd²⁺. The Pd 3d₃/₂ peaks also shifted to higher values due to the presence of ammonium groups. Pd²⁺ species in the fresh sorbent could be assigned to PdO that were from the oxidation of the Pd²⁺ by the lattice oxygen of Fe₂O₃. PdO can react with H₂S to form PdS. Pd²⁺ on the surface of the used and the regenerated sorbents may be assigned to PdS²⁺.

Table 1. Concentrations of elements on the surface of the fresh and used Fe₃O₄–NH₂–Pd sorbents according to the XPS results.

| Samples | Pd²⁺/Pd (%) | Fe²⁺/Fe³⁺ (%) | Sₐd (wt.%) | Hg (wt.%) |
|---------|-------------|---------------|-------------|-----------|
| fresh   | 28.83       | 4.36          | 91.82       | —         |
| used    | 79.08       | 5.99          | 91.80       | 0.38      |

Mechanism of the Hg⁰ removal of Fe₃O₄–NH₂–Pd sorbent. The experimental results indicated that the Fe₃O₄–NH₂–Pd sorbent showed a good activity in removing Hg⁰. Based on the experimental result, the mechanism of the Hg⁰ removal over Fe₃O₄–NH₂–Pd sorbent could be discussed as follows: there were two paths in removing Hg⁰ from coal derived fuel gas over the Fe₃O₄–NH₂–Pd sorbent.

\[
\text{Pd} + \text{Hg} \rightarrow \text{Pd} - \text{Hg} \text{ amalgam}
\]
Conclusion

The magnetic Fe₃O₄–NH₂–Pd sorbent was successfully synthesized using a facile one-pot template-free method combined with a metal adsorption-reduction procedure on the Fe₃O₄–NH₂. The performances of the Hg° removal over the Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents showed that the loaded Pd on the amine-functionalized magnetite nanoparticles could greatly enhance the efficiency in removing Hg° at a higher operation temperature range between 200 and 300 °C. The Fe₃O₄–NH₂–Pd sorbent with a 5% Pd loaded exhibited significantly high activity and stability in Hg° capture, affording over 93% capture efficiency at 200 °C for more than 8 hrs. In term of the mechanism, it was considered that the Hg° was removed on the Fe₃O₄–NH₂–Pd sorbent by forming Pd-Hg amalgam and HgS. By contrast, the Hg° was mainly converted as HgS over the Fe₃O₄–NH₂ sorbent. With regard to the recyclable utilization, the used sorbents could be easily regenerated at 300 °C under N₂ atmosphere. The activity in removing Hg° for the regenerated Fe₃O₄–NH₂–Pd sorbent slightly decreased, however, the magnetic properties after two regenerations were still stable. These findings proved that the Fe₃O₄–NH₂–Pd sorbent could be considered as a recyclable candidate for the Hg° removal from coal derived fuel gas.

Method

Ferric chloride hexahydrate (FeCl₃·6H₂O), anhydrous sodium acetate (NaAc), ethylene glycol (EG), 1,6-hexanediamine and ethanol, potassium borohydride (KBH₄), Pd(NO₃)₂, all chemicals were purchased form Aladdin Industrial Corporation and used as received without further treatment. De-ionized water was used throughout the experiments.

The Fe₃O₄–NH₂ nanoparticles were prepared according to the reference and we do some modification on it. Typically, a solution of 6.5 g 1,6-hexanediamine, 2.0 g anhydrous sodium acetate and 1.2 g FeCl₃·6H₂O as a ferric source in 35 mL ethylene glycol was stirred at 50 °C to give a transparent solution. The solution was then transferred into a teflon-lined autoclave and then kept at 200 °C for 6 hrs. The magnetic nanoparticles were then rinsed with water and ethanol for several times to effectively remove the solvent and unbound 1, 6-hexanediamine, and then dried under vacuum at room temperature to obtain a black powder for further use. During each rinsing step, the nanoparticles were separated from the supernatant by using a magnetic force.

The Fe₃O₄–NH₂–Pd nanoparticles were prepared according to the reported method with some modification. 0.5 g of synthesized Fe₃O₄–NH₂ nanoparticles was placed in a 50 mL ethanol solution and then treated with ultrasonic for 0.5 hrs. This black suspension solution was mixed with 3.0 mM of a Pd(NO₃)₂ solution for 1 hrs with ultrasonic. Then the sorbent was reduced by an excess 0.1 M KBH₄ aqueous solution. It was slowly dropped into the above mixture with stirring. The solid sorbent was separated by magnet and was washed by deionized water after 2 hrs of reduction. The sorbent was dried at 45 °C under vacuum. The Pd loading amounts in the sorbent ranged from 0 to 10 wt %. Finally, all samples were pressed for tabletting and then sieved at 40–60 mesh.

