Experimental Study on the Elemental Mercury Removal Performance and Regeneration Ability of CoOₓ–FeOₓ-Modified ZSM-5 Adsorbents

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Abstract: Herein, a series of Co–Fe mixed oxide modified ZSM-5 adsorbents were synthesized using the ultrasonic-assisted impregnation method for the capture of elemental mercury. In comparison with other samples, Co₁Fe₁-ZSM-5 produced a relatively better performance, with the removal efficiency of around 96.6% Hg⁰ and the adsorption capacity of around 901.63 ug/mg Hg⁰ achieved at 120 °C. The interaction between CoOₓ and FeOₓ improved the reducibility of oxygen species, thus promoting the oxidation of Hg⁰. Among a variety of other gas components, O₂ and NO exerted a positive effect on Hg⁰, which improved its removal to a certain extent. By contrast, SO₂ caused an adverse effect on the capture of Hg⁰, which could be reversed to some degree by the introduction of 5% O₂. After five cycles, the mercury removal efficiency of Co₁Fe₁-ZSM-5 remained above 90%, suggesting excellent recyclability. Finally, XPS analysis was conducted to reveal that Mars–Maessen mechanisms are dominant in the process of mercury adsorption.

Keywords: Hg⁰ adsorption; ZSM-5; cobalt oxide; iron oxide; regeneration

1. Introduction

Mercury is a universal contaminant due to its toxicity, worldwide migration, and bioaccumulation in the food chain and the environment. Among various sources of contamination, coal-fired power plants have been found responsible for the large majority of atmospheric mercury emission [1]. In general, the mercury released from coal-fired flue gas can be classified into three categories: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺), and particulate-bonded mercury (Hg⁰) [2,3]. As for Hg¹⁺ and Hg²⁺, they can be easily removed by the existing air pollution control devices (APCDs) [4]. Nevertheless, it is practically difficult to control Hg⁰ due to its low solubility and high volatility [5]. Therefore, it is necessary to develop an efficient and environmentally friendly technology that is applicable to remove Hg⁰ from flue gases.

Up until now, there have been various technologies tested to reduce Hg⁰ emissions, such as adsorbent injection, plasma, catalytic oxidation, photochemical oxidation, and so on [6–10]. Among them, adsorbent injection, as represented by activated carbon injection (ACI), has been widely recognized as the most promising method of Hg⁰ removal [11]. In the meantime, however, it is also disadvantaged by drawbacks such as low Hg⁰ removal efficiency, high operational cost, and the deteriorating quality and reusability of fly ash, all of which impede the extensive application of this technology in practice [12–14]. Therefore, it is imperative to develop a less costly but more efficient kind of mercury adsorbent. Recently, ZSM-5 has been proposed as an extraordinary candidate adsorbent for mercury removal due to its high specific surface area and adjustable pore size [15,16]. However, considering the lack of surface-active sites for virgin ZSM-5, it is necessary to improve
Hg\(^0\) removal performance by modifying ZSM-5 [17]. As reported in the relevant literature, halides, selenides, and metal oxides can be applied as the active additives for Hg\(^0\) capture [18–22]. Due to the ease of operation, environmental friendliness, and low cost, metal oxide additives are deemed more attractive than others.

Cobalt oxides, with their unique redox couple Co\(^{2+}/Co^{3+}\), have now attracted widespread attention for Hg\(^0\) removal [23–28]. In the research conducted by Zhang et al., it was suggested that the excellent Hg\(^0\) removal performance could be achieved at 180 °C, which synthesized a CoO\(_4\)-based catalyst by one-step calcination method for Hg\(^0\) oxidation [29]. Xu et al. reported that CoO\(_4\)-modified fly ash by the wet impregnation method showed good Hg\(^0\) removal performance [30]. Using a single-step hydrothermal method to produce the cobalt-doped CeO\(_2\) catalyst for Hg\(^0\) removal, Yang et al. achieved a Hg\(^0\) removal efficiency of over 90% under a simulated low-rank coal-burning atmosphere [31]. Moreover, Fe-based catalysts performed equally well in the Hg\(^0\) removal process. As indicated by Xu et al., Fe-modified HZSM-5 produced a remarkable Hg\(^0\) removal performance [32]. Yang et al. proposed that the synthesized magnetic Fe-based adsorbent achieved a satisfactory performance in mercury removal [33]. In spite of this, there is still limited research conducted on the efficiency of Co-Fe-modified ZSM-5 adsorbent in Hg\(^0\) removal. Given the above-mentioned advantages of ZSM-5, CoO\(_x\), and FeO\(_x\), it is believed that the efficiency of Hg\(^0\) removal could be further enhanced for Co-Fe-modified ZSM-5 materials.

