

# Screening of Metal Modified HKUST-1 to Enhance Mercury Removal Efficiency

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**Abstract.** In this work, HKUST-1 and different metal modified HKUST-1 materials were investigated in Hg<sup>0</sup> removal performance under air condition. Results showed that the pristine HKUST-1 only has a mercury removal rate of around 20%. After metal modification of HKUST-1, the removal efficiency was significantly improved. Among different modification materials employed in this study, HKUST-1 modified by manganese chloride exhibited the highest Hg<sup>0</sup> removal efficiency of 95% at 250 °C. This value is relatively high compared with most previously reported catalysts. In addition, this study reveals that the enhanced Hg<sup>0</sup> removal efficiency results from the increase of Brønsted acid sites on the sample surface, which is vital to Hg<sup>0</sup> removal. Furthermore, it is found that SO<sub>2</sub> produced little toxicity to Mn(Cl)/HKUST-1 in the presence of O<sub>2</sub>. This is beneficial to remove Hg<sup>0</sup> in the industrial flue gas, where SO<sub>2</sub> is a common component. Therefore, Mn(Cl)/HKUST-1 synthesized here is a promising catalyst for Hg<sup>0</sup> removal.

## 1 Introduction

Mercury control has become increasingly important because mercury is a poisonous material that results in a detrimental impact on ecosystems and human beings [1]. Countries are beginning to develop documents to control mercury emissions. In 2015, China began to implement pollutant emission standards (GB13223-2011) [2], which put forward the mercury emission limit of 0.03 mg/m<sup>3</sup>. Mercury is mainly divided into three forms: particle-bound mercury (Hg<sup>p</sup>), gaseous divalent mercury (Hg<sup>2+</sup>) and elemental mercury (Hg<sup>0</sup>) [3]. Among these, Hg<sup>2+</sup> can be removed by wet flue gas desulfurization device because of its high-water solubility. The electrostatic dust removal equipment can be used to remove Hg<sup>p</sup>, while Hg<sup>0</sup> exists in a stable form and persist for a long time due to its high volatility and low solubility [4]. Hg<sup>0</sup> affects the growth of crops and contaminates aquatic life, it can also poison the brain and digestive tract when entering human body [5]. Therefore, there is a considerable interest in developing a novel catalyst to control the emission of elemental mercury (Hg<sup>0</sup>).

Many studies have indicated that a new material, metal organic framework material (MOF), has a good prospect of mercury removal due to its high porosity, large specific surface area and diverse structural morphology [6, 7]. HKUST-1 is a copper-based MOF material with each Cu<sup>2+</sup> binds to a water molecule. The water molecules can be easily removed and thus generating open metal sites. Moreover, HKUST-1 shows a lot of acid sites on the surface which is beneficial to Hg<sup>0</sup> adsorption and catalytic

oxidation [8, 9]. Chen et al. found that HKUST-1 exhibited superior Hg<sup>0</sup> removal efficiency when adding HCl into the gas [9]. However, HCl was proved to be toxic and corrosive. Additionally, many researchers have reported that metal oxides like CeO<sub>x</sub> and MnO<sub>x</sub> et al. have excellent performance on Hg<sup>0</sup> removal [10]. Therefore, it is speculated that modification by metal or metal oxides on HKUST-1 can improve the Hg<sup>0</sup> removal performance. Furthermore, there is a certain amount of SO<sub>x</sub> existed in the coal-fired flue gas and SO<sub>2</sub> is the major component. It is difficult for air pollution equipment (APCDs) to completely remove SO<sub>2</sub>. Many reports demonstrated that SO<sub>2</sub> played a negative role in Hg<sup>0</sup> removal. Hence, the effect of SO<sub>2</sub> on Hg<sup>0</sup> removal is significant to study.

In this work, different metal modified HKUST-1 composites were prepared. MnCl<sub>2</sub> was found to be the optimal modification agent for HKUST-1 in terms of Hg<sup>0</sup> removal performance. Moreover, the SO<sub>2</sub> effect on the Hg<sup>0</sup> removal when using the optimal was also investigated.

