Journal of Hazardous Materials 320 (2016) 556–563

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

UiO-66 and its Br-modified derivates for elemental mercury removal

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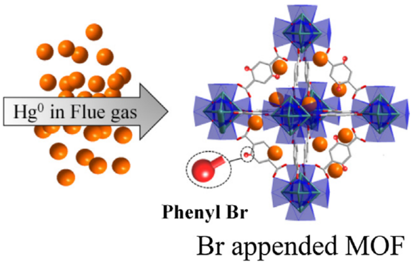
HIGHLIGHTS

- Metal-organic frameworks were prepared and used for elemental mercury adsorption.
- The phenyl bromine appended on the UiO-66 was the main chemisorption site for Hg^0.
- The appended phenyl bromine showed high stability in leaching experiment.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 March 2016
Received in revised form 25 July 2016
Accepted 15 August 2016
Available online 16 August 2016

Keywords:
Metal-organic frameworks
Elemental mercury removal
Phenyl bromide functionalization
Bromine stability
Flue gas

ABSTRACT

Phenyl bromine-appended metal-organic frameworks (Br-MOFs) were synthesized and applied in elemental mercury (Hg^0) removal from simulated flue gas, considering the stability of bromine on the materials at the same time. The techniques of PXRD, nitrogen adsorption, TGA and XPS were used to characterize the materials. Phenyl bromide on the MOFs was the main active site for Hg^0 capture. The optimal Br-MOF showed high Hg^0 removal efficiency of more than 99% for 48 h at 200 °C, whereas the efficiency of un-functionalized MOF and conventional bromine impregnated active carbon dropped to 59.8% and 91.2% within 5 h, respectively. The crystalline integrity of the Br-MOF was maintained after Hg^0 adsorption. Br-MOF exhibited enhanced Hg^0 removal efficiency when SO_2 was introduced to the flue gas. However, exposure Br-MOF to flue gas with steam resulted in low Hg^0 removal efficiency. Bromine leaching experiments proved that Br-MOFs have high bromine stability over the Hg^0 adsorption process, avoiding the possible bromine pollution caused by the conventional bromine impregnated adsorbents. All of these results demonstrated the phenyl bromine-appended MOFs to be potential Hg^0 adsorbent regarding its high Hg^0 capture efficiency and low environmental risk.

1. Introduction

Mercury is an important environmental pollutant that aroused worldwide concern due to its volatility, persistence and bioaccumulation in the ecosystem. Anthropogenic mercury emissions accounts for approximately 60% of the total atmospheric emissions and coal-fired power plants are considered to be the largest source of anthropogenic mercury emissions [1,2]. Mercury in coal combustion flue gas exists in three forms including oxidized mercury (Hg_{oxi}), particle-bound mercury (Hg_p) and elemental mercury (Hg^0). Among them, Hg_{oxi} can be removed by wet flue gas desulfurization units, and Hg_p can be effectively collected by particulate control devices units such as fabric filtering and electrostatic precipitation [3,4]. However, due to the high volatility and low solubility in water, Hg^0 in flue gas is very difficult to be captured through conventional pollution control technologies. Once emitted to the atmosphere, Hg^0 has an atmospheric residence time of approximately one year [5].

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http://dx.doi.org/10.1016/j.jhazmat.2016.08.039
0304-3894/

Among various Hg^0 removal methods, adsorption is one of the most promising pathways because of its simplicity and efficiency [6,7]. Various adsorbents have been studied for Hg^0 removal from flue gas [8–13]. Since the Hg^0 removal efficiencies of the virgin materials are undesirable, active additives such as halogens and sulfur species are typically doped to the surface of the sorbents to improve their Hg^0 capture capabilities [7,14–17]. Bromine impregnated sorbent was found very effective in Hg^0 adsorption from flue gas [16]. However, the impregnation functionalization technique normally creates chemistries on the sorbent in mobile phase [18]. The unstable chemistries could loss easily during the application process as a result of deleterious interactions within the substrate, leading to poor aging characteristics [18]. Yao et al. developed activated carbon fibers with covalently incorporated bromine groups, which showed extremely stable performance in a long Hg^0 adsorption experiment [19]. Another issue that deserves concern for the bromine impregnated Hg^0 adsorption is the potential bromine hazards to the environment [11]. World Health Organization (WHO) promulgated strict bromine emission criterion in drinking water [20], bromine in the environment also relates to the ozone consumption reaction in the stratosphere [21]. So it is essential to develop Hg^0 adsorbents with stable bromine considering the disposal of the used sorbents.