To achieve this purpose, Co-Fe-decorated ZSM-5 adsorbents were produced in this study to explore their potential in the abatement of Hg\(^0\) in flue gases. To be specific, the physicochemical properties of the adsorbents were characterized through a combination of X-ray diffraction (XRD), N\(_2\) adsorption, scanning electron microscope (SEM), and X-ray photoelectron spectroscopy (XPS). Then, it was investigated as to how the Hg\(^0\) removal performance of the adsorbents would be affected by Co/Fe mass ratio, reaction temperature, and flue gas components (O\(_2\), NO, SO\(_2\)). Finally, the level of recyclability and mechanisms of Hg\(^0\) adsorption were examined.

2. Experimental

2.1. Sample Preparation

Commercial Zeolite Socony Mobil-5 (ZSM-5 for short), the Si/Al molar ratio (n(SiO\(_2\))/n(Al\(_2\)O\(_3\))) of which is around 140, was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China)

The mercury adsorbent was synthesized using the ultrasound-assisted impregnation method. Firstly, ZSM-5 was calcined at 500 °C for 2 h to remove all impurities, thus enhancing the validity and reliability of the research result. Then, the cobalt nitrate and ferric nitrate of calculated amount were dissolved in deionized water to obtain a transparent solution, before being mixed with a certain amount of ZSM-5. After 12 h of stirring and 45 min of ultrasonic treatment, the sample was dried at 105 °C for 6 h and finally calcined at 450 °C in a muffle furnace in the air for 4 h. The obtained sample was labeled Co\(_x\)Fe\(_1\)-ZSM-5, where x denotes the Co/Fe mass ratio. The Co/Fe mass ratio of the prepared samples ranged from 1 to 4. A similar method was used to synthesize Co-ZSM-5 and Fe-ZSM-5 with the mixed solution replaced by ferric nitrate aqueous solution and cobalt nitrate aqueous solution. The (Co + Fe) mass ratio of all the samples was set to 8 wt%.

2.2. Sample Characterization

IR spectra were obtained through a FTIR spectrometer (GanDong SCI.&TECH. Co., Ltd., Tianjing, China) ranging from 400 to 4000 cm\(^{-1}\) at a spectral resolution of 4 cm\(^{-1}\).

An N\(_2\) adsorption experiment was carried out for several adsorbents on an AutosORB-iQ (Quantachrome Instruments, Boynton Beach, Florida) instrument. Prior to the experiment, the tested sample was degassed at 200 °C for 6 h. The specific surface areas of the tested samples were calculated using the Brunauer–Emmett–Teller (BET) equation, while the density functional theory (DFT) method was used to determine pore size distributions.
The crystal structure of a series of adsorbents was determined using an Empyrean (PANalytical B.V., Almelo, The Nederlands) X-ray diffraction device equipped with Cu Ka as the radian source in the range of 5–80° at a scanning rate of 2°/min. Microstructure and morphology of the modified samples were investigated on an EVO 18 (ZEISS, Oberkochen, Germany) coupled with energy dispersive X-ray spectroscopy to examine the chemical composition.

H₂ temperature-programmed reduction (H₂-TPR) was analyzed by means of AutoChem II 2920 (Micromeritics Instruments, Norcross, GA, USA). Before the experiment was conducted, the tested sample was pretreated at 300 °C for 30 min. After cooling to room temperature, its temperature was raised again to 800 °C at a heating rate of 10 °C/min. The H₂ signal was continuously recorded by a thermal conductivity detector (TCD).

The element chemical state and chemical composition of the samples were examined using a Thermo ESCALAB 250XI (Thermo Fisher Scientific Inc., Waltham, MA, USA) equipped with Al Kα X-ray source. All the binding energies were calibrated with the C1s line at 284.6 eV.

The metal contents of modified samples were analyzed by an Inductively Coupled Plasma-Atomic Emission Spectrometry (SPECTRO Analytical Instruments, Kleve, Germany).

### 2.3. Experimental Setup and Procedure

The experimental configuration intended for Hg⁰ adsorption is illustrated in Figure 1. The entire experimental system consists of a mercury generation system, an electric tube furnace reactor, an online mercury detector, an online data acquisition system, and an exhaust gas absorption device.