## 2 Materials and Methods

All chemicals were purchased from Sinopharm and used directly without any treatment.

### 2.1 Preparation of samples

HKUST-1 powder preparation

The preparation of HKUST-1 was carried out by hydrothermal method as described in Ref [11]. Copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, 7.5 g) and trimetric (TMA, 4 g)

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were first dissolved in ethanol. The mixed solution was heated under stirring at 50 °C for 3 h. The mixture was then centrifuged to separate the solid. The solid was placed in an oven at 120 °C overnight. The dried powder was then washed by methanol to remove impurities. The final product was obtained after centrifugation and drying.

#### HKUST-1/Al<sub>2</sub>O<sub>3</sub> preparation

A certain amount of Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was dissolved in ethanol and impregnated on Al<sub>2</sub>O<sub>3</sub> by incipient wetness impregnation method. It was heated at 50 °C for 3 h. Then, TMA was excessive impregnated on the product and the reaction was heated at 50 °C for another 3 h. Finally, the sample (HKUST-1/Al<sub>2</sub>O<sub>3</sub>) was washed by methanol and dried at 120°C.

#### A/HKUST-1 preparation

A metal salt with a mass fraction of 10% was dissolved in ethanol and deionized water (40 mL, 1:1). About 1g of HKUST-1 was mixed into the solution. The mixture was stirred at room temperature and ambient pressure for 6 h. After drying at 100 °C overnight, the solid was calcined at 250 °C for 2 h under N<sub>2</sub> atmosphere. The samples referred in the following were denoted as HKUST-1 and A/HKUST-1, respectively. (A was europium nitrate, cerium nitrate, manganese nitrate, manganese acetate or manganese chloride).

## 2.2 Characterization of the samples

The structure of the solid phase was examined by powder X-ray diffraction (XRD SmartLab3KW) with a scanning rate of 0.02°/s. The scanning range is 5-40°. The temperature-programmed reduction with H<sub>2</sub>/He test was conducted by a chemisorption analyser (H<sub>2</sub>-TPR Auto Chem II 2920). Around 0.05 g sample was used for each test. The test temperature was set from 50-500 °C at the heating rate of 10 °C/min in the flow of 2.5% H<sub>2</sub> in He. Thermal stability test was conducted by using the thermogravimetric analyser (TGA NETZSCH STA49 F3) under nitrogen atmosphere, and the temperature was heated from 30 °C to 600 °C at 10°C/min [12]. In-situ diffuse reflectance infrared Fourier transform spectroscopy (in-situ DRIFT VERTEX 70) was adopted to study the acid sites on the surface, with NH<sub>3</sub> as the probe molecule [13].

## 2.3 Hg<sup>0</sup> catalytic oxidation performance evaluation

The Hg<sup>0</sup> removal performance evaluation device consists of a Tekran3300 Hg<sup>0</sup> continuous monitoring module, an elemental Hg<sup>0</sup> calibration module (3310), a dilution probe controller (3340), a sample controller (3320) and a fixed bed quartz (D=12 mm). Teflon pipelines and quartz reactors were selected to avoid mercury adsorbed to the equipment. The reaction temperature range is 30-300 °C with a heating rate of 2°C/min. The Hg<sup>0</sup> removal efficiency was calculated by the following equation:

$$E = \frac{[\text{Hg}^0]_{\text{in}} - [\text{Hg}^0]_{\text{out}}}{[\text{Hg}^0]_{\text{in}}} \times 100\%$$

