A Novel Nano-sized Co₃O₄@C Catalyst Derived from Co-MOF Template for Efficient Hg⁰ Removal at Low Temperatures with Outstanding SO₂ Resistance

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**A novel nano-sized Co₃O₄@C catalyst derived from Co-MOF template
for efficient Hg⁰ removal at low temperatures with outstanding SO₂
resistance**

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Abstract

Co_3O_4 is a promising Hg^0 removal catalyst for industrial application. Operating temperature and low sulfur resistance are two of the main problems that hinder its industrial application in Hg^0 removal. Herein, a metal-organic framework (Co-BDC) was introduced as a sacrificial template to obtain the catalyst nano-sized $\text{Co}_3\text{O}_4@\text{C}$ by calcination. Part of the organic ligands carbonized during the calcination. Carbon wrapped Co_3O_4 and reduced metal agglomeration. The optimal Hg^0 removal temperature of the existing cobalt oxides catalysts was always around 150 °C, but H_2 -TPR showed that the oxygen atoms on the $\text{Co}_3\text{O}_4@\text{C}$ were more active than those on commercial Co_3O_4 , causing the Hg^0 removal temperature window of $\text{Co}_3\text{O}_4@\text{C}$ to shift to lower temperatures. The Hg^0 removal efficiency of $\text{Co}_3\text{O}_4@\text{C}$ could reach almost 100% even at 25 °C. In the meanwhile, $\text{Co}_3\text{O}_4@\text{C}$ also showed a strong SO_2 resistance at ambient temperature. Experimental results and characterization proved that SO_2 did not compete with Hg^0 on the surface of Co_3O_4 at low temperatures. On the contrary, it participated in the oxidation of Hg^0 . This is a great improvement for Co_3O_4 catalyst in Hg^0 removal. It reduces the restrictions on the application of Co_3O_4 in Hg^0 removal. $\text{Co}_3\text{O}_4@\text{C}$ shows considerable potential as an Hg^0 removal catalyst.

Keywords: $\text{Co}_3\text{O}_4@\text{C}$, Hg^0 removal, MOFs, Sulfur-resistance

1. Introduction

Power plants are the largest point source of mercury released into the atmosphere. The burning of fossil fuels (primarily coal) is the largest single source of emissions from human sources, accounting for about 45% of the total anthropogenic emissions.(Pacyna et al., 2006; Ji et al., 2018; Zhang et al., 2020b) Nowadays, injecting activated carbon is the most mature technology for Hg^0 removal and has been employed by many coal-fired power plants.(Bisson and Xu, 2015; Xu et al., 2018) Activated carbon can adsorb Hg^0 , but its low efficiency leads to high operation costs.(Cao et al., 2017) Therefore, the desire for more efficient and low-cost Hg^0 removal agents has focused research on catalysts.

Transition metal oxide Co_3O_4 has proved to have good Hg^0 oxidation performance.(Zhang et al., 2019a; Yang et al., 2020) It's a promising non-noble metal catalyst for Hg^0 removal. It can remove mercury efficiently at high temperatures, and it is more economical than precious metal catalysts. However, it is not easy for Co_3O_4 to achieve industrial applications. It is well known that the performance of the catalyst was always affected by temperature. Previous studies have shown that only in a specific temperature range can Co_3O_4 reach its best state for Hg^0 oxidation. For instance, the cobalt oxide loaded magnetosphere catalyst reported by Yang et al. had its best Hg^0 removal performance around 150 °C.(Yang et al., 2014) The Hg^0 removal temperature windows of the Ce-Co catalyst and Co_3O_4 nanorods synthesized by He et al. were 150-350 °C and 100-300 °C, respectively.(Zhang et al., 2017; Zhang et al., 2019b) Therefore, users need to create a specific temperature environment for Co_3O_4 to achieve its best performance. In the meanwhile, the internal environment of the flue gas purification system was complicated. The flue gas contained various chemical substances, such as SO_2 , NO_x , and so on. It is

inappropriate to put Co_3O_4 in front of Wet Flue Gas Desulfurization(WFGD) equipment because of the existence of SO_2 , which can inactivate Co_3O_4 .(Yang et al., 2015) Co_3O_4 showed low SO_2 resistance at high temperatures, so it needs to ensure the catalyst does not come into contact with SO_2 , which is complicated to operate and uneconomical. If Co_3O_4 is placed after the WFGD equipment, the flue gas needs to be reheated to meet the temperature requirement of Co_3O_4 because the temperature of the WFGD outlet airflow can usually drop to around 45 °C.(Cheng et al., 2020) Given the above, if Co_3O_4 can oxidize Hg^0 efficiently at low temperatures and have good SO_2 resistance, it will be a promising Hg^0 removal agent for large-scale applications.

