

Application of metal-organic frameworks in efficient mercury adsorption

Dapeng Wang¹, Zhenqi Jing², Yaqin Wang³, Tianyu Liu², Chang Wen^{1,2,3*}

¹ China-EU Institute for Clean and Renewable Energy, Huazhong University of Science and Technology, Wuhan 430074, China.

² State Key Laboratory of Coal Combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

³ Department of New Energy Science and Engineering, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan 430074, China.

ABSTRACT

The bimetallic oxide copper–manganese based metal–organic frameworks (CuMnOx/MIL-100(Fe)) were easily synthesized and used to remove elemental mercury (Hg⁰) in flue gas. The mercury removal performance on the CuMnOx/MIL-100(Fe) was studied through a variety of characterization and analysis methods. The results suggest that the synthesized CuMnOx/MIL-100(Fe) have good crystallinity and high dispersity of constituent elements. The Hg⁰ removal performance was investigated under different conditions. The increase in O₂ and NO concentration can obviously promote the removal efficiency of Hg⁰. The obtained adsorption capacity is 1.128 mg/g, which is higher than the adsorption capacity of most same type adsorbents. Finally, the Hg⁰ removal mechanism on the bimetallic oxide CuMnOx/MIL-100(Fe) has been proposed with various characterization analysis. The removal process of Hg⁰ follows the Langmuir-Hinshelwood and Mars-Maessen mechanism.

Keywords: Mercury removal, MIL-100(Fe), Bimetallic oxide copper–manganese

1. INTRODUCTION

The combustion of coal will release dust, NO_x, SO_x, and heavy metal pollution. On the one hand, in the process of carbon neutrality, coal-fired power plants in China play the role of ballast for power grid peak shaving. Under low-load operation, incomplete combustion of coal leads to increased pollutant emissions, and the control of Hg⁰ is a key issue. On the other hand, mercury released during the possible co-processing of coal with waste, sludge, etc. also requires attention. The mercury species in flue gas mainly is of three different forms: Hg_p, Hg²⁺, and Hg⁰. The removal of elemental mercury (Hg⁰)

from flue gas is a major problem at present. The current mercury emission control methods are mainly catalytic oxidation and adsorption. The SCR catalyst is used to promote the conversion of Hg⁰ to Hg²⁺ in the flue gas. Spraying activated carbon into the flue gas, which uses the porous structure of the carbon for physical adsorption as well as the active sites on its surface for chemisorption. However, the adsorption efficiency of this process is low, the adsorbent is consumed in large quantities and it is difficult to separate and recover effectively, which increases the cost and reduces the utilization rate of the adsorbent. Thus, it is necessary to develop a new type of adsorbent with high adsorption efficiency and recyclable.

Metal-organic frameworks (MOFs), consisting of organic ligands and an active metal center, have more potential than the traditional porous materials. Yoon et al. [1] studied that the iron species in MIL-100(Fe) can form a large number of coordination unsaturated metal sites (CUSs) after vacuum drying, which can provide Lewis acid sites for adsorption and heterogeneous catalytic reactions. Zhang et al. [2] synthesized Mn/MIL(Fe) and found that ultra-highly dispersed and homogeneous Fe sites on MIL(Fe) significantly promoted Hg⁰ adsorption and oxidation via the synergy effect with MnOx.

In this work, easily synthesized MIL-100(Fe) with impregnation copper oxide and manganese oxide to form CuMnOx/MIL-100(Fe), as a medium and low temperature SCR catalyst for Hg⁰ removal in the flue gas. Its removal performance of Hg⁰ was evaluated under different simulated flue gas atmospheres. The catalyst recovery and recycling performance were also discussed.

2. EXPERIMENTAL

2.1 Preparation of catalysts

CuMnOx/MIL-100(Fe) was synthesized via the following two-step process. Firstly, CuMnOx/MIL-100(Fe) was prepared at room temperature and normal pressure. Trimeric acid (2.52 g) and NaOH (1.44 g) were dissolved in 95 mL of deionized water named solution 1 (PH \approx 11). FeCl₂ · 4H₂O (3.5786g) was dissolved in 95 mL of deionized water named solution 2 (PH \approx 2.7). Solution 1 was added dropwise to solution 2 with constant stirring, resulting in a mixture with a molar ratio of 1.5 Fe/1.0 H₃BTC/3.0 NaOH/880 H₂O with a pH of about 5.2. When all the additions of solution 1 and solution 2 were complete, the reaction time was recorded as zero. Stirring was continued for 24 hours at room temperature. The solid was recovered by centrifugation at 3700 rpm, which was then washed with deionized water and ethanol at room temperature. Finally, the samples obtained was dried at room temperature to yield MIL-100(Fe).