![Schematic diagram of the experimental setup.](image)

*Figure 1. Schematic diagram of the experimental setup.*

The performance test was carried out using a 0.4 g sample. Hg⁰ vapour (≈200 µg/m³) was generated through a mercury permeation tube placed in a U-shaped quartz tube. The temperature of the water bath was maintained at 50 °C. The total flow rate of the flue gas was set to 600 mL/min, with 5% O₂ 500 ppm NO (when used), 800 ppm SO₂ (when used), and N₂ contained as the balanced gas. Both inlet and outlet Hg⁰ concentrations were
monitored by an online mercury analyzer RA-915M (LUMEX Ltd., St. Petersburg, Russia). Hg\textsuperscript{0} removal efficiency was calculated using the following equation [33]:

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

where \(\eta\) represents the Hg\textsuperscript{0} removal efficiency (%), while \(C_{\text{in}}\) and \(C_{\text{out}}\) (\(\mu\text{g/m}^3\)) refer to the inlet and outlet mercury concentrations.

Hg\textsuperscript{0} uptake capacity \(q_t\) (\(\mu\text{g/g}\)) was determined for the sample using Equation (2) [33], where \(M\) represents the mass (g) of samples, \(f\) indicates the total flow rate (mL/min) of flue gas, and \(t\) denotes the adsorption time (min) required for Hg\textsuperscript{0} capture. Each test lasted for 90 min to calculate Hg\textsuperscript{0} removal efficiency and Hg\textsuperscript{0} adsorption capacity.

\[
q_t = \frac{1}{M} \int_{t_1}^{t_2} (C_{\text{in}} - C_{\text{out}}) \, dt \tag{2}
\]

The pseudo-first-order model and pseudo-second-order model were applied to analyze the process of Hg\textsuperscript{0} capture for the estimate of Hg\textsuperscript{0} adsorption capacity. The pseudo-first-order model is expressed as follows [23,34]:

\[
q_t = q_e \times \left(1 - e^{-k_1 t}\right) \tag{3}
\]

The pseudo-second-order model is expressed as the following equation [34]:

\[
q_t = \frac{q_e^2 \cdot k_2 \cdot t}{1 + q_e \cdot k_2 \cdot t} \tag{4}
\]

where \(q_t\) and \(q_e\) represent the level of mercury adsorption capacity at time \(t\) (\(\mu\text{g/g}\)) and the equilibrium point, respectively, while \(k_1\) and \(k_2\) refer to the rate constant of pseudo-first-order-model and pseudo-second-order-model, respectively.

Recyclability of the adsorbents was carried out in the above-mentioned fixed-bed micro-reactor. Briefly, after the adsorption process, the spent Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 was treated in certain flue gases at different temperatures for 2 h. Then, the sample was cooled down to the desired temperature point for the next Hg\textsuperscript{0} removal performance evaluation cycle.

3. Results and Discussion

3.1. Performance of a Series Samples

Figure 2 shows the performance of the adsorbents at different Co/Fe mass ratios in O\textsubscript{2}-containing flue gas at a temperature ranging between 60 and 180 °C. The pure ZSM-5 sample exhibited a relatively low level of efficiency in Hg\textsuperscript{0} removal. Given the modification to CoO\textsubscript{x} or FeO\textsubscript{x}, there was an obvious improvement detected in the efficiency of Hg\textsuperscript{0} removal. The mercury removal efficiency of Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 sorbents was enhanced with the increase of Co mass ratio. Compared with other samples, Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 and Co-ZSM-5 achieved a satisfactory performance in mercury removal. Hg\textsuperscript{0} removal efficiency reached up to around 96%. In order to identify the variation in performance between Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 and Co-ZSM-5, the theoretical capacity of Hg\textsuperscript{0} adsorption by these samples was calculated (Figure S1). It was found out that Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 performed better in Hg\textsuperscript{0} removal, as evidenced by the higher theoretical capacity of Hg\textsuperscript{0} adsorption. According to these results, there must be a significant synergistic effect at play between cobalt oxides and iron oxide, thus promoting mercury removal. Moreover, Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 is applicable as an optimal sample for further experimentation. The theoretical capacity of Hg\textsuperscript{0} capture by Fe-ZSM-5 is extremely low, which is consistent with the result of Hg\textsuperscript{0} removal efficiency, as shown in Figure 2a. Additionally, it is worth noting that the Hg\textsuperscript{0} removal efficiency profiles of Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 resemble a volcano, which is attributable to the increasingly active reactant with the rise of temperature and the desorption of mercury species from the adsorbent.
surfaces at an excessively high reaction temperature [33,35]. Compared with the reported adsorbents (Table S1), it seems that Co₄Fe₁ZSM-5 can be a potential adsorbent for the practical application.