The performance of Hg° removal over the as-synthesized Fe₃O₄–NH₂ and Fe₃O₄–NH₂–Pd sorbents was detected by a fixed-bed reactor. It includes four parts: Hg generation, gas mixture, a reactor and an online mercury analyzer (Lumex RA-915 M). Hg vapor was brought into the evaluation system using ultrahigh purity N₂ as a carrier. The flow rate through the U tube was accurately controlled by a mass-flow controller. The simulated fuel gas consisted of 10 vol.% H₂, 20 vol.% CO, 300 ppm H₂S, 45 °C ± 0.5 °C. Hg vapor was brought into the evaluation system using ultrahigh purity N₂ as a carrier. The flow rate through the U tube was accurately controlled by a mass-flow controller. The simulated fuel gas was consisted of 10 vol.% H₂, 20 vol.% CO, 300 ppm H₂S, 45 °C ± 0.5 °C. Hg vapor, balancing gas N₂ (470 ml/min) and carrier gas N₂ (500 ml/min).

A total of 0.50 g sorbent was placed in the horizontal quartz reactor (5 mm of the inner diameter) and then packed with quartz wool to support the sorbent layer and avoid its loss. Subsequently, the simulated fuel gas was switched into the reactor at the desired temperature. Hg vapor concentrations at the inlet and outlet of the reactor containing sorbents were monitored using a Lumex mercury analyzer. The removal efficiency (η) of Hg° was used to evaluate the performance of the sorbents for the capture of Hg° from coal derived fuel gas. η is calculated by the following formula:

\[
\eta(\%) = \frac{C_0 - C_1}{C_0} \times 100\%
\]

where \(C_0\) and \(C_1\), μg/m³ or ppm, are the concentrations of Hg° in the feed and effluent gases, respectively.

Mercury content of the sorbent after evaluating is defined as mercury capacity (MC) and it can be directly detected by the pyrolysis accessories (PYRO-915+) of mercury analyzer. All the mercury species can be detected by the pyrolysis accessories of mercury analyzer. Theoretical adsorption mercury capacity (MC_T) of the sorbents can be calculated by the curve of the Hg° removal efficiency, the formulas is showed as bellow:

\[
MC_T (\mu g/g) = \sum \eta \frac{C_0 Q t_i}{G} \times 1000
\]
where \( \eta \) is the mercury removal efficiency at \( t \), which is the adsorption time in the \( i \) reactive time (min), \( C_0 \) is the initial concentration (\( \mu g/m^3 \)) of \( Hg^2+ \) in the feed gas, \( Q_i \) is the flow rate of coal derived fuel gas, \( G \) is the weight of sorbent in the reactor (g).

After the mercury removal test, the used sorbents were regenerated by heating to 300 °C in pure \( N_2 \) carrier gas for 2 hrs. Several capture–regeneration cycles were conducted to evaluate the regeneration performance of \( FeO_x-NH_2-Pd \) sorbent.

The fresh and used \( FeO_x-NH_2 \) and \( FeO_x-NH_2-Pd \) sorbents were determined by Fourier transform infrared (FTIR, Bruker Vertex 70) and the scan range is from 4000 cm\(^{-1} \) to 400 cm\(^{-1} \).

Morphology and particle dispersion of the as-synthesized \( FeO_x-NH_2 \) and \( FeO_x-NH_2-Pd \) were investigated by scanning electron microscopy (SEM) (Cam scan MV2300). The chemical compositions of the synthesized nanostructures were measured by EDS performed of SEM. Transmission electron microscopy (TEM) images were obtained on a Hitachi H-800 transmission electron microscope with an accelerating voltage of 200 kV.

X-ray diffraction (XRD) was employed to investigate the crystal structures of the synthesized sorbents. The instrument was a Rigaku Miniflex 600 diffractometer, fitted with a nickel-filtered Cu K\( \alpha \) radiation source operating at a voltage of 40 kV and 100 mA. The scan rate was 8°/min in the range from 15° to 80°.

X-ray photoelectron spectroscopy (XPS) surface analysis was conducted to determine the elemental speciation and concentration on the surface of \( FeO_x-NH_2-Pd \) sorbents, using an ESCALAB 250 spectrometer (VG Scientific Ltd., UK) equipped with an Al K\( \alpha \) source (1486.6 eV, 150 W). Energy calibration was performed using C 1s peak at 284.6 eV. No smoothing routine of data was applied to analyze the results.