Secondly, the preparation of CuMnOx/MIL-100(Fe) catalyst was synthesized by excess impregnation of MIL-100(Fe). Cu(NO₃)₂·3H₂O (121.8 mg) and Mn(NO₃)₂ (90.2 mg) were added to 40 mL of deionized water to obtain a manganese-copper mixed solution with molar ratio of Mn/Cu=1/1 and 6 wt% loadings of Mn and Cu). MOF (1 g) was magnetically stirred at 80°C for 5 hours with vigorous stirring. The solid samples were then dried in an oven at 60°C for 12 h, and then calcined at 200°C, 300°C, 400°C, 500°C for 3 h to obtain CuMnOx/MIL-100(Fe), denoted as α -CuMnOx/MIL-100(Fe), and α represents the loading (3%, 6%, 9%).

In order to compare the effective improvement of the mercury removal effect of different carriers, Fe₂O₃·5H₂O was used as the carrier to synthesize traditional CuMnOx/Fe₂O₃ for comparative experiments. The synthesis steps were basically the same as the above.

2.2 Material characterization

The morphology of samples were observed by a scanning electron microscope (SEM, GeminiSEM 300). Using energy dispersive X-ray spectroscopy (EDS, OxfordX-MAX) to release the element distribution. Brunauer–Emmett–Teller (BET) surface area was measured using ASAP 2020. All the samples were characterized by powder X-ray diffraction (XRD) with a diffractometer (D8 Advance). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on an ESCALAB 250XI X-ray photoelectron spectroscope. Magnetic test was using Vibrating Sample Magnetometer (VSM, JDM-13).

2.3 Elemental mercury removal experiments

The experimental system for evaluating mercury removal performance was composed by three units, including a Hg⁰ analyzer unit, a fixed bed unit, and a simulated flue gas unit. A given concentration of gaseous Hg⁰ vapor (140 μ g/m³) was produced through a mercury permeation tube, which was heated in a temperature-controllable water bath. The flow rate of total flue gas was set as 1.0 L/min (N₂ as balance gas). In each experimental case, 0.02 g CuMnOx/MIL-100(Fe) samples were introduced into the quartz tube of the reactor. At the same time, 0.98 g quartz sand was selected as the diluent to mix with CuMnOx/MIL-100(Fe) samples to increase the length of heterogeneous reaction field, thereby promoting the contact between the flue gas and sample. The temporal Hg⁰ concentration was obtained using a mercury analyzer (Lumex RA-915M). A blank test was carried out to obtain a stable inlet Hg⁰ concentration before each test. The mercury mass balance during different cases is in the range from 95 to 105%. The temporal Hg⁰ removal efficiency (η) was defined through the following equation:

$$\eta = \frac{Hg_{in}^0 - Hg_{out}^0}{Hg_{in}^0} \times 100\% \quad (1)$$

Where Hg_{in}⁰ and Hg_{out}⁰ were Hg⁰ concentration in the inlet and outlet of the reaction system, respectively.

The mercury adsorption capacity per unit mass q (ug/g) was defined through the following equation:

$$q = \frac{1}{m} \left(\int_0^t Hg_{in}^0 \cdot v_t - \int_0^t Hg_{out}^0 \cdot v_t \right) \quad (2)$$

Where m (mg) was the mass of adsorbent, t (min) was the time of removal mercury, v_t (L/min) was the speed of flue gas.

3. Results and discussion

3.1 Success preparation of MIL-100(Fe)

The XRD data of synthesized MIL-100(Fe) was shown in Fig.1 (a). The results showed that the synthesized MIL-100(Fe) has developed crystal structure, high crystallinity, and high purity. The peak value was mainly focused on 6.3°, 10.2°, 20°, which means we have synthesized MIL-100(Fe) successfully. The morphology of the MIL-100(Fe) was characterized and shown in Fig. 1 (b). The MIL-100(Fe) presented a relatively regular three-dimensional block structure with clear edges and corners, with crystal size of about 200 nm. It also confirmed the successful synthesis of the material.

