Smart Modification of HZSM-5 with Manganese Species for the Removal of Mercury

Haining Wang,* Wei Ma, Jiangbo Yan, and Dong Ye

ABSTRACT: In this study, a series of Mn-modified HZSM-5 samples were synthesized using the solid-state ion-exchange method, and the effects of the manganese loading amount, calcination temperature, reaction temperature, and gas components on mercury removal efficiency were systematically explored. Given that the mass ratio of HZSM-5 to KMnO₄ and the calcination and reaction temperatures were set to 10:2.6 and 400 and 150 °C, Hg⁰ removal efficiency could reach a peak value of 96.4% when exposed to the flue gas containing 5% O₂ and N₂ as the balance. Among the various gas components, O₂ and NO showed a positive impact on Hg⁰ removal; Hg⁰ removal efficiency could even reach ca. 100% when O₂ and NO were simultaneously introduced. In contrast, the introduction of SO₂ led to a decline of Hg⁰ removal efficiency by ca. 16%. In addition, Hg⁰ removal efficiency could still retain ca. 92% of that for the fresh sample after six regeneration and reuse cycles, which is indicative of a satisfactory stability and renewability. Finally, Mars–Maessen mechanisms dominated in the mercury chemical adsorption process.

1. INTRODUCTION

Mercury in the flue gases of power plants has been a major environmental problem throughout the world because of this species’ high toxicity, volatility, and bioaccumulation.¹ In order to cut down the mercury emissions from the power stations, Ministry of Environment Protection of China renewed the emission standard of air pollutants for thermal power stations. The emission limit value of Hg is set to be 0.03 mg m⁻³. Faced with such an urgent environmental problem, effective mercury removal methods should be adopted.

Mercury in the flue gases can be divided into three categories: particle-bound mercury (Hg⁰), oxidized mercury (Hg²⁺), and element mercury (Hg⁰). Among these three kinds of mercury species, Hg⁰ and Hg⁴⁺ could be effectively captured by electrostatic precipitators (ESPs) and wet flue gas desulfurization (WFGD), respectively.² Because of this species’ low water solubility and high vapor pressure, it is hard to realize the effective removal of Hg⁰ relying on the present desulfurized and particulate control devices.³ Therefore, developing superior mercury sorbents constitutes the vital task to reduce the emission of mercury.⁴

Activated carbon, a typical kind of sorbent, has been widely used in power stations for the removal of mercury.⁵ However, the high cost, low adsorption capacity, and low adsorption rate constitute the main barrier to the industrialization of activated carbon.⁶ Therefore, developing a new kind of sorbent material with a satisfactory performance and a low cost has been the hotspot in the environmental field. Thanks to this material’s satisfactory thermal stability and high specific surface area, among all the materials, metal-modified molecular sieve material is regarded as a potential sorbent for the adsorption of mercury.⁷ Generally, some transition metals and rare earth metals, such as Cu, Fe, Mn, and Ce, have been always used to decorate the molecular sieve materials.⁷ Due to the superior
redox properties of metals, introducing these metals could provide abundant active sites for the adsorption of mercury, thereby leading to an increased mercury removal efficiency. Fan found that Cu-modified molecular sieve material exhibits a satisfactory Hg\textsuperscript{0} removal efficiency and deNO\textsubscript{x} activity at 250 °C. Zhou claimed that Hg\textsuperscript{0} removal efficiency could be increased to a certain extent upon the introduction of CeO\textsubscript{2} or La\textsubscript{2}O\textsubscript{3}. In the case of Mn-HZSM-5 material for the removal of mercury in the flue gases, scanty research has been conducted. However, this research can provide a theoretical basis for the development and commercialization of new mercury sorbents with a low cost and a superior performance.

In this study, a series of Mn-modified HZSM-5 samples were synthesized using the solid-state ion-exchange method. X-ray diffraction (XRD), N\textsubscript{2} adsorption, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) were conducted to study the physicochemical properties of the series samples. X-ray photoelectron spectroscopy (XPS) was carried out to discover the detailed mechanisms of mercury adsorption on Mn-HZSM-5 materials.