Figure 2. (a) Removal of mercury over various samples; (b) calculation of adsorption capacity for the pseudo-first-order model and pseudo-second-order model.

3.2. Physicochemical Properties of the Samples

3.2.1. FTIR Analysis

FTIR was involved in exploring the surface nature of various samples. As shown in Figure 3, all of the samples exhibited six characteristic peaks in the range of 400 and 2000 cm⁻¹, suggesting no significant effect of loading Co-Fe mixed oxides on the surface functional groups of ZSM-5. As demonstrated in the previous research, the bands at 796 and 1233 cm⁻¹ are related to the symmetric stretching vibrations of Si-O-Si [36]. Moreover, the peaks at 448 and 1102 cm⁻¹ corresponded to the Si-O-Si asymmetric stretching vibrations. Conversely, the characteristic peak at 543 cm⁻¹ was assigned to the double six-membered ring, which indicates the existence of micropore structure in ZSM-5 [17,36]. Moreover, the bending vibration of hydroxyl species accounted for the appearance of the peak at 1632 cm⁻¹ [37].

Figure 3. FTIR spectra of a series of samples.
3.2.2. XRD Analysis

Figure 4 shows the XRD patterns of these four samples under study. All of the samples exhibited typical ZSM-5 peaks (2θ = 23.1°, 23.3°, and 24.4° PDF-ICDD 44-0003), suggesting the presence of MFI structure. Moreover, it can be seen that there were no evident variations in the peaks of XRD diffraction that could be detected for these three modified samples, indicating the limited impact of doping active components on the crystal structure of the support [38]. As for Co-ZSM-5 and Fe-ZSM-5 samples, the peaks at 36.8° indexed to Co3O4 (PDF-ICDD 42-1467) and 33.1° attributed to Fe2O3 (PDF-ICDD 33-0664) were found distinct, suggesting the loading of Co and Fe beyond the theoretical monolayer coverage on the ZSM-5 surface. As for CoFe1-ZSM-5, the appearance of diffraction peaks was attributed to the disappearance of iron oxides, suggesting the potential existence of iron oxides in a highly dispersed state on the surface of ZSM-5 [39,40]. Moreover, compared with CoFe1-ZSM-5 and Co-ZSM-5, the peaks indexed to cobalt oxides were weakened and widened, implying that the introduction of Fe2O3 exerts an inhibitory effect on the growth of Co3O4, thus reducing the size of cobalt oxide particles. As a consequence, there might be more active sites provided for the reactions [41].

![XRD patterns of a series of samples](image)

**Figure 4.** XRD patterns of a series of samples.

3.2.3. BET Analysis

N2 adsorption experiments were conducted to investigate the structural properties of these samples. As shown in Figure 5a, all of these samples exhibited typical type IV isotherms and type H3 hysteresis loops, implying the existence of mesopores with slit-shaped structures [2]. In addition, it is worth noting that all these samples displayed a sharp rise of nitrogen uptake in low relative pressure regions, signaling the presence of abundant micropore structures [42]. Figure 5b shows the corresponding pore size distributions of various samples, which confirms the co-existence between micropores and mesopores [41,43]. The N2 adsorption data are listed in Table 1, from which it can be found out that the adsorbent micropore surface area shrunk upon the introduction of the active species, but with no obvious variations detected in the external surface area. This result indicates that most of the added metal oxides entered the micropore channels to obstruct them. In addition, the CoFe1-ZSM-5 sample had the largest external surface area, which means the existence of iron oxide contributes to a satisfactory outcome of cobalt oxide distribution. This is consistent with the result of XRD measurement. Moreover, the relatively large specific surface area might provide an increased number of active sites for Hg0 capture, which can partially explain the higher Hg0 removal efficiency of CoFe1-ZSM-5 than the other samples.
Figure 5. (a) N$_2$ adsorption–desorption isotherms and (b) pore distributions of a series samples.