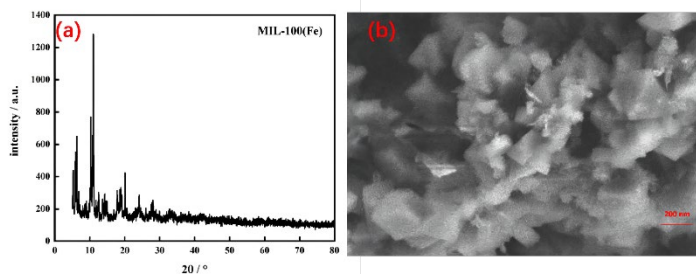


Fig. 1 Characterization of MIL-100(Fe): (a) XRD patterns, (b) SEM image

Bimetallic loading of Cu and Mn included the benefits of particle size reduction and the interaction between metal oxides and MIL-100(Fe). Fig. 2 showed the image of the loading of Cu-Mn bimetals, including large particles with clear edges and corners, and uneven particle size, as well as agglomerated, unevenly distributed, and disorderly distributed small particles. This distribution would promote the transfer of electrons between metals, thereby improving the mercury removal efficiency.

The element distribution of CuMnOx/MIL-100(Fe) were shown in Fig. 3, it could be seen that Cu, Mn, Fe, O elements were evenly distributed on the surface, this highly dispersed phase could provide abundant active sites and oxidative intermediates for the removal of element mercury in the flue gas. The synergistic interaction between MnOx and CuOx led to stronger reducibility and good oxygen mobility, which would form more reactive oxygen species.

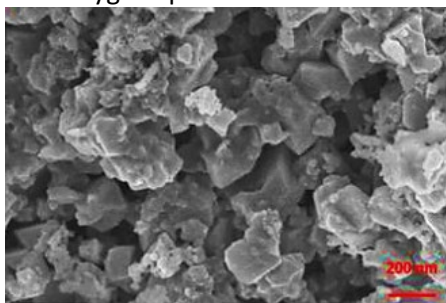


Fig. 2 SEM image of 500°C-CuMn/MIL-100(Fe)

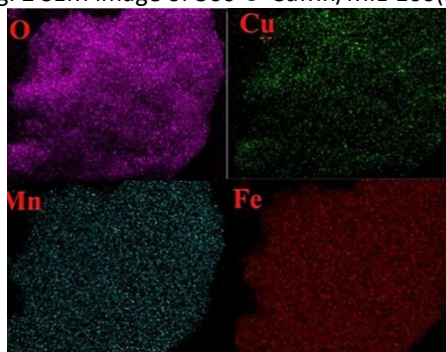


Fig. 3 EDS image of CuMnOx/MIL-100(Fe)

MIL-100(Fe) exhibited a large BET surface area of 1266.12 m²/g. The calcination at 200°C did not destroy

the spatial structure of MIL-100(Fe) material. A little decrease in BET surface area was caused by a small part of the generated Cu-Mn binary metal oxides deposited in the pore structure of MOFs, which blocked the micropores. Although increasing of calcination temperature would decrease BET surface area, abundant active sites were formed on the surface. High-valence metal oxides will provide sufficient lattice oxygen to facilitate the oxidation of Hg⁰, which ensures excellent mercury removal performance.

The XRD patterns of CuMnOx/MIL-100(Fe) under different calcination temperature were shown in Fig. 4. The characteristic peaks of 200°C-CuMnOx/MIL-100(Fe) were generally consistent with MIL-100(Fe), which indicated that the crystal structure of MIL-100(Fe) was not destroyed and the formation of copper and manganese oxides were limited. With the temperature gradually increased, the organic components of MIL-100(Fe) were thermally decomposed, the crystal structure was destroyed, and some iron elements be oxidized to form high-valence iron oxide. When the temperature reached 500°C, it showed a clear iron element diffraction peak, but not show the diffraction peak of CuMnOx, which may due to the light and evenly distributed loading of only 6.wt % Cu and Mn.