References

1. Park, C.-L. & Kim, B.-G. The optimization of low-rank coal grinding for transport coal gasification by robust design. *Fuel* **95**, 282–286, doi:10.1016/j.fuel.2011.09.031 (2012).

2. Johari, K., Saman, N., Song, S. T., Mat, H. & Stuckey, D. C. Utilization of coconut milk processing waste as a low-cost mercury sorbent. *Ind. Eng. Chem. Res.* **52**, 15648–15657 (2013).

3. Li, H., et al. Role of flue gas components in mercury oxidation over TiO\(_2\)-supported MnO\(_x\)-CeO\(_2\), mixed-oxide at low temperature. *J. Hazard. Mater.* **243**, 117–123 (2012).

4. Pavlish, J. H., et al. Status review of mercury control options for coal-fired power plants. *Fuel Process. Technol.* **82**, 89–165 (2003).

5. Wang, J., et al. Simultaneous removal of hydrogen sulfide and mercury from simulated syngas by iron-based sorbents. *Fuel* **103**, 73–79, doi:10.1016/j.fuel.2011.10.056 (2013).

6. Hou, W., Zhou, J., Qi, P., Gao, X. & Luo, Z. Effect of H\(_2\)S/HCL on the removal of elemental mercury in syngas over CeO\(_2\)-TiO\(_2\). *Chem. Eng. J.* **241**, 131–137 (2014).

7. Granite, E. J., Myers, C. R., King, W. P., Stanko, D. C. & Pennline, H. W. Sorbents for mercury capture from fuel gas with application to gasification systems. *Ind. Eng. Chem. Res.* **45**, 4844–4848 (2006).

8. Zhao, Z., et al. One pot synthesis of tunable Fe\(_3\)O\(_4\)–MnO\(_2\) core–shell nanoplates and their applications for water purification. *J. Mater. Chem. B* **22**, 9052, doi:10.1039/c2tb0153e (2012).

9. Gu, Y. et al. Evaluation of elemental mercury adsorption by fly ash modified with ammonium bromide. *J. Therm. Anal. Calorim.* **119**, 1663–1672 (2015).

10. Zhang, Y., et al. Effects of modified fly ash on mercury adsorption ability in an entrained-flow reactor. *Fuel* **128**, 274–280 (2014).

11. Jurg, J. et al. Mercury removal from incineration flue gas by organic and inorganic adsorbents. *Chemosphere* **47**, 907–913 (2002).

12. Lee, S.-H. & Park, Y.-O. Gas-phase mercury removal by carbon-based sorbents. *Fuel Process. Technol.* **84**, 197–206 (2003).

13. Ghorishi, S. B., Keeney, R. M., Serre, S. D., Gullett, B. K. & Jozewicz, W. S. Development of a Cl-impregnated activated carbon for entrained-flow capture of elemental mercury. *Environ. Sci. Technol.* **36**, 4454–4459 (2002).

14. Zeng, H., et al. Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. *Fuel* **83**, 143–146, doi:10.1016/s0016-2361(03)00235-7 (2004).

15. Granite, E. J., Pennline, H. W. & Harigr, R. A. Novel sorbents for mercury removal from flue gas. *Ind. Eng. Chem. Res.* **39**, 1020–1029 (2000).

16. Bisson, T. M. et al. Chemical–mechanical bromination of biomass ash for mercury removal from flue gases. *Fuel* **108**, 54–59 (2013).

17. Bisson, T. M. & Xu, Z. Potential Hazards of Brominated Carbon Sorbents for Mercury Emission Control. *Environ. Sci. Technol.* **49**, 2496–2502 (2015).

18. Yang, S. et al. Gaseous elemental mercury capture from flue gas using magnetic nanosized (Fe\(_3\)O\(_4\). \( \text{Mn}_n \) \(_{1-x}\)-O\(_x\)). *Environ. Sci. Technol.* **45**, 1540–1546 (2011).

19. Yang, S. et al. Low temperature selective catalytic reduction of NO with NH\(_3\) over Mn-Fe spinel: performance, mechanism and kinetic study. *Appl. Catal., B: Environ.* **110**, 71–80 (2011).

20. Poulston, S. et al. Metal sorbents for high temperature mercury capture from fuel gas. *Fuel* **86**, 2201–2203 (2007).

21. Baltrus, J. P., Granite, E. J., Stanko, D. C. & Pennline, H. W. Surface characterization of Pd/Al\(_2\)O\(_3\) sorbents for mercury capture from fuel gas. *Main Group Chem. 7*, 217–225 (2008).

22. Baltrus, J. P. et al. Surface characterization of palladium-alumina sorbents for high-temperature capture of mercury and arsenic from fuel gas. *Fuel* **89**, 1323–1325 (2010).