In the present work, a 2D MOFs Co-BDC was used as the sacrificial template, and $\text{Co}_3\text{O}_4@\text{C}$ was formed by burning it at 500 °C.(Dai et al., 2017) Metal-organic frameworks (MOFs) are a series of novel porous materials with regular pores and large surface area, which consists of metal ions and organic ligands.(Shekhah et al., 2011) It is a promising precursor of nano-sized metal oxides.(Tao et al., 2018) In MOFs, metal clusters are connected by organic ligands. Organic ligands can hinder the agglomeration of metal ions to a certain extent during the calcination process. It can change the particle size of Co_3O_4 and increase the number of low-coordination atoms located at the edges and corners, which can improve the Hg^0 removal performance of the catalyst.(Li et al., 2017a) The experimental results indicated that the temperature window of $\text{Co}_3\text{O}_4@\text{C}$ shifted to a low-temperature range. It can remove Hg^0 efficiently even at room temperature. Meanwhile, it showed strong SO_2 resistance at ambient temperature. Experimental results and characterization proved that SO_2 did not compete with Hg^0 on the surface of Co_3O_4 at low temperatures. On the contrary, it participated in the oxidation of Hg^0 . This is a great

improvement for Co_3O_4 catalyst in Hg^0 removal. It reduces the restrictions on the use of Co_3O_4 , making Co-based catalysts more energy-saving and flexible to combine with the flue gas treatment system.

2. Experimental procedure

2.1 Materials

The chemicals used in this study are shown below. Cobalt(II) acetate tetrahydrate ($\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$, 99.5%) and p-Phthalic acid (PTA, $\text{C}_8\text{H}_6\text{O}_4$, 99%) were purchased from Aladdin Industrial Corporation. N,N-Dimethylformamide (DMF, $\text{C}_3\text{H}_7\text{NO}$, 99.5%) was purchased from Shanghai Aladdin Biochemical Technology. Ethanol ($\text{C}_2\text{H}_5\text{OH}$, $\geq 99.7\%$) was purchased from Shanghai Titan Scientific Co., Ltd. Commercial tricobalt tetraoxide (Co_3O_4 , 99.9%) was purchased from Shanghai Macklin Biochemical Co., Ltd. All chemicals purchased from commercial sources were used as received without further purification.

2.2 Catalyst preparation

Co-BDC is chosen as the sacrificial template for the form of cobalt oxide nanoparticles (NPs) and Co-BDC was prepared according to previous publication with some changes. Its preparation was carried out as follows: PTA (0.206 g, 1.24 mmol) and $\text{C}_4\text{H}_6\text{CoO}_4 \cdot 4\text{H}_2\text{O}$ (0.612 g, 2.46 mmol) were dissolved in 15 mL of DMF and stirred for 30 min. Then the solution was transferred into a 50 mL Teflon-lined pressure vessel and heated in the oven at 110 °C for 24 h. After cooling to room temperature, the purple solid product was washed and sonicated with DMF (3×30 mL) and fresh ethanol (3×30 mL) to remove the unwanted particles and unreacted reactants. Finally, the obtained powder was dried at 70 °C overnight to gain the sacrificial template Co-BDC and then $\text{Co}_3\text{O}_4@\text{C}$ was prepared by calcining Co-

BDC at 400/500/600 °C for 3 h in an oven.

2.3 Characterization

The properties of the samples were characterized and analyzed. The crystal structures of samples were characterized by powder X-ray diffraction (XRD) with a D/max2550V apparatus, Cu-K α radiation source ($\lambda=1.5406 \text{ \AA}$) as the X-ray source and its scanning angle of the samples was ranged from 5° to 75°. The surface area and pore properties of the samples were measured by the Brunauer-Emmett-Teller (BET) method with an apparatus (Micromeritics Tristar 3020 SIN 993). The composition data of the samples was given by a Falion 60S energy dispersive X-ray (EDX) spectrometer. The morphologies of the samples were observed by a scanning electron microscope (SEM) S-3400N. A JEM-2100 transmission Electron Microscopy (TEM) was used to observe the morphology and lattice of the samples. The sample's Fourier transform infrared spectroscopy (FT-IR) was measured by Thermo Nicolet iS10. The surface elemental state changes of the samples before and after Hg⁰ removal were determined via X-ray photoelectron spectroscopy analysis (XPS) using an ESCALAB 250Xi apparatus with an Al-K α radiation source at an energy step size of 0.05 eV. H₂-Temperature programmed reduction (H₂-TPR) was performed using an Autochem II2920. The temperature range explored was from 50 °C to 600 °C with a heating rate of 10 °C/min.