2. RESULTS AND DISCUSSION

2.1. Performance of the Series Samples. 2.1.1. Effect of the Mass Ratio of HZSM-5 to KMnO\textsubscript{4}. As is shown in Figure 1, Hg\textsuperscript{0} removal efficiency of a pure HZSM-5 sample is quite low, whose value is just 26.3%. Given the decoration of manganese species, this value continuously increases. This can be ascribed to the fact that adding manganese species could activate the catalyst lattice oxygen; Hg\textsuperscript{0} is prone to being oxidized to Hg\textsuperscript{2+} by the activated catalyst lattice oxygen. Compared to Hg\textsuperscript{0}, Hg\textsuperscript{2+} seems to be somewhat easier to remove. Given that the mass ratio of HZSM-5 to KMnO\textsubscript{4} is 10:2.6, mercury removal efficiency reaches a peak value of ca. 94.6%. Further increasing the doping amount of manganese species, Hg\textsuperscript{0} removal efficiency drops down. This might be because the introduction of excess manganese species would block the pore structures of HZSM-5, which exerts an inhibitory effect on the interactions between the active sites and mercury, thereby resulting in a declined Hg\textsuperscript{0} removal efficiency.

2.1.2. Effect of Calcination Temperature. As is demonstrated in Figure 2, the samples calcined at 400 °C exhibit the highest mercury removal efficiency of 96.4%. Given that the calcination temperature increases, Hg\textsuperscript{0} removal efficiency decreases to some extent. This is because a high-temperature calcination process might damage the pore structures of the samples, which would decrease the specific surface area and total pore volume of the samples. In addition, highly dispersed surface active sites tend to aggregate together to form large particles, which would consequently decrease the mercury removal efficiency.

As is mentioned above, the sample, whose mass ratio of HZSM-5 to KMnO\textsubscript{4} and calcination temperature are set to 10:2.6 and 400 °C, exhibits the highest Hg\textsuperscript{0} removal efficiency. Therefore, this sample could be chosen to investigate the effect of other factors on the adsorbent Hg\textsuperscript{0} removal efficiency. Together with the pure HZSM-5 sample, this sample can also be selected for the following characterizations to investigate the variations in the physicochemical properties of the samples upon the modification of manganese species. For convenience, this sample can be denoted as Mn-HZSM-5 for short.

2.1.2.1. Effect of Reaction Temperature. As is revealed in Figure 3, it can be seen that Hg\textsuperscript{0} removal efficiency increases from 93.1 to 96.4% with the reaction temperature going up to 150 °C. Further increasing the temperature to 250 °C, Hg\textsuperscript{0} removal efficiency sharply decreases. Figure 3 also illustrates the Hg\textsuperscript{0} adsorption capacity of the series samples. At 150 °C, Hg\textsuperscript{0} adsorption capacity reaches the highest value of 1.3 mg/g, which then continuously decreases to 0.5 mg/g as the temperature rises to 250 °C. A relatively higher temperature decreases to some extent. This is because a high-temperature calcination process might damage the pore structures of the samples, which would decrease the specific surface area and total pore volume of the samples. In addition, highly dispersed surface active sites tend to aggregate together to form large particles, which would consequently decrease the mercury removal efficiency.

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could help to activate the reactants, hence promoting the adsorption of Hg⁰ to a certain extent. Further increasing the temperature, mercury would easily desorb from the sample surface, thereby resulting in a decreased adsorption capacity.