### Table 1. N$_2$ adsorption results of a series samples.

| Samples      | Surface Area/(m$^2$/g) | Micropore Surface Area/(m$^2$/g) | External Surface Area/(m$^2$/g) | Total Pore Volume/(cm$^3$/g) |
|--------------|------------------------|----------------------------------|---------------------------------|-----------------------------|
| ZSM-5        | 356                    | 289                              | 67                              | 0.18                        |
| Co-ZSM-5     | 336                    | 260                              | 76                              | 0.16                        |
| Fe-ZSM-5     | 343                    | 269                              | 74                              | 0.19                        |
| Co$_4$Fe$_1$-ZSM-5 | 351                | 264                              | 87                              | 0.18                        |

3.2.4. SEM Analysis

Figure 6 shows the SEM images of virgin ZSM-5 and Co$_4$Fe$_1$-ZSM-5. As can be seen from Figure 6a,b, the surface of ZSM-5 showed smoothness. Differently, there were some tiny particles emerging on the surface of ZSM-5 for Co$_4$Fe$_1$-ZSM-5, suggesting the successful introduction of active species. Meanwhile, there were no significant variations detected in the structure of the modified samples, suggesting that morphology is not the main reason for the variations in the Hg$^0$ removal efficiency of the serial adsorbents.

EDX was used to characterize the distributions of Fe and Co species over ZSM-5. As shown in Figure 7b, Co$_3$O$_4$ with bright contrast was dispersed over the entire surface of ZSM-5. The corresponding elemental maps of ferric also imply that Fe$_2$O$_3$ was well distributed throughout the ZSM-5. EDX analysis (Figure 7d) displays that the Fe/Co mass ratio of Co$_4$Fe$_1$-ZSM-5 was 3.9, which matched the ICP result well (Table S2).
3.2.5. H₂-TPR Analysis

The redox properties of ZSM-5 and modified ZSM-5 were studied using H₂-TPR, the results of which are shown in Figure 8. Regarding virgin ZSM-5, there were a few signs of hydrogen consumption detected, suggesting the absence of reducible species available
for the capture of Hg$^0$. For all the modified ZSM-5, there were a number of evident peaks of H$_2$ reduction. The reduction of Fe-ZSM-5 after deconvolution can be divided into two stages. Located at 346 °C, the first sub-peak is possibly attributed to the reduction of Fe$_2$O$_3$ to Fe$_3$O$_4$, whereas the reduction of Fe$_3$O$_4$ to FeO can account for the appearance of the peak at 485 °C [44]. In respect of Co-ZSM-5, the peaks centered at 328 and 357 °C were associated with the reduction of Co$_3$O$_4$ to CoO and CoO to metallic cobalt, respectively [45]. Co$_4$Fe-ZSM-5 manifests four peaks at 316, 361, 404, and 436 °C. The first one is suspected to result from the reduction of Co$_3$O$_4$ to CoO, the second and third ones are probably attributable to the reduction of CoO and Fe$_2$O$_3$, and the last one is ascribed to the reduction of Fe$_3$O$_4$. Notably, there appears to be a decline of temperature for the reduction peaks, suggesting the improved reducibility of Co$_4$Fe$_1$-ZSM-5 due to the synergistic effect between CoO$_x$ and FeO$_x$ [23]. This would facilitate the oxidation of Hg$^0$, constituting another reason for the elevated Hg$^0$ removal efficiency of Co$_4$Fe$_1$-ZSM-5.

![Figure 8. H$_2$-TPR patterns of a series of samples.](image)

3.2.6. XPS Analysis

To demonstrate the chemical properties of the adsorbent surface, the XPS method was used to explore the atom environment of the samples. As shown in Figure 9, for Co 2p spectra, there were two distinct peaks detected at around 780 and 795 eV, which can be attributed to Co 2p$_{3/2}$ and Co 2p$_{1/2}$, respectively. Following deconvolution, there were two spin-orbit doublets (D$_1$ and D$_2$) emerging, along with three satellite peaks observed (S$_1$, S$_2$, and S$_3$). Located at 780.0–780.1 eV and 795.0–795.1 eV, D$_1$ bands were attributable to Co$^{3+}$ species. By comparison, the D$_2$ bands located at 781.7 and 797.4 eV corresponded to Co$^{2+}$ species, suggesting the co-existence between Co$^{2+}$ and Co$^{3+}$ [2]. A similar conclusion can be drawn for Fe atoms that both Fe$^{3+}$ and Fe$^{2+}$ were observable in the samples [46]. Upon calculation (Table 2), it can be found out that the addition of Fe$_2$O$_3$ into Co-ZSM-5 increased the ratio Co$^{3+}$/Co$^{2+}$ from 0.77 to 1.37 and caused the ratio Fe$^{3+}$/Fe$^{2+}$ to drop sharply from 1.62 to 1.29 with the Fe-containing samples as modified by CoO$_x$, which indicates that the conversion of Co$^{2+}$ to Co$^{3+}$ can be accelerated by the interaction between Co species and Fe species. This has been proved as highly active in catalytic reactions, thus enhancing the activity of the Co$_4$Fe$_1$-ZSM-5 sample.
Figure 9. XPS spectra of fresh Co-ZSM-5, Fe-ZSM-5, and fresh Co$_4$Fe$_1$-ZSM-5: (a) Co 2p, (b) Fe 2p.