2.4 Experimental apparatus and procedure

A specific experimental system was set up for testing the Hg⁰ capture ability of the catalyst, as shown in our previous studies(Zhou et al., 2019). In a test, 50 mg of a sample was placed in a quartz tube with an inner diameter of 6 mm and fixed with quartz wools. The quartz tube contacted the temperature measuring rod of the fixed bed reactor and it can adjust the

temperature of the sample. The Hg^0 concentration of the inlet gas was controlled by a water bath and it was $400 \mu\text{g}/\text{m}^3$. The Hg^0 concentrations of the inlet and outlet gas were measured by the Hg^0 vapor analyzer (SG-921, Jiangsu Jiangfen Electroanalytical Instrument Co., Ltd, China.). The Hg^0 removal efficiency(η) was determined by the following equation:

$$\eta = \left(\frac{C_0 - C}{C_0} \right) \times 100 \quad (1)$$

where C_0 and C are the Hg^0 concentration of inlet gas and outlet gas, respectively.

The total gas flow was 100 ml/min and the height of the sample was 10 mm, resulting in a Gas hourly space velocity of $3.06 \times 10^4 \text{ h}^{-1}$. The temperature-programmed desorption of Hg^0 (Hg-TPD) was used to investigate the catalyst performance and its regeneration temperature. The N_2 or air flow rate was 100 ml/min. All the samples were heated from 50 to 350 °C and the heating rate was 1 °C/min.

3. Results and discussion

3.1 Hg^0 removal performance of $\text{Co}_3\text{O}_4@\text{C}$

Figure 1. (a) Effect of temperature on Hg^0 removal performance of commercial Co_3O_4 and $\text{Co}_3\text{O}_4@\text{C}$; (b) Effect of calcination temperature on Hg^0 removal performance of $\text{Co}_3\text{O}_4@\text{C}$.

Commercial Co_3O_4 was introduced to this study to compare Hg^0 removal performance with

Co₃O₄@C. The effect of temperature on the Hg⁰ removal performance of catalysts was analyzed, as shown in Figure 1a. The experimental results showed that the Hg⁰ removal temperature window of commercial Co₃O₄ and Co₃O₄@C was 150 °C to 350 °C and 25 °C to 200 °C respectively. The Hg⁰ removal temperature window of Co₃O₄@C shifted to a lower temperature region compared to that of commercial Co₃O₄. Commercial Co₃O₄ did not perform well in removing Hg⁰ at ambient temperature (25 °C→18.5%). Physical adsorption was considered the major contributor to its Hg⁰ removal at room temperatures, but its efficiency was low because of the dense structure of commercial Co₃O₄ (3.47 m²g⁻¹, Table 1).(Yang et al., 2014) When reaction temperature rose, the reactants attained more kinetic energy, thus enhancing the catalytic activity for Hg⁰ oxidation, resulting in an increase in Hg⁰ removal performance at high temperatures.(Mochida et al., 2000) Commercial Co₃O₄ got its peak efficiency (about 95%) at 200 °C. However, Co₃O₄@C performed much better than Commercial Co₃O₄ at low temperatures. It could efficiently remove Hg⁰ at ambient temperature.

The effect of calcination temperature on Hg⁰ removal performance of Co₃O₄@C was studied in the temperature range of 400 to 600 °C. The samples obtained at 400 °C performed well in mercury removal. Its Hg⁰ removal efficiency can reach 100% at 25 and 150 °C. Its Hg⁰ removal capacity at 25 and 150 °C is 0.3 and 0.89 mg/g, respectively. When the calcination temperature increased from 400 °C to 500 °C, the sample Co₃O₄@C maintained excellent Hg⁰ removal performance. However, when the calcination temperature was increased to 600 °C, the Hg⁰ removal efficiency of the sample dropped abruptly. The precursor is sintered into larger particles at too high temperature, which is not conducive to the catalytic reaction. The Hg⁰ removal ability of the sample is closely

related to the appropriate calcination temperature. Accordingly, 500 °C was chosen as the calcination temperature of Co₃O₄@C in this study.

3.2 The characterization of Co₃O₄@C

Co₃O₄@C showed excellent Hg⁰ removal efficiency (almost 100%) at low temperatures.

The properties of the catalyst Co₃O₄@C depend on its micromorphology, crystal forms, and sizes. The X-ray diffraction (XRD) patterns of Co₃O₄@C and commercial Co₃O₄ were shown in Figure 2a. They both agree well with simulated Co₃O₄ (PDF#74-2120) and the peaks of Co₃O₄@C at 19°, 31.3°, 36.8°, 38.5°, 44.8°, 55.7°, 59.4°, and 65.2° corresponded to the crystal planes (111), (220), (311), (222), (400), (422), (511) and (400) of Co₃O₄ respectively (Chen et al., 2019). Co₃O₄ was successfully synthesized by the calcination of Co-BDC in Co₃O₄@C at 500 °C.

