



# Combined effects of Ag and UiO-66 for removal of elemental mercury from flue gas

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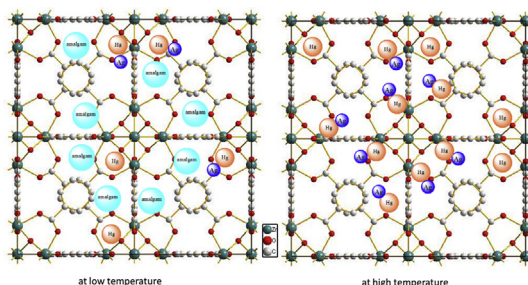
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## HIGHLIGHTS

- Ag nanoparticles were introduced into UiO-66 for Hg<sup>0</sup> removal.
- Ag and UiO-66 presented a synergistic effect.
- The temperature window of UiO-66-Ag was wide.

## GRAPHICAL ABSTRACT



## ARTICLE INFO

### Article history:

Received 22 June 2017

Received in revised form

2 October 2017

Accepted 6 January 2018

Available online 9 January 2018

Handling Editor: Min Jang

### Keywords:

Ag nanoparticles

UiO-66

Mercury

Removal

## ABSTRACT

The zirconium metal-organic framework material UiO-66 was doped with Ag nanoparticles and investigated for the removal of elemental mercury (Hg<sup>0</sup>) in flue gas. Physical and chemical characterization of the adsorbents showed that adding Ag did not change the crystal structure and morphology of the UiO-66. Ag doping can improve the redox activity of UiO-66, and the adsorbent exhibited high thermal stability and surface area. Hg<sup>0</sup> removal experiments indicated that UiO-66 exhibited the higher performance compared with P25 and activated carbon, and the addition of Ag exhibited a significant synergistic effect with the UiO-66, which had highest Hg<sup>0</sup> adsorption capacity (3.7 mg/g) at 50 °C. Furthermore, the Hg<sup>0</sup> removal mechanism was investigated, revealing that Hg<sup>0</sup> is removed by the formation of an Ag amalgam and channel adsorption at low temperature, and through Ag-activated oxygen oxidation and channel capture at high temperature.

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## 1. Introduction

Environmental pollution with mercury has attracted increasing attention in recent years because of its volatility, persistence, bio-accumulation, and neurological toxicity. Coal combustion is

considered to be one of the major anthropogenic mercury sources due to the huge global consumption of coal (Yuan et al., 2012). Most of the mercury in coal is associated with pyrite, and other forms of mercury are organically bound, elemental, and in sulfide and selenide minerals (Gao et al., 2013). During combustion, mercury is released into the exhaust gas as elemental mercury vapor, which may then be oxidized via homogeneous and heterogeneous reactions. Therefore, mercury species emitted from coal-fired flue gas

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are present in three forms: elemental mercury ( $\text{Hg}^0$ ), oxidized elemental mercury ( $\text{Hg}^{2+}$ ), and particle-bound elemental mercury ( $\text{Hg}^p$ ). Generally speaking,  $\text{Hg}^{2+}$  and  $\text{Hg}^p$  are relatively easy to remove from flue gas using typical air pollution control methods, such as wet-flue gas desulfurization (wet-FGD) and electrostatic precipitators (ESPs) (Zhao et al., 2017). However,  $\text{Hg}^0$  is the main mercury component of flue gas (Liu et al., 2011), and is difficult to remove owing to its high volatility and low solubility in water. Furthermore, all Hg species including  $\text{Hg}^0$  can transform into highly toxic methylmercury, which can enter the food chain where it poses a serious threat to human health. Therefore, removal of  $\text{Hg}^0$  from coal-fired flue gas is a very important issue.

Adsorption and oxidation are considered the two main methods for  $\text{Hg}^0$  removal. Many adsorbents and catalysts for  $\text{Hg}^0$  removal have been proposed in recent years, such as active carbon, selective catalytic reduction (SCR) catalysts, metal oxides, and noble metals (Abad-Valle et al., 2011; Li et al., 2011; Wdowin et al., 2014). Morency et al. reported the treated zeolite sorbent can effectively remove mercury from flue gases, and had similar capture rate with activated carbon (Morency, 2002). Malgorzata et al. prepared manganese oxides supported on zirconium dioxide for  $\text{Hg}^0$  removal, and found the rate of  $\text{Hg}^0$  capture on the particle surface area is dependent on manganese content and distribution (Wiatros-Motyka et al., 2013). However, few of them show any clear merit in either conversion efficiency or economy.

Metal-organic frameworks (MOFs) are an emerging class of porous materials comprised of different organic linkers and metal ions that have attracted widespread attention because of their ordered crystalline structures, controllable porosities, large internal surface areas, and countless structural topologies (Xu et al., 2015). Given these unique features, MOFs have motivated research for wide-ranging applications such as in gas storage and separation, drug delivery, and heterogeneous catalysis (Kim et al., 2011). MOFs can also be applied in  $\text{Hg}^0$  removal because of their high surface areas and high volume fractions of active metal (Shahat et al., 2013).