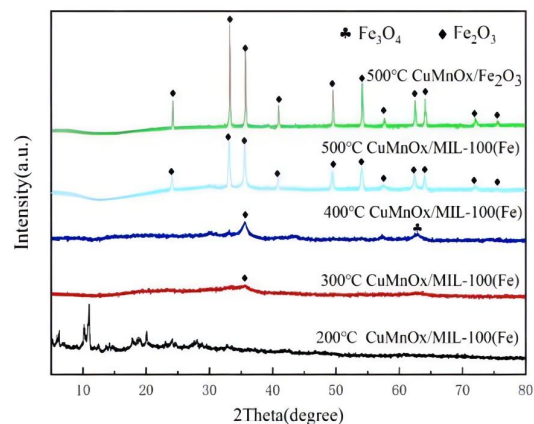


Fig. 4 XRD patterns of CuMnOx/MIL-100(Fe) under different calcined temperature

Under the atmosphere of 5% O₂+N₂, the catalyst samples under three conditions of unreacted, reacted for 8 hours and reacted for 16 hours were taken for XPS analysis. As displayed in Table 1, during the first 8 hours of reaction, the low-valence state of transition metal elements showed an upward trend, which indicated that high-valence metal elements as the reactive sites participate in the oxidation of Hg⁰ and were reduced to a low-valence state. The ratio of Cu⁺/Cu showed an upward trend with the progress of the reaction of next 8 hours, while Fe²⁺/Fe showed an opposite trend, which indicated that the reaction transformed from Cu²⁺ and

Fe²⁺ to Cu⁺ and Fe³⁺. The existence of Cu⁺ will facilitate the adsorption and activation of oxygen, thereby improving the oxidation activity of the catalyst. The valence state of Mn³⁺/Mn didn't change significantly during the last 8 hours of reaction, which indicated that the conversion of Mn³⁺ and Mn⁴⁺ was in a balanced state, reflecting the stability of manganese during the catalyst reaction process.

Table 1 The proportion of each active component of the catalyst

	Fe ²⁺	Fe ³⁺	Cu ⁺	Cu ²⁺	Mn ²⁺	Mn ³⁺	O _w	O _w
	Fe ²⁺ + Fe ³⁺	Fe ²⁺ + Fe ³⁺	Cu ⁺ + Cu ²⁺	Cu ⁺ + Cu ²⁺	Mn ²⁺ + Mn ³⁺	Mn ²⁺ + Mn ³⁺	O _w + O _w + O _w	O _w + O _w + O _w
CuMnOx/MIL-100(Fe)	0.40	0.60	0.20	0.80	0.48	0.52	0.69	0.31
CuMnOx/MIL-100(Fe)-Sh	0.54	0.46	0.29	0.71	0.57	0.43	0.68	0.32
CuMnOx/MIL-100(Fe)-16h	0.45	0.55	0.33	0.67	0.56	0.44	0.71	0.29

3.2 Hg⁰ removal performance of CuMnOx/MIL-100(Fe)

In order to explore the difference in mercury removal effect of catalysts at different calcination temperature, 6%-CuMnOx/MIL-100(Fe) was calcined at different temperature for 3 hours in this experiment. It can be seen from Fig. 5(a) that with the increase of calcination temperature, the mercury removal effect was gradually enhanced, reaching 94.8% at 500°C, which indicated that the 6%-CuMnOx/MIL-100(Fe) prepared at higher calcination temperature were beneficial to the removal of Hg⁰. The large specific surface area and abundant metal active sites of CuMnOx/MIL-100(Fe) could promote adsorption of Hg⁰. Although the specific surface area of 500°C-CuMnOx/MIL-100(Fe) dropped sharply, it promoted the formation of CuMnOx and Fe₂O₃, which would provide abundant active sites and high-valence metal oxides for the oxidation of mercury. However, when the calcination temperature continued to increase, metal oxides would agglomerate and block the pores, therefore the optimal calcination temperature was selected as 500°C.