Table 2. XPS data of a series of samples.

| Samples               | Concentration of the Oxygen | \(\text{Co}^{3+}/\text{Co}^{2+}\) | \(\text{Fe}^{3+}/\text{Fe}^{2+}\) |
|-----------------------|----------------------------|---------------------------------|---------------------------------|
| Fresh Co-ZSM-5        | -                          | 0.77                            | -                               |
| Fresh Fe-ZSM-5        | -                          | -                               | 1.62                            |
| Fresh Co$_4$Fe$_1$-ZSM-5 | 7.8%                      | 92.2%                           | 1.37                            |
| Spent Co$_4$Fe$_1$-ZSM-5 | 5.9%                      | 94.1%                           | 0.84                            |

3.3. Effects of Gas Components

3.3.1. Effects of O$_2$

As shown in Figure 10, the mercury removal efficiency of Co$_4$Fe$_1$-ZSM-5 in N$_2$ reached 73.4% at 120 °C. In this process, the lattice oxygen of the adsorbents played an important role. With O$_2$ concentration rising to 5%, the mercury removal efficiency showed a significant increase to 96.6%. This was because O$_2$ could compensate for the lattice oxygen consumed in the reaction, thus improving the outcome of Hg$^0$ capture [47].

Figure 10. Effect of gas components on Hg$^0$ removal efficiency. T = 120 °C.
3.3.2. Effects of NO

As shown in Figure 10, the introduction of 500 ppm NO into pure N\textsubscript{2} flue gas led to a significant improvement of Hg\textsuperscript{0} removal efficiency, which can be accounted for by the capability of NO to react with the surface oxygen species of CoO\textsubscript{x} and FeO\textsubscript{x} from reactive NO\textsubscript{x} species. This promotes the Hg\textsuperscript{0} heterogeneous oxidation occurring on the adsorbent surface [48]. However, in the context of O\textsubscript{2}- and NO-containing flue gas, the impressive removal efficiency of Hg\textsuperscript{0}, close to 100%, was achievable. It is suggested that NO is conducive to the removal of Hg\textsuperscript{0}, regardless of the presence of O\textsubscript{2}, which is supposed to result from O\textsubscript{2} accelerating the formation of reactive NO\textsubscript{x} species. Thus, the enhancement of Hg\textsuperscript{0} removal efficiency is achieved [35].

3.3.3. Effects of SO\textsubscript{2}

With 600 ppm SO\textsubscript{2} added into the reaction system, Hg\textsuperscript{0} removal efficiency declined from 73.4% to 56.1% in the absence of O\textsubscript{2}. Notably, the level of Hg\textsuperscript{0} removal efficiency in the presence of SO\textsubscript{2} and O\textsubscript{2} remained lower than in the flue gas without SO\textsubscript{2}, which implies that SO\textsubscript{2} negatively affects Hg\textsuperscript{0} removal. Immediately after the increase of concentration of SO\textsubscript{2}, such an inhibitory effect was enhanced, for which there were two reasons. On the one hand, SO\textsubscript{2} and Hg share the same adsorption sites on the adsorbent surface site, with competitive adsorption occurring between Hg\textsuperscript{0} and SO\textsubscript{2} [49]. On the other hand, SO\textsubscript{2} reacts with surface-active components to form metal sulfate salts, which reduces the number of available surface-active sites, thus interfering with the Hg\textsuperscript{0} adsorption process [50].

After the addition of 5% O\textsubscript{2}, this inhibitory effect diminishes, which is accompanied by a slight increase in the level of Hg\textsuperscript{0} removal efficiency. This is suspected to result from the capacity of O\textsubscript{2} to compensate for the consumed lattice oxygen. Eventually, the oxidation of Hg\textsuperscript{0} to HgO as deposited onto adsorbent surface subsequently is enhanced [42].