However, weak thermal stability is a major disadvantage of MOFs. The zirconium MOF (UiO-66) is recently synthesized and shows high chemical and thermal stability. Consequently, several investigations into its functionalization and application in catalysis have been reported (Cao et al., 2014). In recent years, there have been several reports on Zr(IV)-based MOFs for  $\text{Hg}^0$  removal. Zhang et al. synthesized phenyl bromine-appended MOFs and applied them to high-efficiency  $\text{Hg}^0$  removal from simulated flue gas (Xiao et al., 2016). Saleem et al. investigated post-synthetically  $\text{NH}_2$ -modified UiO-66 for the adsorptive removal of heavy metal ions including  $\text{Hg}^{2+}$  from aqueous solution, and showed that  $-\text{NH}_2$  functionalization markedly improved its metal removal efficiency (Saleem et al., 2016). Thus, UiO-66 could become a highly desirable and promising material or support for  $\text{Hg}^0$  removal.

As a unique feature, Hg atoms can dissolve certain metal atoms to form amalgams, and amalgams decompose to release mercury to the gas phase at higher temperatures (Luglie et al., 2005). Given this feature, Ag has been widely studied as an adsorbent in  $\text{Hg}^0$  removal due to its efficiency and low cost (Liu et al., 2008; Yuan et al., 2012). Furthermore, Ag can enhance the oxidizing ability of some metallic oxides for  $\text{Hg}^0$  removal (Zhao et al., 2014). However, Ag atoms tend to coalesce into oligomers, which themselves progressively grow into larger clusters and eventually precipitate during preparation and calcination. Thus, it is necessary to seek a suitable carrier with large surface areas to provide highly dispersed Ag nanoparticles.

In this study, Ag and UiO-66 were combined to form an adsorbent for the removal of  $\text{Hg}^0$  from flue gas. The physical and chemical properties of the adsorbents, as well as their  $\text{Hg}^0$  removal efficiencies, were investigated. In addition, the mechanism involved in  $\text{Hg}^0$  removal was discussed.

## 2. Experimental section

### 2.1. Materials

All chemicals used for adsorbent preparation were of analytical grade. Zirconium tetrachloride ( $\text{ZrCl}_4$ , >99%), 1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ , 99%), and N,N'-dimethylformamide (DMF, 99.5%) were purchased from Aladdin Co. (Shanghai, China); glacial acetic acid ( $\text{CH}_3\text{COOH}$ , >99.5%) and silver nitrate ( $\text{AgNO}_3$ , >99.8%) were purchased from Shanghai Ling Feng Chemical Reagent Co., Ltd. (Shanghai, China). Sodium borohydride ( $\text{NaBH}_4$ , 96%) was purchased from Sinopharm Chemical Reagent Co., Ltd.

### 2.2. Preparation of adsorbents

The synthesis of UiO-66 was performed using a modified procedure as described in the literature (Cao et al., 2014). Standard synthesis of UiO-66 was performed by dissolving  $\text{ZrCl}_4$  (0.53 g, 2.27 mmol) and  $\text{H}_2\text{BDC}$  (0.35 g, 2.11 mmol) in DMF (100 mL) at room temperature. Acetic acid (3.5 mL) was then added to the mixture. The obtained mixture was sealed and placed in a pre-heated oven at 120 °C for 24 h. Crystallization was carried out under static conditions. After the solution was cooled to room temperature in air, the resulting solid was filtered and washed with DMF three times, and finally dried at 150 °C in an oven for 24 h. An amount of UiO-66 was dissolved in the solution of  $\text{AgNO}_3$ , and the molar ratio of Ag and Zr was 0.05. Then the solution of  $\text{NaBH}_4$  (0.1 mol/L) was slowly added to the Ag and UiO-66 solution, which was finally dried at 150 °C in an oven for 24 h. The prepared adsorbent was labeled UiO-66-Ag. Because the activated carbon and P25 was a commonly used adsorbent/catalyst carrier, adding silver onto activated carbon and P25 were selected for performance comparison, marked as: C-Ag and P25-Ag.

### 2.3. Removal activity evaluation

The removal activity was evaluated in accordance with the previously described criteria (Zhao et al., 2015), including a simulative gas formulating system and reaction device (SHKD-1, Tongsheng Lida Digital Technology Co., Ltd., Beijing), a cold vapor atomic absorption spectrometer (CVAAS), and an online data acquisition system, shown in Fig. 1. The reaction system included eight mass flow controllers to adjust the simulated flue gas compositions and a fixed-bed reactor. The adsorbent was packed into the quartz tube, which was plugged with quartz wool. An  $\text{Hg}^0$  permeation tube was used to generate  $\text{Hg}^0$  vapor carried by pure  $\text{N}_2$ , which was then introduced to the inlet of the gas mixer. A cold vapor atomic absorption spectroscopy (CVAAS) analyzer was employed as an online continuous detector that could only detect  $\text{Hg}^0$ . The concentration of  $\text{Hg}^0$  was measured using Lumex RA 915+. At the beginning of each test, the gas containing  $\text{Hg}^0$  was first passed through a bypass without adsorbents to determine the baseline. When the concentration of  $\text{Hg}^0$  had fluctuated within  $\pm 5\%$  for more than 30 min, the gas was diverted to pass through the fixed-bed reactor containing the adsorbents. The amount of adsorbents were 20 mg and the gas flow rate was  $500 \text{ mL min}^{-1}$ , corresponding to a space velocity (SV) of  $2.13 \times 10^5 \text{ h}^{-1}$ , using  $\text{N}_2$  as carrier gas, and the  $\text{O}_2$  content was 4%. The concentration of  $\text{Hg}^0$  was approximately  $250 \mu\text{g/m}^3$ .

The  $\text{Hg}^0$  removal efficiency and adsorption capacities were calculated according to Eqs. (1) and (2):

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