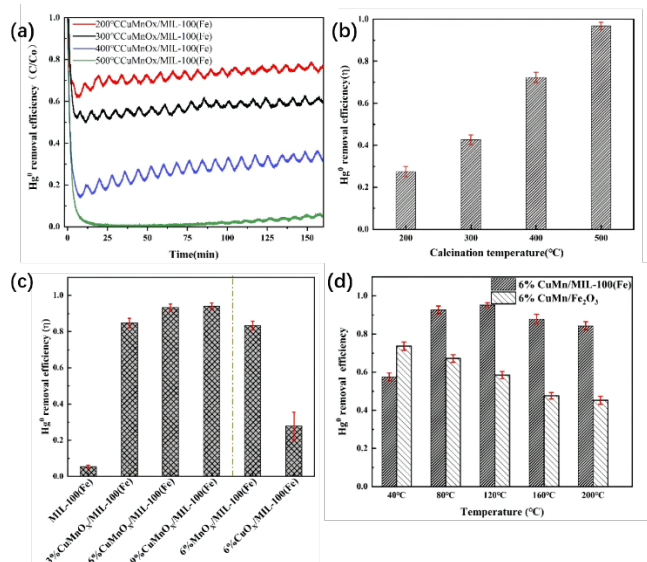


Fig. 5 Effect of Synthesis conditions of CuMnOx/MIL-100(Fe) in the 5% O₂+N₂: (a) (b) calcination temperature, (c) CuMnOx loading mass, (d) reaction temperature between 6%-CuMnOx/MIL-100(Fe) and 6%-CuMnOx/Fe₂O₃

The content of active components was related to the dispersion, aggregation, crystallinity, and redox properties of metal oxides on the carrier. As shown in Fig. 5 (c), the Hg⁰ removal efficiency of MIL-100(Fe) was only 8.4% without metal loading, which indicated that although it had a large specific surface area, it represented low reactivity at 120°C. As the loading increased from 3. wt% to 9. wt%, the efficiency of Hg⁰ removal increased from 82.5% to 91.7%, which attributed to the larger specific surface area of MIL-100(Fe), Cu and Mn can be better dispersed on the surface. It promoted the formation of CuMnOx during calcination, which would make the sample have stronger oxidizing ability and oxygen storage capacity, so it would increase the oxidation and chemisorption of Hg⁰. There was little improvement in efficiency of Hg⁰ removal when the loading was increased from 6% to 9%, because too high loading will lead to agglomeration of active ingredients, clogging pores, and unfavorable reaction. The efficiency of Hg⁰ removal by using 6%-MnOx/MIL-100(Fe) and 6%-CuOx/MIL-100(Fe) are lower than 6%-MnCuOx/MIL-100(Fe). This indicated that the bimetallic loading will form more lattice oxygen on the sample surface, enhancing the oxygen storage capacity of the catalyst.

In order to explore the low temperature activity of the catalyst, five temperature gradients (40 °C, 80 °C, 120 °C, 160 °C, 200 °C) were selected to test the mercury removal performance of the catalyst. The results were shown in Fig. 5 (d). When the reaction temperature increased from 40°C to 120°C, the mercury removal efficiency gradually increased, and the best mercury removal efficiency was reached at 120°C, which indicated that an appropriate increase in the reaction temperature was beneficial to the removal of Hg⁰. This catalyst has good mercury removal efficiency at low temperature. The increase of reaction temperature will usually weaken the physisorption between the catalyst and Hg⁰, but chemisorption will be enhanced. If the temperature is too high, the result will be the opposite. Therefore, 120°C was considered as the optimum reaction temperature. Compared with 6%-CuMnOx/MIL-100(Fe), 6%-CuMnOx/Fe₂O₃ showed lower efficiency of Hg⁰ removal. It is attributed to the difference of the carrier. Many factors contributed to this result: Firstly, the large specific surface area and abundant pore structure of MIL-100(Fe) make the CuMnOx uniformly

distributed on the surface of the carrier. Secondly, the highly crystalline nature and uniformly dispersed metallic Fe sites of MIL-100(Fe) enable to form a good mutual synergy with CuMnOx, thereby promoting the removal of Hg⁰.

From above discussion, we found the 6%-CuMnOx/MIL-100(Fe) with calcination temperature of 500°C, and under reaction temperature of 120°C, the catalyst would have optimal performance. We would use it in the following discussion.

O₂ played an important role in Hg⁰ removal by CuMnOx/MIL-100(Fe). When the carrier gas was 2%, 5%, and 10% O₂, the performances of all the catalysts, as shown in Fig. 6 (a), were excellent and far better than those using pure N₂ as the carrier gas. With the introduction of oxygen, the oxygen species consumed by the reaction on the catalyst surface can be replenished in time. Meanwhile, oxidizing low-valence metal oxides and adding to the lattice of metal oxides to form chemisorbed oxygen.