2.1.3. Effect of Gas Components. 2.1.3.1. Effect of O₂. The impact of gas components on Hg⁰ removal efficiency of Mn-HZSM-5 is displayed in Figure 4. Compared with that under a

N₂ atmosphere, Hg⁰ removal efficiency significantly increases from 76.6 to 96.4% when 5% O₂ is added, which is indicative of the positive effect of O₂ on Hg⁰ removal and could be explained by replenishing the consumption of surface oxygen during the adsorption period.¹⁰

2.1.3.2. Effect of NO. NO has a positive effect on Hg⁰ removal both in the presence and absence of O₂. This is because NO could be adsorbed onto the active sites of the adsorbent and react with surface oxygen to form NO₃ species, which have been proved to be beneficial for Hg⁰ oxidation.¹¹ Once NO and O₂ were simultaneously added into the reaction system, nearly 100% Hg⁰ removal efficiency could be obtained, which could be explained by the fact that the as-introduced O₂ could accelerate the oxidation of NO to NO₃ and replenish the consumption of surface oxygen.¹²

2.1.3.3. Effects of SO₂. Given that 800 ppm SO₂ was purged into the reaction system, Hg⁰ removal efficiency decreases to a certain extent. This inhibitory effect could be summarized as the following two aspects. One is that SO₃ competes with Hg⁰ for the adsorption on the active sites of the samples.¹³ The other is that SO₂ could react with metal oxides to form Inertial structures, thereby impeding the oxidation of Hg⁰. It should be noted that adding 5% O₂ exerts a slightly promotional effect on Hg⁰ removal, which could be explained by the supplement of surface oxygen species consumed by SO₂.¹⁴

2.1.4. Stability and Renewability. Stability and renewability are considered as an important index for adsorbents in practical applications. The spent adsorbents were regenerated in air at 350 °C for 30 min. Figure 5 shows the mercury removal efficiency of the series regenerates. It could be seen that after six regeneration and reuse cycles, the relative activity slightly decreases to 92%, which could be ascribed to the decrease in the active sites and destruction of the pore structures.¹⁶ This result also indicates that this sample exhibits good stability and renewability and can be a potential adsorbent for industrialization.

![Figure 4. Effect of gas components on Hg⁰ removal efficiency.](image)

![Figure 5. Stability and renewability of the adsorbent.](image)

| Regeneration Cycles | Relative activity (%) |
|--------------------|----------------------|
| 1                  | 100                  |
| 2                  | 98                   |
| 3                  | 96                   |
| 4                  | 94                   |
| 5                  | 92                   |
| 6                  | 90                   |

Figure 4. Effect of gas components on Hg⁰ removal efficiency.

Figure 5. Stability and renewability of the adsorbent.

2.2. Physicochemical Properties of the Samples. N₂ adsorption experiments were conducted to explore the specific surface areas and pore size distributions of the series samples. As is shown in Figure 6, all the samples exhibit the typical type IV isotherms, which is closely related to capillary condensation in mesopores.¹⁷ In addition, it seems that the hysteresis loops of the series samples are suggested to be the H3 type, indicating the existence of a slit-shaped structure.¹⁸ In addition, it should be noted that these two samples possess abundant micro pore structures, as is evidenced by the micropore filling phenomena.¹⁹ This would enable these two samples with a relatively large specific surface area. For the pure HZSM-5 sample, the specific surface, micropore volume, and average pore size are 253.4 m² g⁻¹, 0.09 cm⁻¹ g⁻¹, and 2.5 nm, respectively. Given that the HZSM-5 sample is decorated with manganese species, it can be seen that the specific surface area and micropore volume decrease to a certain extent, while the pore size slightly increases to 2.9 nm (Table 1). This is because the part of the pore structures would be blocked by the introduced manganese species, thereby resulting in the variations in the physical properties of the series samples.

![Figure 6. N₂ adsorption/desorption isotherms of the series samples.](image)

Table 1. Physicochemical Properties of the Samples.

| Sample       | Specific Surface Area (m² g⁻¹) | Micropore Volume (cm⁻¹ g⁻¹) | Average Pore Size (nm) |
|--------------|-------------------------------|-----------------------------|------------------------|
| Pure HZSM-5  | 253.4                         | 0.09                        | 2.5                    |
| Mn-HZSM-5    | 230.4                         | 0.08                        | 2.8                    |
| Mn-MHZSM-5   | 210.4                         | 0.07                        | 3.0                    |

XRD patterns in Figure 7 demonstrate that the crystal phase of the HZSM-5 sample remains almost unchanged upon the addition of manganese species. However, it should be noted that the peak intensity of the HZSM-5 sample decreases to some extent through introducing manganese species, suggesting that manganese species have been successfully introduced and the added MnO₂ sometimes interacts with the support HZSM-5. This exerts an inhibitory effect on the crystal growth.
of HZSM-5. In addition, weak peaks indexed to MnO2 come out for the modified sample, suggesting that Mn loading is beyond the theoretical monolayer coverage on the HZSM-5 support.