The SEM images revealed the microscopic morphology of the sample. Figure 2b-2c showed that Co₃O₄@C was made up of nano-sized particles. The N₂ adsorption-desorption isotherm of Co₃O₄@C is shown in Figure 2d. It is a type IV curve, according to Brunauer-Deming-Deming-Teller classification, and it exhibited an H3 hysteresis loop which was characteristic of aggregates of plate-like particles. The pore size distribution of the sample (inset Figure 2d) showed that the pore diameter of Co₃O₄@C was mainly distributed around 40 nm, indicating the existence of mesopores. The BET surface area of Co₃O₄@C was 49.79 m²·g⁻¹, and its pore volume and pore size (Table 1) was 0.26 cm³·g⁻¹ and 21.04 nm, respectively. Transmission electron microscopy further analyzed the structure of the sample, as shown in Figure 2e. the sample exhibited an ordered lattice structure, and its interplanar spacing of 0.24 nm corresponded to Co₃O₄ (311). However, there were gray areas without lattice fringes on the edge of the particle, which was considered to be

199 amorphous carbon. As seen from the figure, amorphous carbon wrapped the Co_3O_4 particle.

Figure 2. The micromorphology of $\text{Co}_3\text{O}_4@\text{C}$ powders. (a) XRD patterns of $\text{Co}_3\text{O}_4@\text{C}$, commercial Co_3O_4 , and the simulated Co_3O_4 (PDF#74-2120) (b-c) SEM images of $\text{Co}_3\text{O}_4@\text{C}$ powders prepared by the calcination method. (d) N_2 adsorption-desorption isotherm of $\text{Co}_3\text{O}_4@\text{C}$ and its pore size distribution. Inset shows the pore size distribution of the sample. (e) TEM image of $\text{Co}_3\text{O}_4@\text{C}$.

Table 1. Textural properties of $\text{Co}_3\text{O}_4@\text{C}$ and commercial Co_3O_4

Catalyst	S_{BET} ($\text{m}^2 \cdot \text{g}^{-1}$)	Pore size (nm)	Pore volume ^c ($\text{cm}^3 \cdot \text{g}^{-1}$)	Element content (at %)		
				C	O	Co
$\text{Co}_3\text{O}_4@\text{C}$	49.79	21.04	0.26	20.3	29.1	50.6
Commercial Co_3O_4	3.47	15.11	0.013	7.9	39.9	52.2

The EDX results (Table 1) showed that the carbon content of $\text{Co}_3\text{O}_4@\text{C}$ was 20.3%, higher than that of commercial Co_3O_4 (7.9%). This is because during the calcination process, the organic ligands in MOFs were not completely decomposed, and carbonization occurred. Table 1 showed that the molar ratio of O to Co content in $\text{Co}_3\text{O}_4@\text{C}$ and commercial Co_3O_4 was 0.575 and 0.764, respectively (simulated Co_3O_4 , O: Co=0.75). The relative content of element oxygen in $\text{Co}_3\text{O}_4@\text{C}$ was less than that of simulated Co_3O_4 significantly.

3.3 The effect of O_2 and temperature

Figure 3. (a) The synergy of temperature and the gas components O_2 on Hg^0 removal performance of $\text{Co}_3\text{O}_4@\text{C}$. (b) The analysis of different experimental conditions on deactivation time of $\text{Co}_3\text{O}_4@\text{C}$.

The catalytic performance of $\text{Co}_3\text{O}_4@\text{C}$ could be greatly improved in the presence of O_2 ,

as shown in Figure 3a. $\text{Co}_3\text{O}_4@\text{C}$ performed poorly on Hg^0 physical adsorption and lost its activity within 100 min in pure N_2 atmosphere at ambient temperature. However, when O_2 was injected into the carrier gas, its deactivation time increased significantly from 100 min to 350 min (the blue line). In the meanwhile, it was found that increasing the O_2 concentration from 4% (the green line) to 21% (the red line) did not improve the Hg^0 removal performance of the sample.

Temperature also had a great influence on the activity of $\text{Co}_3\text{O}_4@\text{C}$. It was found that the Hg^0 oxidation activity of $\text{Co}_3\text{O}_4@\text{C}$ could also be improved by heating in the absence of O_2 (the orange line, in Figure 3a). When the ambient temperature rose from 25 °C to 150 °C, the deactivation time of $\text{Co}_3\text{O}_4@\text{C}$ was extended by 250 minutes in the N_2 atmosphere, as shown in Figure 3b. Figure 3b also exhibited the synergy of temperature and O_2 on the Hg^0 removal performance. High temperature and O_2 could increase the deactivation time by 150 min and 250 min, respectively. However, the sample could maintain its activity within 800 min when there was O_2 in the carrier gas, and the ambient temperature was 150 °C. It extended the deactivation time by 700 minutes, proving the synergistic effect of oxygen and high temperature.

Figure 4. (a) Synergistic effect of temperature and SO₂ on Hg⁰ removal efficiency of the sample. (b) Synergistic effect of O₂ and SO₂ on the deactivation time of the sample. Experimental conditions: catalyst mass, 50 mg; experimental temperature, 25 °C; gas stream contents, 285 mg/m³ SO₂+4% O₂/N₂; gas flow rate, 100 mL/min. (c) the effect of NO_x on Hg⁰ removal efficiency.