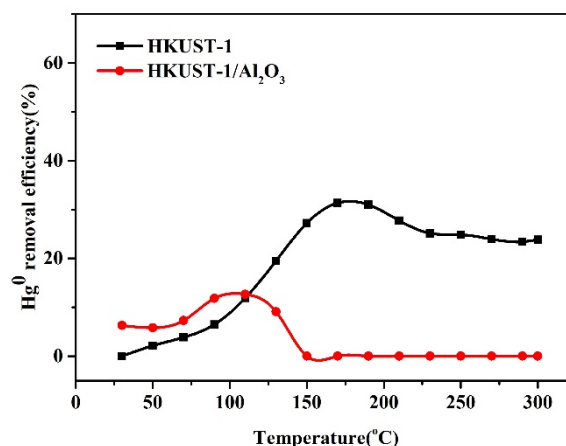
## 3 Results and discussion

### 3.1 Activity comparison of HKUST-1 and HKUST-1/Al<sub>2</sub>O<sub>3</sub>

The Hg<sup>0</sup> removal performance of HKUST-1 powder and HKUST-1/Al<sub>2</sub>O<sub>3</sub> with the same amount of HKUST-1 were conducted. The concentration of Hg<sup>0</sup> source was 30 µg/m<sup>3</sup>, and 1500ml/min flow rate of air was injected into the reactor. The comparison results were shown in Fig. 1. Before 112 °C, the Hg<sup>0</sup> removal efficiency of powder HKUST-1 was lower than that of HKUST-1/Al<sub>2</sub>O<sub>3</sub>. This can be attributed to the distribution of HKUST-1 was more uniform than the powder. As the temperature continued to increase, the removal efficiency of powder HKUST-1 gradually increased, which reached the highest value of 31.15% at around 175 °C. Then the removal rate decreased gradually with the increasing temperature and kept stable between 250-300 °C. However, the removal efficiency of HKUST-1/Al<sub>2</sub>O<sub>3</sub> dramatically declined after 112°C and became zero at 150°C. This is probably caused by the structure decomposition of HKUST-1 supported on Al<sub>2</sub>O<sub>3</sub> under this reaction condition. This matches with its colour change observed from light blue to grey, which was not found for HKUST-1 powder.

During the Hg<sup>0</sup> removal process for HKUST-1 powder, both adsorption and catalytic oxidation of Hg<sup>0</sup> occurred. The oxidation reaction rate rose with the temperature increasing, while the adsorption rate decreased. According to the curve shown in Fig. 1, it can be inferred that the oxidation reaction dominates before 175°C. However, due to the limited adsorption capacity of HKUST-1, as well as the dropped adsorption rate at high temperature (>175°C), the whole Hg<sup>0</sup> removal efficiency obviously went down.

By comparing the results for two materials, the conclusion can be drawn that HKUST-1 powder was superior to HKUST-1/Al<sub>2</sub>O<sub>3</sub> for Hg<sup>0</sup> removal performance. Therefore, powder HKUST-1 was selected as the pristine sample for the later modification.

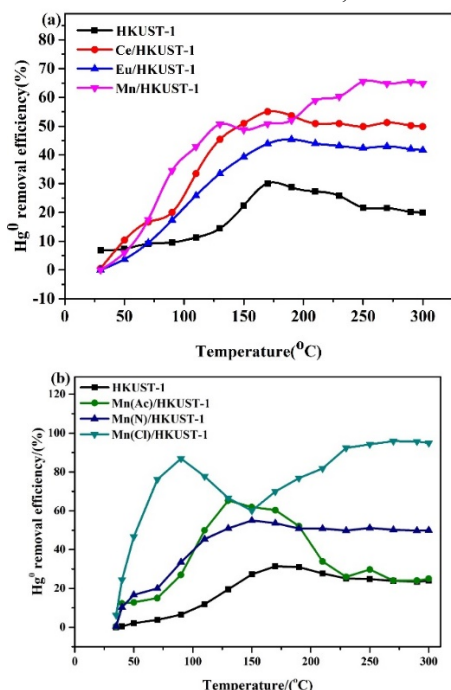


**Figure 1** Dynamic activity test trend of prepared samples (Reaction condition: Hg<sup>0</sup>=30 µg/m<sup>3</sup>, GHSV=1.74×10<sup>5</sup> h<sup>-1</sup>, Temperature 30 -300 °C.)