SEM was used to study the variations in the morphology of the HZSM-5 before and after the addition of manganese species. As is shown in Figure 8a,b, the pure HZSM-5 sample exhibits a typical angular hexagonal structure with a pretty smooth surface. While for the Mn-HZSM-5 sample, a few teeny particles could be clearly seen on the surface of HZSM-5, which could be attributed to the introduced manganese species. In addition, some variations in the morphology occur upon the decoration of manganese species, which might be ascribed to the grinding procedure during the sample preparation process (Figure 8c,d).

FTIR spectra of the series samples are shown in Figure 9. The IR peak centered at 448 and 1093 cm$^{-1}$ can be assigned to the asymmetric stretching vibrations of Si–O–Si bonds. The symmetric stretching vibrations of Si–O–Si species can explain the appearance of the bands at 792 and 1224 cm$^{-1}$. In addition, the characteristic peak at 543 cm$^{-1}$ could be attributed to the double six-membered ring, which is indicative of the existence of the micropore structure in HZSM-5, while the band at 1632 cm$^{-1}$ could be indexed to the vibrations of H$_2$O on the sample surfaces. It should be noted that no obvious variations in the characteristic peaks could be observed for the Mn-HZSM-5 sample, suggesting that adsorbent surface functional groups remain almost unchanged regardless of the introduction of manganese species.

2.3. Reaction Mechanisms. XPS spectra were used to study the adsorption mechanisms of Hg$^0$ on the Mn-modified sample. As is shown in Figure 10a, Mn 2p photoelectron peaks can be clearly seen. This result indicates that Mn species are successfully loaded onto the HZSM-5 surface, which is consistent with the XRD patterns in Figure 7. After deconvolution, we can see that at 641, 642.3, and 643.8 eV come out three subpeaks (Figure 10b). Based on previous studies, peaks in the range of 640.5–641.5 eV can be attributed to Mn$^{2+}$; bands between 641.5 and 642.8 eV could be related to Mn$^{3+}$, and the peaks with the binding energies of 642.8–643.8 eV can be assigned to Mn$^{4+}$. Thus it can be concluded that Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$ co-exist in these samples. After the adsorption of mercury, the content of Mn$^{4+}$ exhibits a downward trend from 25.8 to 22.9% (Table 2), demonstrating that in the Hg$^0$ adsorption process, Mn$^{4+}$ might act as a redox site for the oxidation of Hg$^0$ to Hg$^{2+}$. As a result, the valence state of Mn species would be decreased to some extent.

Table 1. N$_2$ Adsorption Results of the Series Samples

| samples   | surface area/(m$^2$·g$^{-1}$) | micropore specific area/(m$^2$·g$^{-1}$) | external surface area/(m$^2$·g$^{-1}$) | total pore volume/(cm$^3$·g$^{-1}$) | micropore volume/(cm$^3$·g$^{-1}$) | pore size/nm |
|-----------|-------------------------------|----------------------------------------|--------------------------------------|-----------------------------------|-----------------------------------|---------------|
| HZSM-5    | 253.4                         | 174.5                                  | 78.9                                 | 0.16                              | 0.09                              | 2.5           |
| Mn-HZSM-5 | 186.5                         | 95.0                                   | 91.5                                 | 0.14                              | 0.05                              | 2.9           |

Figure 7. XRD patterns of the series samples.

Figure 8. SEM images of (a, b) HZSM-5 and (c, d) Mn-HZSM-5.

Figure 9. FTIR spectra of the series samples.