(d) the Hg⁰ removal performance. (e) The Hg⁰ removal performance of Co₃O₄@C in the simulate gas at ambient temperature. The gas components: 400 μg/m³ Hg⁰+4%O₂+2286 mg/m³ SO₂+402 mg/m³ NO+N₂.

3.3 The effect of SO₂

The concentration of chemical substances in flue gas is always higher than that of Hg⁰, and their influence on Hg⁰ removal is an important index to evaluate the performance of catalysts(Liu, 2008). Many studies indicated that SO₂ played the role of inhibitor, which competed with mercury on the surface of metal oxides.(Li et al., 2011; Yang et al., 2011; Zhang et al., 2014) The negative effect of SO₂ was also found at high temperatures (150 °C) in this study, as shown in Figure 4a. The Hg⁰ removal efficiency of commercial Co₃O₄ and Co₃O₄@C both dropped to about 40% when SO₂ was injected into the carrier gas, and the ambient temperature rose to 150 °C. Co₃O₄@C deactivated as fast as commercial Co₃O₄, demonstrating its poor SO₂ poisoning resistance at high temperatures as Co₃O₄ in the literature.(Yang et al., 2014) Nevertheless, Co₃O₄@C showed excellent SO₂ resistance at room temperature (the blue part, Figure 3a). Its Hg⁰ removal efficiency was above 90% when SO₂ was injected into the gas flue, and the increase in SO₂ concentration did not reduce the Hg⁰ removal performance of Co₃O₄@C. Its Hg⁰ removal efficiency is maintained at 90% even in the presence of 2286 mg/m³ SO₂. In the meanwhile, the catalyst deactivation experimental results showed that SO₂ not only had no negative effects on the sample, but also promoted the removal of Hg⁰ at ambient temperature, as shown in Figure 4b. The deactivation time of the sample in the SO₂+N₂ atmosphere was 430 min, better than that in the O₂+ N₂ atmosphere (340 min). The presence of SO₂ in the O₂ atmosphere can prolong the deactivated time of Co₃O₄@C from 340 min to 860 min. In summary, SO₂ played a role in promoting Hg⁰ removal at ambient temperature.

3.4 The effect of NO_x

NO can be oxidized by lattice oxygen or adsorbed oxygen on the surface of metal oxide, forming new species like NO₂ and NO⁺, so it might compete with Hg⁰ and inhibit Hg⁰ oxidation on the surface of Co₃O₄@C.(Li et al., 2008) Nevertheless, NO is weakly adsorbed on the surface of metal oxides to form NO₂, nitrite, and nitrate species and cannot repel Hg⁰ from the surface of the catalyst.(Jin et al., 2010; Li et al., 2012) Figure 4c showed that NO slightly inhibited the oxidation of Hg⁰ removal in the N₂ atmosphere. The Hg⁰ removal efficiency of Co₃O₄@C dropped to about 90% when 402 mg/m³ NO was injected into N₂. However, this negative effect did not appear when the carrier gas contained O₂. The Hg⁰ removal efficiency of Co₃O₄@C was maintained at 100% when NO was injected into 4% O₂ atmosphere regardless of temperature and NO concentration changes. Figure 4d showed the real-time change of mercury removal efficiency when NO was injected into the carrier gas. When 402 mg/m³ of NO was injected into the N₂ gas flow, the Hg⁰ removal efficiency of Co₃O₄@C decreased from 99% to 96%. NO occupied part of active sites on the surface of the sample and inhibited the Hg⁰ removal performance of Co₃O₄@C. The same phenomenon occurred when the gas flow change from N₂ to air but the Hg⁰ removal efficiency of the sample gradually recovered within 60 minutes in the presence of O₂, which may be due to the adsorbed NO being oxidized and then reacting with Hg⁰.

3.5 The Hg⁰ removal performance in simulated flue gas

It is necessary to test the Hg⁰ removal capacity of the sample under the simulated flue gas atmosphere to study the comprehensive influence of all kinds of chemical compositions. In this study, the composition of simulated gas was 400 µg/m³ Hg⁰+4%O₂+2286 mg/m³ SO₂+402 mg/m³ NO+N₂, and Co₃O₄@C maintained excellent Hg⁰ removal efficiency (>

90%) for about 800 minutes when it was exposed to the gaseous environment where NO, SO₂ and Hg⁰ were present simultaneously, as shown in Figure 4e. It showed great adaptability to the complex simulated flue gas at ambient temperature.

3.6 The Hg⁰ removal mechanism of Co₃O₄@C

Figure 5. (a) The Co 2p XPS spectra of Co₃O₄@C before and after the treatment; (b) Peak area of Co 2p and the ratio change of Co³⁺/Co²⁺. (c) The Hg 4d XPS spectra of Co₃O₄@C after the treatment.