It can be seen from Fig. 6 (b) that when the SO₂ concentration introduced into the flue gas gradually increased from 400 ppm to 1200 ppm, the removal efficiencies of Hg⁰ gradually decreased from 87.4% to 60.9%. The higher the concentration of SO₂, the more obvious the inhibitory effect on CuMnOx/MIL-100(Fe). It was attributed to the irreversibility of sulfate and sulfite generated by the catalyst reacting with SO₂.

As shown in Fig. 6 (c), when 5% H₂O and 10% H₂O was introduced, the mercury removal efficiencies decreased from 88.3% to 79.8% and 69.1% respectively, which indicated that water vapor had a slight inhibitory effect on mercury removal. It attributed to the competitive adsorption of H₂O and Hg⁰, because H₂O occupied the active sites on the reactant surface. Under the atmosphere of 400 ppm SO₂ and 5% H₂O, the mercury removal efficiency decreased greatly. With the progress of the reaction, a high concentration of H₂O would accumulate on the surface of the catalyst to form a water film, which together with SO₂ inhibits the oxidation of Hg⁰.

In order to explore the mechanism of NO on CuMnOx/MIL-100(Fe), under the condition of N₂+5%O₂, 300 ppm, 600 ppm and 900 ppm NO were introduced respectively, as shown in Fig. 6 (d), and it was found that the removal efficiency of Hg⁰ increased, which indicated that NO promotes the catalyst performance. It proved that NO can be oxidized by chemically adsorbed oxygen or lattice oxygen on the catalyst surface to generate new active species NO⁺ and NO₂. Therefore, when these newly formed reactive species were generated during

the removal of Hg⁰, they can react with the adsorbed Hg⁰ to generate HgO and Hg(NO₃)₂, thereby facilitating the removal of Hg⁰.

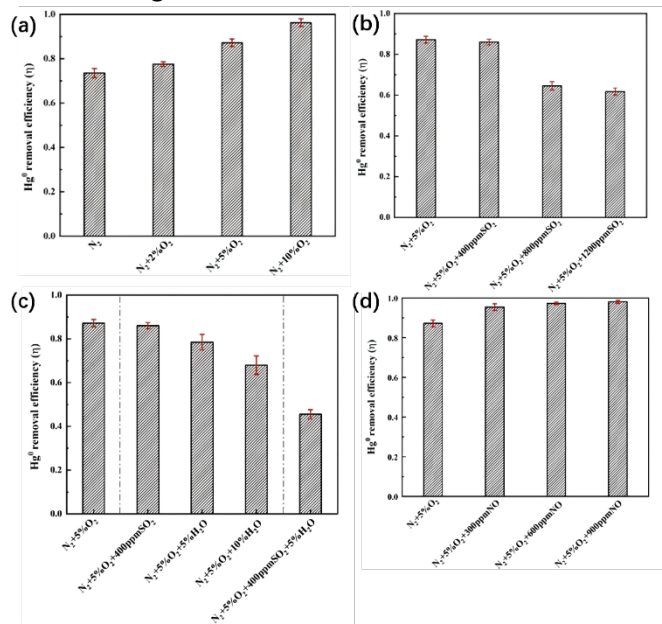


Fig. 6 Effect of flue gas concentration on Hg⁰ removal performance:(a) oxygen concentration, (b) SO₂ concentration, (c) H₂O and SO₂ concentration, (d) NO concentration

3.3 The mechanism of Hg⁰ removal

The removal of Hg⁰ follows the Langmuir-Hinshelwood and Mars-Maessen mechanism, that was, the gaseous elemental mercury (Hg⁰) in the flue gas was first adsorbed on the catalyst surface and then catalyzed by adjacent active substances. The oxygen in the flue gas was adsorbed on the surface of the catalyst through van der Waals force to form O_{phy-ad}. When the metal element in the metal oxide changes from high valence to low valence, oxygen migrates from the lattice, and the migrated oxygen is called O_{lat}. When it was the sole source of oxygen, it would be quickly depleted. When the metal component existed in a low valence state, it exhibited the ability to accept oxygen and form oxygen vacancies. The oxygen on the catalyst surface replenished the oxygen vacancies in time, and the formed oxygen was called O_{chem-ad}. O_{chem-ad} were combined in the form of chemical bonds, and it was considered to be the most reactive reactive oxygen species.