For O 1s spectra, after deconvolution, the subpeak in the range of 530.1–531.4 eV can be ascribed to lattice oxygen of MnO$_2$ (O$^\alpha$), while the subpeak ranging between 532.3–532.5 eV is indexed to lattice oxygen of HZSM-5 (O$^\beta$) (Figure 10c). After the adsorption of mercury, the ratio of lattice oxygen belonging to MnO$_2$ (O$^\alpha$) decreases from 12.2 to 8.8%. At the same time, the content of lattice oxygen of HZSM-5 (O$^\beta$) increases from 87.8 to 91.1%, suggesting that lattice oxygen belonging to MnO$_2$ is involved in the adsorption of Hg$^0$.

For Hg 4f spectra, after deconvolution, at 102.8 and 103.6 eV come out two photoelectron peaks (Figure 10d). The
The former one can be attributed to the Si 2p peak, and the latter one can be ascribed to the Hg 4f peak.\textsuperscript{22b} According to the binding energy of the Hg peak, it can be concluded that Hg exists in the +2 oxidation state.\textsuperscript{8a} However, it should be noted that no peaks ascribed to Hg\textsuperscript{0} can be observed. This might be because a vacuum environment could promote the desorption behavior of Hg\textsuperscript{0} from the absorbent surface and the amount of Hg\textsuperscript{0} remaining on the sample surface is under the detection limit of the XPS detector.

It is well accepted that physical and chemical adsorptions are involved in the Hg\textsuperscript{0} adsorption process onto the HZSM-5 surface. For the chemical adsorption process, when Hg\textsuperscript{0} is chemically adsorbed onto the HZSM-5 surface, lattice oxygen of the samples plays a decisive role in the oxidation of Hg\textsuperscript{0}. In this process, Mn\textsuperscript{4+} is reduced to a lower valence state. After this, O\textsubscript{2} is used to re-oxidize the reduced Mn species. That is to say, the Mars–Maessen reaction pathway dominates in the chemical adsorption process. The detailed reaction steps are listed as follows:

\begin{equation}
\text{Hg}^0(\text{g}) \rightarrow \text{Hg}^0(\text{ads})
\end{equation}

\begin{equation}
\text{Hg}^0(\text{ads}) + \text{MnO}_x \rightarrow \text{Hg}^\text{O=O MnO}_{x-1}
\end{equation}

3. CONCLUSIONS

This study illustrated the physicochemical properties of Mn-modified HZSM-5, together with this sample’s mercury removal performance. Some conclusions are listed below:

(1) A series of Mn-modified HZSM-5 samples were prepared using the solid-state ion-exchange method. When the mass ratio of HZSM-5 to KMnO\textsubscript{4} is 10:2.6 and the calcination temperature is set at 400 °C, Hg\textsuperscript{0} removal efficiency can reach 96.4% at 150 °C, 70.1% higher than that of the pure HZSM-5 sample.

(2) The introduced manganese oxides could activate the catalyst lattice oxygen species, which would promote the oxidation of Hg\textsuperscript{0} to Hg\textsuperscript{2+}, thereby leading to an enhanced mercury removal performance.

(3) In the mercury removal process, the introduction of O\textsubscript{2} and NO favors the removal of element mercury, whereas the presence of SO\textsubscript{2} exerts an inhibitory effect on Hg\textsuperscript{0} removal.
After six cycles of regeneration and reuse, the Mn-HZSM-5 sample could still exhibit a satisfactory Hg\(^0\) removal efficiency. Finally, the Mars–Maessen routine dominates in the chemical adsorption process.

4. EXPERIMENTAL SECTION

4.1. Preparation of the Samples. Protonated Zeolite Socony Mobil-5 (denoted as HZSM-5 for short), whose molar ratio of Si/Al is 50:1, was purchased from the Catalyst Plant of Nankai University, China. First, the HZSM-5 sample was calcined in a muffle furnace at 550 °C for 2 h to remove the impurities and adsorbed H\(_2\)O. After cooling down to room temperature, the HZSM-5 sample, which was used as the support of the mercury sorbent, was placed in a drying bottle.