The structural defects of the lattice stimulated the formation of active surface species that are conducive to Hg⁰ oxidation (Machida et al., 2008; Hu et al., 2019). As mentioned before, the EDX result showed that the sample Co₃O₄@C had a lack of coordination oxygen (molar ratio O:Co=0.575), which may be caused by oxygen competition inside the sacrificial template during calcination. The incomplete combustion of organic ligands produced carbon. The carbon wrapped Co₃O₄ and robbed the oxygen of the cobalt ions, causing the exposure of the cobalt ions and the lack of lattice oxygen in the structure of Co₃O₄. The Co

2p XPS spectra of $\text{Co}_3\text{O}_4@\text{C}$ before and after the treatment showed in Figure 5a. The binding energies at approximately 794.8, 779.7, 796.8 and 781.6 eV were assigned to $\text{Co}^{3+} 2p_{1/2}$, $\text{Co}^{3+} 2p_{3/2}$, $\text{Co}^{2+} 2p_{1/2}$ and $\text{Co}^{2+} 2p_{3/2}$, respectively.(Wei et al., 2008) During the treatment, the oxygen in the air continuously filled structural defects on the surface of the catalyst and combines with the exposed Co ions, so that the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio rose from 1.73 to 2, as shown in Figure 5b. The lack of lattice oxygen led to a reduction in the valence of cobalt in $\text{Co}_3\text{O}_4@\text{C}$. As Hg^0 was continuously oxidized on the surface of $\text{Co}_3\text{O}_4@\text{C}$, the number of structural defects decreased. When the catalyst was deactivated, it could be seen that the $\text{Co}^{3+}/\text{Co}^{2+}$ ratio was 2, which was the correct ratio of Co^{3+} to Co^{2+} in Co_3O_4 . Thus, the structural defects on the surface of $\text{Co}_3\text{O}_4@\text{C}$ were considered to be one of the factors contributing to its outstanding Hg^0 performance.

Under the synergy of temperature and O_2 , the Hg^0 removal effect of the sample was further improved. As mentioned above, it could be confirmed that both O_2 and lattice oxygen on the catalyst surface participated in the oxidation of Hg^0 . HgO was found in the sample after the experiment through an X-ray photoelectron spectroscopy. In Figure 5c, the binding energy of $\text{Hg } 4d_{3/2}$ and $\text{Hg } 4d_{5/2}$ peaks was 359.9 and 379.3 eV, respectively, which matched well with the peak data of HgO in the NIST XPS database. Thus, it can be confirmed that Hg^0 was oxidized to HgO by $\text{Co}_3\text{O}_4@\text{C}$.

Figure 6. (a) H₂-TPR spectra of Co₃O₄@C and commercial Co₃O₄; (b) Hg-TPD spectra of Co₃O₄@C and commercial Co₃O₄; (c) Extended X-ray adsorption fine structure-Fourier transform (EXAFS-FT) of Co₃O₄@C before and after Hg⁰ removal.

At the same time, temperature experiments confirmed that the lattice oxygen on the surface of Co₃O₄ also played an important role in Hg⁰ oxidation. When there was no O₂ in the carrier gas, the lattice oxygen on the surface of Co₃O₄@C could be activated and reacted with Hg⁰ as the ambient temperature rose from 25 °C to 150 °C, resulting in an increase in deactivation time of Co₃O₄@C (the orange line in Figure 3a). H₂-TPR was conducted to explore the Co-O bond strength difference between commercial Co₃O₄ and Co₃O₄@C in this study. Its data was revealed in Figure 6a. The peaks of commercial Co₃O₄ at 376.3 °C and 402.9 °C were related to the reduction of Co₃O₄ to CoO and CoO to Co, respectively. The H₂-TPR spectra of Co₃O₄@C could be divided into two parts (inset of Figure 6a). It had two small reduction peaks at 346.1 °C and 355.8 °C, and this might be

due to the presence of bulk Co_3O_4 . Its main reduction peaks were at 281.5 °C and 317.6 °C. The reduction temperatures of $\text{Co}_3\text{O}_4@\text{C}$ were lower than those of commercial Co_3O_4 , showing the weaker Co-O bond strength in $\text{Co}_3\text{O}_4@\text{C}$. The lattice oxygen on the surface of $\text{Co}_3\text{O}_4@\text{C}$ was easier to be activated, which means that the temperature required for the lattice oxygen activation of $\text{Co}_3\text{O}_4@\text{C}$ is lower, and it has more activated lattice oxygen than commercial Co_3O_4 at the same temperature. This makes $\text{Co}_3\text{O}_4@\text{C}$ perform better than commercial Co_3O_4 in Hg^0 removal and shifts the Hg^0 removal temperature window of $\text{Co}_3\text{O}_4@\text{C}$ to the low-temperature range.