### 3.2 Modified HKUST-1 for Hg<sup>0</sup> removal test

Different metal salts were used to modify HKUST-1 and the Hg<sup>0</sup> removal results were displayed in Fig. 2(a). It can be seen that Hg<sup>0</sup> removal efficiencies of the samples modified are all higher than that of the sample without modification. When the temperature is higher than 200 °C, the high-to-low order of mercury removal rate is as follows: Mn/HKUST-1 > Ce/HKUST-1 > Eu/HKUST-1 > HKUST-1. The material modified by manganese nitrate exhibited the highest mercury removal efficiency, reaching about 65%. This indicates that Mn is more helpful to improve the efficiency of Hg<sup>0</sup> removal compared to the other metals. Many previous literatures have reported that Mn-based catalyst is one of the best candidate catalysts for the removal of Hg<sup>0</sup> [14]. Therefore, the Hg<sup>0</sup> removal performance of manganese modified HKUST-1 was mainly studied.

The precursor is one of the important factors affecting the efficiency of adsorbent/catalyst. In this section, manganese nitrate, manganese acetate and manganese chloride were used to modify HKUST-1 (Mn(N)/HKUST-1, Mn(Ac)/HKUST-1 and Mn(Cl)/HKUST-1) respectively, and the results were displayed in Fig. 2 (b). The mercury removal efficiency of unmodified HKUST-1 increased with the increase of temperature, reaching its maximum value of 31.15% at 175 °C, and then remained basically flat between 20-30%. The mercury removal efficiency of the samples modified by different manganese precursors was higher than that of HKUST-1 during 30-300 °C. Among different kinds of manganese precursor, HKUST-1 modified by MnCl<sub>2</sub> shows the highest removal efficiency, up to 95% in the range of 250-300 °C, which could be attributed to the combined effect of Cu, Mn and Cl.

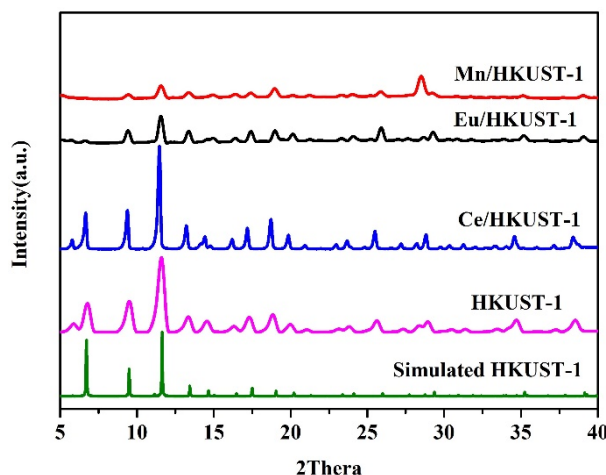


**Figure 2** (a) Test of different metal modified HKUST-1  
 (b) Different manganese Mn precursors modification on HKUST-1 test results (Reaction condition: Hg<sup>0</sup>=30 μg/m<sup>3</sup>, GHSV=1.74×10<sup>5</sup> h<sup>-1</sup>, T= 30-300 °C)

### 3.3 Characterization of samples

#### 3.3.1 XRD analysis

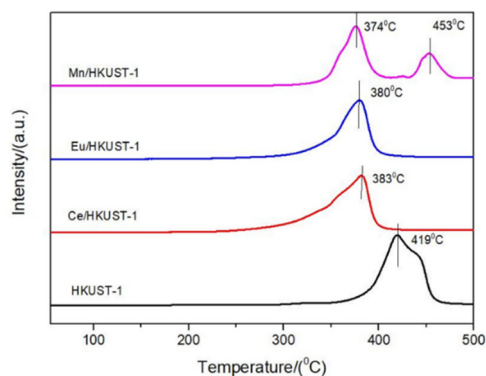
The XRD patterns reveal the crystallographic structures of the catalysts, as shown in Fig. 3. The pattern of HKUST-1 matches well with the simulated one, suggesting the material was prepared successfully with high purity [11]. There were still intact characteristic peaks of HKUST-1 after loading metals, indicating that the main structure was not affected by the impregnation loaded metal salt. In addition, there were no diffraction peaks of metal salts shown in the other three patterns. This means that Ce, Eu and Mn were well distributed and stayed as amorphous. The uniform dispersion of metal element was beneficial to Hg<sup>0</sup> oxidation [15]. The low crystallinities of the modified materials were conducive to the formation of surface defects of the samples and thus providing more reaction sites [16]. Therefore, it was believed that metal modified HKUST-1 can remove Hg<sup>0</sup> much more efficient compared to pristine HKUST-1 [17].