23. Baltrus, J. P. et al. Effect of palladium dispersion on the capture of toxic components from fuel gas by palladium-alumina sorbents. *Fuel* **90**, 1992–1998 (2011).

24. Rupp, E. C., Granite, E. J. & Stanko, D. C. Laboratory scale studies of Pd/\( \gamma \)-Al\(_2\)O\(_3\) sorbents for the removal of trace contaminants from coal-derived fuel gas at elevated temperatures. *Fuel* **108**, 131–136 (2013).

25. Sasmaz, E., Aboud, S. & Wilcox, J. Hg Binding on Pd Binary Alloys and Overlays. *J. Phy. Chem. C* **113**, 7813–7820, doi:10.1021/jp8112478 (2009).

26. Lim, D.-H., Aboud, S. & Wilcox, J. Investigation of Adsorption Behavior of Mercury on Au(111) from First Principles. *Environ. Sci. Technol.* **46**, 7260–7266, doi:10.1021/es300046d (2012).

27. Aboud, S., Sasmaz, E. & Wilcox, J. Mercury adsorption on PdAu, PdAg and PdCu alloys. *Main Group Chem. 7*, 205–215, doi:10.1080/10242200802465213 (2008).

28. Suarez Negreira, A. & Wilcox, J. Role of WO\(_3\) in the Hg Oxidation across the V2O\(_5\)–WO\(_3\)–TiO\(_2\) SCR Catalyst: A DFT Study. *J. Phy. Chem. C* **117**, 24397–24406, doi:10.1021/jp707794z (2013).

29. Zhang, F. et al. Pd immobilized on amine-functionalized magnetite nanoparticles: a novel and highly active catalyst for hydrogenation and Heck reactions. *Green Chem. 13*, 1238–1243 (2011).

30. Hou, W. et al. Pd/Al\(_2\)O\(_3\) sorbents for elemental mercury capture at high temperatures in syngas. *Ind. Eng. Chem. Res.* **53**, 9909–9914 (2014).
31. Kumar, G., Blackburn, J., Albridge, R., Moddeman, W. & Jones, M. Photoelectron spectroscopy of coordination compounds. II. *Palladium complexes*. *Inorg. Chem.* 11, 296–300 (1972).

32. JoseAmalis, A. & Kumarrana, R. Trapping Pd(0) in nanoparticle-assembled microcapsules: an efficient and reusable catalyst. *Chem. Commun.* 4165–4167 (2008).

33. Ma, M. et al. Preparation of high-magnetization Fe₃O₄–NH₂–Pd(0) catalyst for Heck reaction. *Catal. Commun.* 17, 168–172 (2012).

34. Yue, C. et al. Effects of pretreatment of Pd/AC sorbents on the removal of Hg 0 from coal derived fuel gas. *Fuel Process. Technol.* 135, 125–132 (2015).

35. Scott, T., Allen, G., Heard, P. & Randell, M. Reduction of U (VI) to U (IV) on the surface of magnetite. *Geochem. Cosmochim. Acta* 69, 5639–5646 (2005).

36. Liu, S., Wang, X., Wang, K., Lv, R. & Xu, Y. ZnO/ZnS–PdS core/shell nanorods: synthesis, characterization and application for photocatalytic hydrogen production from a glycerol/water solution. *Appl. Surf. Sci.* 283, 732–739 (2013).

37. Hyland, M., Jean, G. & Bancroft, G. XPS and AES studies of Hg (II) sorption and desorption reactions on sulphide minerals. *Geochem. Cosmochim. Acta* 54, 1957–1967 (1990).

38. Zhang, H., Zhao, J., Fang, Y., Huang, J. & Wang, Y. Catalytic oxidation and stabilized adsorption of elemental mercury from coal-derived fuel gas. *Energy Fuels* 26, 1629–1637 (2012).

39. Hutson, N. D., Attwood, B. C. & Scheckel, K. G. XAS and XPS characterization of mercury binding on brominated activated carbon. *Environ. Sci. Technol.* 41, 1747–1752 (2007).

40. Wang, L., Bao, J., Wang, L., Zhang, F. & Li, Y. One-pot synthesis and bioapplication of amine-functionalized magnetite nanoparticles and hollow nanospheres. *Chem. Eur. J.* 12, 6341–6347 (2006).

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**Author Contributions**

Lina, Qinglian and Jiancheng designed/carried out the experiments, Qinglian and Shuai Chen preformed the sample characterization measurements, Lina and Qinglian wrote the main manuscript text. all the authors analyzed the results and reviewed the manuscript.

**Additional Information**

**Competing Interests:** The authors declare that they have no competing interests.

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