Metal oxides can oxidize Hg^{0(ad)} to Hg²⁺, which can react with chemisorbed oxygen and lattice oxygen to form HgO. As shown in Figure 7, the reduced metal oxides can be oxidized by O₂ in the flue gas, and the XPS analysis results showed that there was a good synergy between the metal oxides, and the metals in this catalyst

continued to undergo high and low valence transitions, as shown in Table 1, which is beneficial to improve the catalytic performance of the metal oxides.

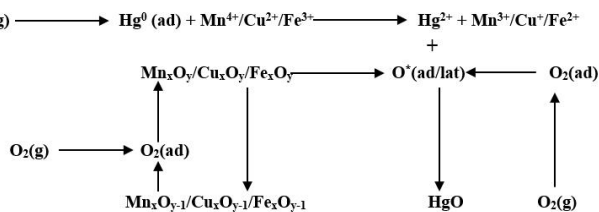


Fig. 7 Mechanism of CuMnOx/MIL-100(Fe) Catalytic Oxidative Removal of Hg⁰

3.4 Adsorbent recycle performance

During the magnetic test of CuMnOx/MIL-100(Fe), we found that in the presence of an external magnetic field, the curve showed a small coercive force hysteresis, which indicated that the adsorbent had good superparamagnetic properties. While MIL-100(Fe) was not magnetic, the iron element in the carrier was converted into magnetic γ -Fe₂O₃ during the calcination process. After the external magnetic field disappeared, CuMnOx/MIL-100(Fe) would not be permanently magnetized, which would be beneficial to the recovery of the adsorbent.

The reuse and utilization efficiency of the separated adsorbent was related to the long-term operation cost of the adsorbent, therefore the multi regeneration performance of the adsorbent was also an important indicator to measure whether it was economical and efficient. The mercury removal performance of 6% CuMnOx/MIL-100(Fe) was tested under the simulated flue gas condition of 120°C. The adsorbent was then heat treated at 350°C for 1 h to regenerate. After 8 cycles, the mercury removal efficiency hardly decreased and remained above 90%. This indicated that 6% CuMnOx/MIL-100(Fe) had good regeneration performance.

3.5 Comparison of adsorbent capacity

In order to further compare the effectiveness of CuMnOx/MIL-100(Fe) adsorbent and the similar MOF-based adsorbent, the mercury removal capacities of MOF-based adsorbent reported in the literature are listed in Table 2. Since the removal time of Hg⁰ by adsorbents in different literatures was not uniform, the time was normalized to 3 hours in this study. It can be seen that the Hg⁰ capture capacity within 3 h at 120°C in this experiment was 1.128 mg/g, which was higher than the adsorption capacity of most reported adsorbents.

Table 2 Comparison of Hg⁰ capture capability of different MOFs materials

sorbents	Hg ⁰ capture	experiment	refs
	capacity (mg.g ⁻¹)	condition	
CuMnOx/MIL-100(Fe)	1.128	120°C, 3h	this work
Cu-MOFs	0.4158	120°C, 3h	[3]
FeCu-MOFs	0.40455	120°C, 3h	[4]
MnOx/MIL-100(Fe)	~ 0.47	200°C, 3 h	[2]
α -MnO ₂ -MIL-96(Al)	0.112	100°C, 3h	[5]

4. Conclusions

MIL-100(Fe) was successfully synthesized under the conditions of room temperature, no corrosive acid, and short time. MIL-100(Fe) has a large specific surface area (1266.12 m²/g), rich pore structure, developed crystal structure and high crystallinity and purity. CuMnOx was loaded on MIL-100(Fe) by excessive impregnation to obtain CuMnOx/MIL-100(Fe). 6%-CuMnOx/MIL-100(Fe) calcined at 500°C had the best Hg⁰ removal performance. The obtained adsorption capacity was 1.128 mg/g, which was higher than the adsorption capacity of most similar adsorbents. The removal process involved the participation of physisorbed oxygen, chemisorbed oxygen, and lattice oxygen. The removal of Hg⁰ follows the Langmuir-Hinshelwood mechanism and Mars-Maessen mechanism. All in all, the designed CuMnOx/MIL-100(Fe) was one of the most promising materials for elemental mercury removal from flue gas with good cycle regeneration performance and large adsorption capacity.

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