**Figure 3** XRD pattern analysis

#### 3.3.2 H<sub>2</sub>-TPR experiment

It was reported that there was a close correlation between the reduction capacity and catalytic property of the catalyst [18]. Therefore, the H<sub>2</sub>-TPR tests were conducted for four different metal-modified HKUST-1 samples to analyse their relative reducibility. As shown in Fig. 4, these four samples have peaks at different temperatures. Some distinctive peaks were displayed on the pattern. It can be found that two peaks appeared on the sample modified by Mn, at the temperature of 374 °C and 453 °C, which corresponded to the reduction process of Cu<sup>2+</sup> to Cu<sup>+</sup> and Mn<sup>4+</sup> to Mn<sup>3+</sup>, respectively [19, 20]. Compared with pristine HKUST-1, the reduction temperature of Cu<sup>2+</sup> was lower, indicating Mn/HKUST-1 has more oxygen species to improve catalytic oxidation performance. Correspondingly, Mn/HKUST-1 showed higher catalytic capacity than the other three samples due to the lower reduction temperature was favourable for higher catalytic performance [21]. Therefore, the H<sub>2</sub>-TPR results gave explanation for the highest Hg<sup>0</sup> removal efficiency of Mn/HKUST-1 among the four samples.



**Figure 4** H<sub>2</sub>-TPR test

### 3.3.3 Thermogravimetric analysis

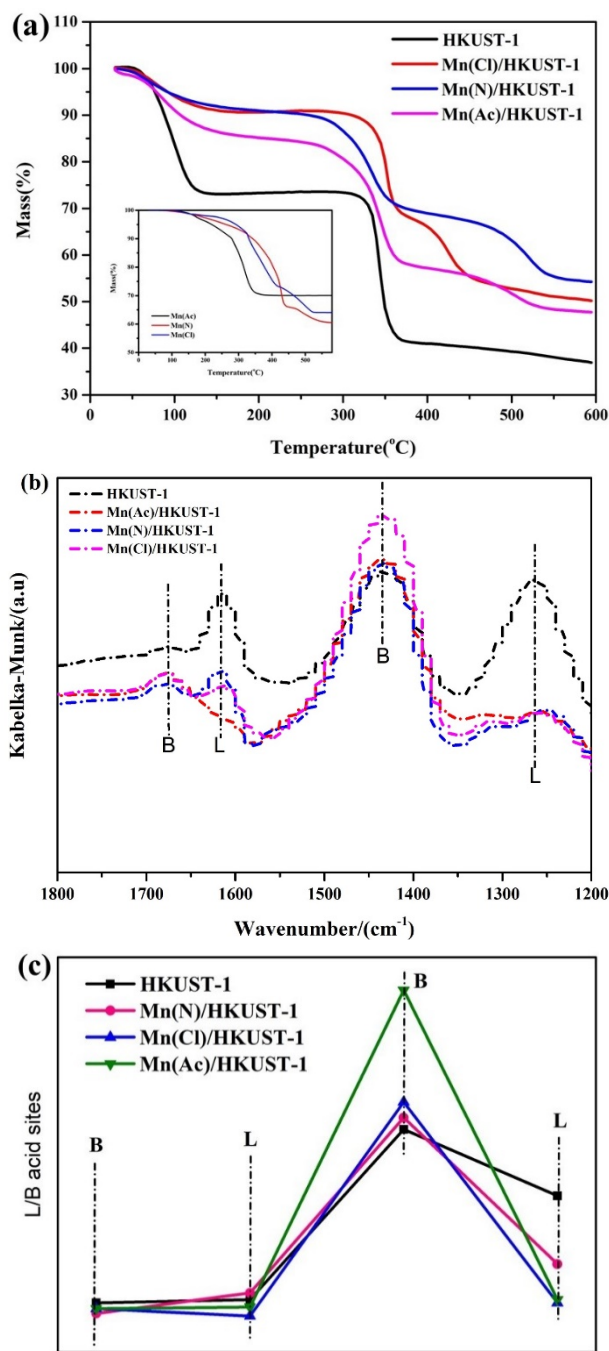
Thermal stabilities of prepared materials were identified by TGA (shown in Fig. 5(a)). Pristine HKUST-1 and modified HKUST-1 experienced similar processes. The first major mass loss before 120 °C was ascribed to the water molecules removal which were physically adsorbed. The second large mass decline after 300 °C was probably due to the decomposition of the HKUST-1 structure [22]. As a whole, HKUST-1 and modified HKUST-1 can keep the stable structure at a relatively high temperature.