3.4. Regeneration Ability

The mercury temperature-programmed desorption method was applied to further analyze the mercury species on Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5, which is also suited to determining the conditions required for regeneration of the adsorbents. As shown in Figure 11a, the Hg-TPD profile of Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 fit well into three peaks, which was ascribed to the desorption of physically adsorbed Hg\textsuperscript{0} and the decomposition of weakly adsorbed HgO (Hg-O) and strong bond HgO (Hg≡O) [51–53]. It suggests the dominance of chemisorption over Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 in the Hg\textsuperscript{0} adsorption process, which means the possibility to obtain a clean adsorbent surface after treatment at 500 °C and achieve a satisfactory performance in Hg\textsuperscript{0} capture. To demonstrate this point, a test was conducted on the Hg\textsuperscript{0} capture efficiency of the adsorbents regenerated at different temperatures, which revealed that the efficiency of the sample regenerated at 500 °C was higher than that regenerated at 300 and 400 °C, confirming that 500 °C is the optimal temperature for the regeneration of the spent adsorbents. Apart from that, the regeneration atmosphere is another important influencing factor in the recyclability of the adsorbents.

As shown in Figure 11c, the Hg\textsuperscript{0} removal efficiency of adsorbent was just around 85%. With the addition of 5% O\textsubscript{2}, however, it improved to around 95%, suggesting that O\textsubscript{2} is conducive to improving the performance of the regenerated sample in Hg\textsuperscript{0} adsorption. Despite a further increase in the level of O\textsubscript{2} concentration, there were no evident variations observed in Hg\textsuperscript{0} removal efficiency, indicating that 5% O\textsubscript{2} is sufficient for restoring the Hg\textsuperscript{0} capture performance of the adsorbent. After five cycles of recycling (Figure 11d), adsorbent Hg\textsuperscript{0} removal efficiency remained basically unchanged above 90%, which could be accounted for by the insignificant variation in the physicochemical properties of the adsorbents after the adsorption and regeneration process (Figure S2, Table S3). It demonstrates the excellent recyclability of the Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 sample and its applicability as an adsorbent.
3.5. Mercury Capture Mechanism

Finally, XPS analysis was conducted to explore the adsorption mechanisms of Co₄Fe₁-ZSM-5. Figure 12a,b shows the Co 2p spectra of the fresh and spent samples. It can be discovered from the figures that both ratios of Co³⁺/Co²⁺ (from 1.37 to 0.84) and Fe³⁺/Fe²⁺ (from 1.29 to 0.93) declined after Hg⁰ adsorption, implying that Co³⁺ and Fe³⁺ play a crucial role in the removal of Hg⁰ and undergo a redox-reduction reaction to a lower valance state [2].

As can be seen from Figure 12c, the asymmetry of O 1s spectra suggested the existence of various oxygen species. After curve-fitting, those peaks in the range of 530.2–530.5 eV could be indexed to the lattice oxygen of metal oxides (denoted as O₁α), while the peaks at 532.9–533.2 eV were associated with the lattice oxygen of ZSM-5 (denoted as O₁β), as shown in Figure 12c [17]. According to Table 2, the concentration of O₁α dropped to 5.9%, suggesting that the lattice oxygen of metal oxides was primarily responsible for the oxidation of Hg⁰.

As for Hg 4f spectra, there were two photoelectron peaks detected at 103.2 and 104.0 eV after deconvolution (Figure 12d). The former can be assigned to Si 2p for SiO₂, while the latter was attributable to Hg 4f⁵⁄₂ for HgO, being consistent with the Hg-TPD result shown in Figure 11a that the captured mercury species existed mainly in the form of HgO on the adsorbent surfaces. Moreover, it can be concluded that the Mars–Maessen reaction routine is dominant in the Hg⁰ adsorption process over Co₄Fe₁-ZSM-5 (Equations (5)–(12)) [45,54,55]. More specifically, Hg⁰ is first physically adsorbed on the adsorbent surface, which is followed by the combination with lattice oxygen of metal oxides to form HgO. Meanwhile, Co³⁺ and Fe³⁺ are reduced. Finally, gaseous O₂ acts as an oxidant to re-oxidize the reduced cobalt and iron species into Co³⁺ and Fe³⁺.
Figure 12. XPS spectra of fresh and spent Co$_4$Fe$_1$-ZSM-5: (a) Co 2p, (b) Fe 2p, (c) O1s, (d) Hg 4f.