The deactivation of $\text{Co}_3\text{O}_4@\text{C}$ was observed as the ambient temperature increased. When the temperature exceeded 200 °C, the Hg^0 removal efficiency of $\text{Co}_3\text{O}_4@\text{C}$ dropped sharply. Hg-TPD experiment could help to explain this phenomenon. Use the sample to remove Hg^0 for one hour in a 4% O_2 atmosphere. Then cut off the Hg^0 source and heat the sample in N_2 or air. The temperature range is from 50 °C to 350 °C with a heating rate of 1 °C/min. Figure 6b showed the Hg-TPD spectra of $\text{Co}_3\text{O}_4@\text{C}$. It had two Hg^0 thermal-desorption peaks around 175 °C and 275 °C when the carrier gas was N_2 . When the carrier gas changed from N_2 to air, the peak around 175 °C disappeared. This peak could be attributed to physically adsorbed Hg^0 because physically adsorbed Hg^0 could be oxidized on the surface of $\text{Co}_3\text{O}_4@\text{C}$ in the presence of O_2 . Chemisorbed Hg^0 would not be affected by O_2 . Thus, the Hg^0 thermal-desorption peak around 275 °C did not disappear when the carrier gas changed from N_2 to air. In summary, the Hg^0 thermal-desorption peaks around 175 °C and 275 °C corresponded to physically adsorbed Hg^0 and chemically adsorbed Hg^0 , respectively.(Yang et al., 2014) It can be seen that the adsorption of Hg^0 onto the surface of $\text{Co}_3\text{O}_4@\text{C}$ would be inhibited when the temperature exceeded 175 °C, and this

temperature was the starting point for the decline in Hg⁰ removal performance of Co₃O₄@C.

Thus, Hg⁰ adsorption is one of the key steps for the catalyst to oxidize Hg⁰.

The analyses of the extended X-ray absorption fine structure (EXAFS) spectrum allowed to determine the atomic structure and the coordinating environment of Co in the sample accurately. This technique helped to analyze the stability of the catalyst during Hg⁰ removal. Figure 6c showed the EXAFS Fourier transform (FT) of Co₃O₄@C before and after Hg⁰ removal. It revealed three main peaks located at 1.90 Å, 2.85 Å, and 3.35 Å which corresponded to Co-O, Co-Co1, and Co-Co2 coordination, respectively. The spectrum showed that there was no obvious peak shift of the sample observed after Hg⁰ removal, indicating the great structure stability of Co₃O₄@C during Hg⁰ removal.

The mechanism of Hg⁰ oxidation by Co₃O₄@C is clear. Firstly, Hg⁰ was adsorbed on the surface of the sample, and then it was oxidized to HgO by activated O₂ or the lattice oxygen of Co₃O₄@C. This was in line with the Mars-Maessen mechanism that Hg⁰ needs to be adsorbed onto the surface of the catalyst before it is oxidized, (Presto and Granite, 2006) and the reactions could be described as following. (Liu et al., 2011; Yang et al., 2014)

(4)

Figure 7. (a-b) Hg^0 adsorption and desorption experiments and their mechanism simulation diagram. Experimental temperature (a) 25 °C; (b) 150 °C. Experimental conditions: catalyst mass, 50 mg; gas stream contents, $\text{N}_2 \rightarrow 2286 \text{ mg}/\text{m}^3 \text{ SO}_2 + \text{N}_2$; gas flow rate, 100 mL/min. (c) the FT-IR spectra of $\text{Co}_3\text{O}_4\text{@C}$ before and after SO_2 injection.

In this work, SO_2 did not show the inhibition of the Hg^0 removal efficiency of $\text{Co}_3\text{O}_4\text{@C}$ at room temperature. A new experiment was introduced to find out its mechanism, and its setting was as follows. Firstly, the sample $\text{Co}_3\text{O}_4\text{@C}$ adsorbed Hg^0 for an hour in pure N_2

at 25 °C or 150 °C. Then the Hg⁰ generator was removed, and 2286 mg/m³ SO₂ was injected into the gas flow. The result was shown in Figure 7a-7b.

A peak of Hg⁰ desorption immediately appeared as SO₂ entered in Figure 7b, proving that there was a competitive adsorption relationship between SO₂ and Hg⁰ at 150 °C. This explained why SO₂ inactivated the sample Co₃O₄@C at high temperatures. Obviously, SO₂ was more competitive than Hg⁰. It could occupy adsorption sites and combine with lattice oxygen on the surface of the sample Co₃O₄@C. This suppressed the occurrence of equation (2), and the subsequent oxidation reactions cannot occur, resulting in a reduction in the Hg⁰ removal performance of the sample. Nevertheless, when the experimental temperature was adjusted to 25 °C, there was no Hg⁰ desorption peak observed with the influx of SO₂. Hg⁰ was not driven away from the surface of the sample by SO₂ at room temperature, indicating that SO₂ did not compete with Hg⁰ at room temperature. As mentioned before, the deactivated time of Co₃O₄@C in the SO₂+N₂ atmosphere is almost the same as that in the O₂+N₂ atmosphere at 25 °C. Both SO₂ and O₂ could improve the Hg⁰ removal performance of the sample independently. The reason for the promotion is due to the generation of SO₃ by SO₂ oxidation on the sample.(Li et al., 2017b) FT-IR analysis corroborated this view. The FT-IR spectra of the sample before and after injection of SO₂ (Figure 7c) indicated the generation of sulfates in Co₃O₄@C during the experiment. The band that appeared around 1200 cm⁻¹ could be ascribed to the sulfates located in the bulk or subsurface of metal oxides.(Zhang et al., 2015) Consequently, SO₂ was converted to SO₄²⁻ on the surface of the sample during the experiment.