The additional weight loss stages of modified HKUST-1 compared to the pristine one was resulted from the decomposition of metal salts when temperature went higher than 350°C. This was in agreement with the TGA curves for different metal salts as shown in Fig. 5(a).

It can be found that HKUST-1 modified by MnCl<sub>2</sub> kept the last stable state at the highest temperature among three modified samples, indicating possessing the highest thermal stability, which is beneficial for Hg<sup>0</sup> removal.

### 3.3.4 In situ DRIFTS

It was reported that Hg<sup>0</sup> could combine with acid gas to form acid sites on the catalyst surface [23]. Therefore, in situ DRIFTS test was carried out to further study the active centres, the results were shown in Fig. 3(b). Some peaks displayed in the range of 1200-1700 cm<sup>-1</sup>. Two peaks centred at 1260 cm<sup>-1</sup> and 1610 cm<sup>-1</sup> were attributed to the Lewis acid sites, and the bands at 1450 cm<sup>-1</sup> and 1670 cm<sup>-1</sup> were Brønsted acid sites [24]. The results showed that the largest amount of Brønsted acid sites presented on Mn(Cl)/HKUST-1 surface, which resulted in the excellent removal performance of Hg<sup>0</sup>. Fig. 3(c) shows the relative amount of Lewis acid sites and Brønsted acid sites corresponding to Fig.3(b). Papers have illustrated that Brønsted acid sites were prior to Lewis sites for Hg<sup>0</sup> removal [25]. Hence, the in situ DRIFTS test also supported the result of the highest Hg<sup>0</sup> removal performance of Mn(Cl)/HKUST-1.



**Figure 5** (a) Thermal stability test (b) In-situ DRIFT experiment (c) B/L acid sites ratio corresponding to (b)

### 3.4 The effect of SO<sub>2</sub> on Mn(Cl)/HKUST-1

It is generally reported that SO<sub>2</sub> causes an inhibition of Hg<sup>0</sup> removal [26]. Therefore, it is vital to study the SO<sub>2</sub> effect on the sample performance, since SO<sub>2</sub> normally exists in the flue gas. MnCl<sub>2</sub> modified HKUST-1, as the optimal Hg<sup>0</sup> removal material obtained in this work were taken as the sample to investigate SO<sub>2</sub> effect on it. A typical temperature of 250 °C was selected to study SO<sub>2</sub> effect, since Hg<sup>0</sup> removal efficiency reached the highest at this temperature. The efficiencies under three different gas conditions were investigated and the results are displayed in Fig. 6.