The mercury sorbent was synthesized using the solid-state ion-exchange method. Certain amounts of HZSM-5 and KMnO\(_4\) were mixed and finely ground (mass ratios of HZSM-5 to KMnO\(_4\) are 10:0, 10:1.6, 10:2.6, and 10:3.1), and then, the mixture was heated to a certain temperature point (300, 400, 500, and 600 °C) at a heating rate of 10 °C min\(^{-1}\) and calcined for 4 h. Finally, the mercury sorbent can be obtained. The sample, whose mass ratio of HZSM-5 to KMnO\(_4\) and calcination temperature were set to 10:2.6 and 400 °C, is denoted as Mn-HZSM-5 for short in this manuscript. The reasons would be illustrated in the following sections.

4.2. Reaction Systems. As is shown in Figure 11, the fixed-bed experimental system mainly consisted of a gas supply system, a mercury vapor generator, a fixed-bed reactor, an online mercury analyzer, a data acquisition computer, and an exhaust gas absorption device. The feed gas contained N\(_2\), 5% O\(_2\) (when used), 500 ppm NO (when used), and 800 ppm SO\(_2\) (when used) at a flow rate of 500 mL/min. The mercury vapor generator was composed of a thermostat water bath and a mercury permeation tube. Hg\(^0\) vapor (~140 μg/m\(^3\)) was generated using a mercury permeation tube with a water bath fixed at 45 °C. The sample (500 mg) was placed in the fixed-bed reactor, which contained a tubular furnace, a quartz tube reactor (10 mm inner diameter × 600 mm length), and a temperature-controller. Inlet and outlet Hg\(^0\) concentrations were determined using an online RA-915 M mercury analyzer (LUMEX Ltd., Russia). Hg\(^0\) removal efficiency and adsorption capacity could be calculated using the following equations.

\[
\eta = (1 - \frac{C_{\text{out}}}{C_{\text{in}}}) \times 100\%
\]

\[
Q = \frac{1}{M} \int_{t_1}^{t_2} (C_{\text{in}} - C_{\text{out}}) dt
\]

In these equations, \(\eta\) represents the Hg\(^0\) removal efficiency (%); inlet and outlet mercury concentrations are denoted as \(C_{\text{in}}\) and \(C_{\text{out}}\) (μg/m\(^3\)); Hg\(^0\) adsorption capacity is named as \(Q\); \(M\), \(f\), and \(t\) are related to the mass (g) of the samples, the total flow rate of flue gas (L/min), and the reaction time of Hg\(^0\) capture (min), respectively. Relative activity \(\eta/\eta_0\) was used to evaluate the stability and renewability of the samples, where \(\eta\) is the Hg\(^0\) removal efficiency for fresh samples and \(\eta_0\) is the Hg\(^0\) removal efficiency for the samples after some cycles of regeneration and reuse. For the calculation of Hg\(^0\) removal efficiency, each mercury removal test lasted for 30 min, while for calculating the Hg\(^0\) adsorption efficiency, each mercury removal test lasted for 3 h.

4.3. Characterizations. Pore structures of the series adsorbents were analyzed through N\(_2\) adsorption measurements (Micromeritics Instrument Corp., USA). Prior to each experiment, all the samples were degassed at 105 °C for 5 h. Specific surface areas and pore size distributions were estimated using the Brunauer–Emmett–Teller (BET) equation and Barrett–Joyner–Halenda (BJH) method. XRD patterns of the tested samples were recorded on an X-ray diffractometer (Siemens D500, Siemens, Japan) with CuK\(_{\alpha}\) as the radiation source in the range of 5–80° at a scanning rate of 2 °/min. X-ray photoelectron spectroscopy analysis was carried on a Thermo ESCALAB 250Xi (Thermo Fisher Scientific, USA) equipped with Al K\(_{\alpha}\) as the radiation source. Microstructures of the samples were observed using a scanning electronic microscope (Hitachi Ltd., Japan). IR spectra were collected on an FTIR spectrometer (Tian Jing Gan Dong SCI.&TECH, China) in the range of 400–4000 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\).
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