Reaction condition: N$_2$ + 5% O$_2$ + 200 µg/m$^3$ Hg$^0$.

\[ \text{Hg}^0 (g) \rightarrow \text{Hg}^0 (\text{ads}) \]  \hspace{1cm} (5)

\[ \text{Hg}^0 (\text{ads}) + \text{Co}_x\text{O}_y \rightarrow \text{Hg-O} \equiv \text{Co}_x\text{O}_y-1 \] \hspace{1cm} (6)

\[ \text{Hg}^0 (\text{ads}) + \text{Fe}_x\text{O}_y \rightarrow \text{Hg-O} \equiv \text{Fe}_x\text{O}_y-1 \] \hspace{1cm} (7)

\[ \text{Hg}^0 (\text{ads}) + \text{Co}_x\text{O}_y \rightarrow \text{HgCo}_x\text{O}_y \] \hspace{1cm} (8)

\[ \text{Hg}^0 (\text{ads}) + \text{Fe}_x\text{O}_y \rightarrow \text{HgFe}_x\text{O}_y \] \hspace{1cm} (9)

\[ \text{HgO} (\text{ads}) \rightarrow \text{HgO} (g) \] \hspace{1cm} (10)

\[ \text{Co}_x\text{O}_y-1 + 1/2\text{O}_2 \rightarrow \text{Co}_x\text{O}_y \] \hspace{1cm} (11)

\[ \text{Fe}_x\text{O}_y-1 + 1/2\text{O}_2 \rightarrow \text{Fe}_x\text{O}_y \] \hspace{1cm} (12)

On the basis of this result, it can be concluded that adsorbent oxidative ability contributed to the capture of Hg$^0$ for the existence of the adsorbed mercury species in the form of Hg-O-M compounds. On the basis of the H2-TPR profiles shown in Figure 7, Co$_4$Fe$_1$-ZSM-5 adsorbent exhibited a relative high oxidative ability, which, to some extent, had a positive effect on the oxidation of Hg$^0$ and thus stimulated the capture of Hg0. Meanwhile, the optimized textural structures could be beneficial for the mass transfer of the reactant, enabling Co$_4$Fe$_1$-ZSM-5 with a satisfactory Hg$^0$ removal performance. In addition, Co$_4$Fe$_1$-ZSM-5 was found to effectively capture Hg$^0$ in SO$_2$- or NO-containing flue gas. It possesses a superior recycle attribute, hindering that this material can be a potential adsorbent for the practical application.
4. Conclusions

This study explored a series of Co-Fe mixed oxides supported on ZSM-5, as synthesized using an ultrasound-assisted impregnation method for the abatement of Hg\textsubscript{0}. The conclusions of this study are presented as follows:

1. Compared with other samples, Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5 performed relatively better, with a roughly 96.6% Hg\textsubscript{0} removal efficiency and a roughly 901.63 µg/g Hg\textsubscript{0} adsorption capacity achieved at 120 °C. The interaction between CoO\textsubscript{x} and FeO\textsubscript{y} enhanced the reducibility of oxygen species, which promoted the oxidation of Hg\textsubscript{0}.

2. Among various gas components, O\textsubscript{2} and NO had a positive impact the removal of Hg\textsubscript{0}, whereas SO\textsubscript{2} inhibited the adsorption of Hg\textsubscript{0} to a certain extent.

3. The Mars–Masson mechanism dominated the Hg\textsubscript{0} adsorption process over Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5. Co\textsuperscript{3+} and Fe\textsuperscript{3+} provided the active sites required to oxidize Hg\textsubscript{0} into Hg\textsubscript{0} for the subsequent deposition onto the adsorbent surface.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/app12083769/s1, Figure S1: (a) simulated adsorption capacity of Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5, Co-ZSM-5 and Fe-ZSM-5; (b) breakthrough curve of Co\textsubscript{4}Fe\textsubscript{1}-ZSM-5, Co-ZSM-5 and Fe-ZSM-5 under N\textsubscript{2} + 5%O\textsubscript{2} + 200 µg/m\textsuperscript{3}, t = 540 min; Figure S2: (a) N\textsubscript{2} adsorption-desorption isotherms and (b) pore distributions of the fresh and regeneration samples; (c) XRD pattern of the fresh and regeneration sample; Table S1: Comparison of the Hg\textsubscript{0} removal performances onto various adsorbents; Table S2: The content of metal in samples obtained by ICP-AES; Table S3: N\textsubscript{2} adsorption results of the fresh and regeneration samples.

Author Contributions: Conceptualization, W.M. and D.Y.; methodology, W.M. and D.Y.; validation, W.M., D.Y. and H.W.; formal analysis, W.M.; investigation, W.M.; resources, H.W.; data curation, W.M.; writing—original draft preparation, W.M.; writing—review and editing, D.Y.; visualization, W.M.; supervision, H.W.; project administration, H.W.; funding acquisition, H.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was supported by the National Natural Science Foundation of China (51568024).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

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