Under the first condition, the fresh catalyst was heated to 250 °C in N<sub>2</sub> for two hours. During this period, Hg<sup>0</sup> removal rate was found to be maintained at about 70%. Then it can be observed that the removal rate of Hg<sup>0</sup> gradually decreased after 100 ppm SO<sub>2</sub> was added into the gas at 120 min, dropping by 30% within two hours. It can be speculated that this phenomenon was caused by the competitive adsorption of SO<sub>2</sub> and Hg<sup>0</sup> on the surface of the sample. It was also reported that Hg<sup>0</sup> would compete adsorption with SO<sub>2</sub> in the literature [27].

For the second condition, 5% oxygen was added and it was found that the mercury removal efficiency could rise to about 95%. The above activity tests proved that a certain amount of O<sub>2</sub> could enhance the Hg<sup>0</sup> removal efficiency. After stabilizing for two hours, 100 ppm SO<sub>2</sub> was also introduced. It was found that the removal efficiency of mercury still kept stable in the following two hours. This phenomenon indicated that O<sub>2</sub> could not only promote the removal of Hg<sup>0</sup>, but reduce the competitive adsorption of SO<sub>2</sub> [28]. It has been reported that part of SO<sub>2</sub> was converted to SO<sub>3</sub> in the presence of O<sub>2</sub>, which promotes the catalytic oxidation of Hg<sup>0</sup> to some extent, thus reducing the toxicity of SO<sub>2</sub> [29].

In order to further study Hg<sup>0</sup> removal mechanism of Mn(Cl)/HKUST-1 with the presence of SO<sub>2</sub>, the experiment under the third condition was carried out. The only difference between the second condition was that the fresh sample was pre-treated by 100 ppm SO<sub>2</sub> for 2 hours at room temperature before Hg<sup>0</sup> removal test. As can be seen from the figure, the removal efficiency kept the same as the second condition during the first 120 min. However, the removal efficiency began to decrease afterwards. This phenomenon may due to the presence of some fresh Mn-based active sites on the surface of the pre-treated sample, which promotes the removal of Hg<sup>0</sup>. While Mn-based active sites were gradually poisoned with the continuous SO<sub>2</sub> injection. It is interested that the removal rate still reached around 60%, the reason was inferred to the new active sites generation on the surface to facilitate the removal of Hg<sup>0</sup>.

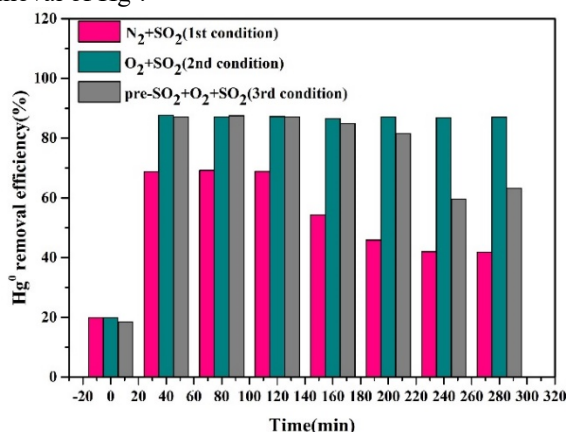


Figure 6 SO<sub>2</sub> effect on Mn(Cl)/HKUST-1 at 250°C

## 4 Conclusion

In conclusion, HKUST-1 and modified HKUST-1 were studied for Hg<sup>0</sup> removal. Among these, Mn(Cl)/HKUST-1 showed the highest Hg<sup>0</sup> removal efficiency of 95%, which

is competitive compared to most reported materials. The In-situ DRIFT result indicated that MnCl<sub>2</sub> promotes Brønsted acid sites generation, thus providing the beneficial factor for Hg<sup>0</sup> removal. It is found that Mn distributed evenly on the HKUST-1 from the XRD result, which is favourable for Hg<sup>0</sup> removal. Moreover, Mn(Cl)/HKUST-1 showed a good SO<sub>2</sub>-resistance in the presence of O<sub>2</sub>. Based on the screening results in this study, Mn(Cl)/HKUST-1 was proved to be a potential Hg<sup>0</sup> removal material. Further studies on the mechanism of Hg<sup>0</sup> removal by Mn(Cl)/HKUST-1 will be carried out in the future progress.

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