In summary, SO₂ was oxidized to SO₃ on the surface of Co₃O₄@C and then oxidizes the adsorbed Hg⁰. The reactions could be described as following.(Zhang et al., 2020a)

(8)

When O₂ appeared in the carrier gas, equation (9) and (10) happened and lattice oxygen got replenishment.

4. Conclusions

The Co₃O₄@C composite material formed by burning the sacrificial template Co-BDC showed excellent Hg⁰ removal capability and strong SO₂ resistance at ambient temperature. Its temperature window shifted to a low-temperature range compared to traditional Co₃O₄ catalysts. Meanwhile, it was found that the competition between SO₂ and Hg⁰ on the surface of Co₃O₄ disappeared, and SO₂ participated in the oxidation of Hg⁰ at ambient temperature. The role of SO₂ in Hg⁰ removal was discussed. This is a great improvement to the application of Co₃O₄ in Hg⁰ removal. It reduces the restrictions on the use of Co₃O₄ in Hg⁰ removal. Co₃O₄@C showed great adaptability to the complex simulated flue gas at ambient temperature.

Availability of data and materials: All data generated or analyzed during this study are included in this published article.

Authors' contributions: All authors (Jiacheng Zhou, Qicheng Shen, Jie Yang, Muhammad Tariq, Wei Sun, Limei Cao and Ji Yang) read and approved the final manuscript.

Declarations

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Ethics approval: Since this study did not recruit any human and/or animal subjects, this section does not apply.

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Figures

Figure 1

(a) Effect of temperature on Hg⁰ removal performance of commercial Co₃O₄ and Co₃O₄@C; (b) Effect of calcination temperature on Hg⁰ removal performance of Co₃O₄@C.

Figure 2

The micromorphology of $\text{Co}_3\text{O}_4@\text{C}$ powders. (a) XRD patterns of $\text{Co}_3\text{O}_4@\text{C}$, commercial Co_3O_4 , and the simulated Co_3O_4 (PDF#74-2120) (b-c) SEM images of $\text{Co}_3\text{O}_4@\text{C}$ powders prepared by the calcination method. (d) N_2 adsorption-desorption isotherm of $\text{Co}_3\text{O}_4@\text{C}$ and its pore size distribution. Inset shows the pore size distribution of the sample. (e) TEM image of $\text{Co}_3\text{O}_4@\text{C}$.

Figure 3

(a) The synergy of temperature and the gas components O₂ on Hg₀ removal performance of Co₃O₄@C.
 (b) The analysis of different experimental conditions on deactivation time of Co₃O₄@C.

Figure 4

(a) Synergistic effect of temperature and SO₂ on Hg⁰ removal efficiency of the sample. (b) Synergistic effect of O₂ and SO₂ on the deactivation time of the sample. Experimental conditions: catalyst mass, 50 mg; experimental temperature, 25 °C; gas stream contents, 285 mg/m³ SO₂+4% O₂/N₂; gas flow rate, 100 mL/min. (c) the effect of NO_x on Hg⁰ removal efficiency. (d) the Hg⁰ removal performance. (e) The Hg⁰

removal performance of Co3O4@C in the simulate gas at ambient temperature. The gas components: 400 µg/m3 Hg0+4%O2+2286 mg/m3 SO2+402 mg/m3 NO+N2.

Figure 5

(a) The Co 2p XPS spectra of Co₃O₄@C before and after the treatment; (b) Peak area of Co 2p and the ratio change of Co³⁺/Co²⁺. (c) The Hg 4d XPS spectra of Co₃O₄@C after the treatment.

Figure 6

(a) H₂-TPR spectra of Co₃O₄@C and commercial Co₃O₄; (b) Hg-TPD spectra of Co₃O₄@C and commercial Co₃O₄; (c) Extended X-ray adsorption fine structure-Fourier transform (EXAFS-FT) of Co₃O₄@C before and after Hg⁰ removal.

Figure 7

(a-b) Hg⁰ adsorption and desorption experiments and their mechanism simulation diagram. Experimental temperature (a) 25 °C; (b) 150 °C. Experimental conditions: catalyst mass, 50 mg; gas stream contents, N₂ 2286 mg/m³ SO₂+N₂; gas flow rate, 100 mL/min. (c) the FT-IR spectra of Co₃O₄@C before and after SO₂ injection.