Metal-organic frameworks (MOFs) are a class of porous, crystalline material constructed from metal cluster nodes and organic ligands. MOFs have been studied and applied in many fields such as separation, catalysis and gas adsorption [22,23]. Besides the advantage of texture properties such as high porosities, specific surface areas and versatility of structure, the most attractive feature of MOFs concerns the modulation of their chemical properties. Functional groups could be stably incorporated into a MOF and react with incoming molecules [24–26]. By reacting $ZrCl_4$ with 2,5-dimercapto-1,4-benzenedicarboxylic acid, thiol (-SH) functions was installed in UiO-66. It was found that the thiol-laced framework showed excellent adsorption ability for both Hg (II) from aqueous solutions and Hg in vapor phase [27,28]. Halogen functionalized UiO series have been well studied in the previous literatures [29,30]. Therefore, we assumed bromine modified MOFs have the potential to be effective and stable Hg^0 capture sorbents. Among kinds of MOFs, zirconium-based UiO-66 framework $(Zr_6O_4(OH)_4(C_6H_4(CO_2)_2)_6(DMF)_x(H_2O)_y)$ was selected as substrate in this work because of its thermal stability and chemical stability [31,32]. Even though the usage of modified MOFs for gases adsorption [28,29,33,34] or Hg^{2+} adsoption [35] have been studied in numerous researches, the application of bromine modified MOFs in Hg^0 adsorption from simulated flue gas has not been reported until now.

In this work, phenyl bromine-appended UiO-66 series were synthesized via solvothermal synthesis. The performance of the phenyl bromine-appended MOF as Hg^0 adsorption was evaluated at different temperatures and flue gas components conditions. The stability of bromine on the fresh and exhausted phenyl bromine-appended MOFs was tested through leach experiments and compared with traditional bromine impregnated Hg^0 adsorbents.

2. Experimental

2.1. Preparation of the materials

All of the reagents were purchased from Beijing J&K Co., Ltd. (Beijing, China) and were used without further purification. UiO-66 and bromine-appended UiO-66 series were synthesized according to the method reported by Biswas and co-workers with some amendments [29]. The frameworks were synthesized from metal ion donor zirconium tetrachloride ($ZrCl_4$) and three different functional organic linkers (H_2BDC-X, BDC: 1,4-benzenedicarboxylate, X = H, Br, Br_2) in polar solvent *N,N*-dimethylformamide (DMF), denoted as UiO-66, Br-UiO-66 and 2Br-UiO-66, respectively. The specific methods are as followed. $ZrCl_4$ (47.8 mg, 0.205 mmol) and acetic acid (2.05 mmol) were dissolved in 8 mL of *N,N*-dimethylformamide (DMF). H_2BDC-Br_2 (66.4 mg 0.205 mmol) was then added into the solution. After 15 min's sonication, the mixture was poured into a 50 mL Teflon-lined high-pressure autoclave and heated at 120 °C in an oven for 24 h. After crystallization, the autoclave was naturally cooled down to room temperature and the resultant powder was collected by centrifugation at 400 rpm for 15 min. Then the resulting powder was immersed in 50 mL DMF and shook at 60 °C for 24 h in order to remove unreacted monomers. Removal of DMF from the pores was achieved by washing the materials with volatile solvent dichloromethane at 60 °C for 36 h. After cooling, this mixture was centrifuged and excess solvent was removed under vacuum at room temperature for 12 h. The obtained pale yellow powder was denoted as 2Br-UiO-66. UiO-66-Br and UiO-66 were synthesized with the same procedure as above described but replaced H_2BDC-Br_2 to H_2BDC- Br_1 or H_2BDC.

The UiO-66 and active carbon (AC) were also functionalized by impregnation method for comparison with the 2Br-UiO-66 and Br-UiO-66 in the Hg^0 capturing and bromine leaching experiments. 17.37 mL KBr solution (0.2 mol/L) and 1 g UiO-66 or AC solid were mixed under vigorous stirring at room temperature for 3 h. Then the mixture was dried in an electric oven at 80 °C for 12 h, the obtained materials were denoted as 2KBr-UiO-66 and 2KBr-AC, respectively. The bromine loaded on the sorbents was designed as 27.79 wt% in this experiment reference to the bromine content of 2Br-UiO- 66 which was determined by XRF spectrometry.

2.2. Mercury removal measurement

All the adsorption experiments were performed with a bench scale Hg^0 adsorption test system, which consisted of a simulated flue gas mixer, a fixed bed reactor, a digital temperature controller and an Hg^0 monitoring device (Fig. 1). Nitrogen was used as the carrier gas to introduce Hg^0 vapor into the gas mixing chamber from an Hg^0 permeation tube which was sealed in a U-shaped tube and immersed in water bath at 44 °C. The oxygen in the simulated flue gas was set at 5%. The sulfur dioxide and moister content in the simulated flue gas were set at 0.01% and 3%, respectively. To avoid mercury condensation, heating belts were used to keep the silicone pipelines warm (120 °C). The simulated flue gas was preheated and mixed in a mixer and then passed through the fixed bed where sorbent was laid in. As shown in Fig. 1, when "a-b" air holes of the valve were connected, the flue gas bypassed the reactor and the inlet Hg^0 concentration was measured. When "a-c" air holes of the valve were connected, the flue gas pass through the adsorbent and the outlet Hg^0 concentration was measured. The Hg^0 removal efficiency defined as η could be calculated by Eq. (1).

$$\eta = (C_{in} - C_{out})/C_{in} \times 100\% \quad (1)$$

where C_{in} and C_{out} represent the Hg^0 concentration at the inlet and outlet of the reactor, respectively. The Hg^0 concentrations were measured by H11-QM201H mercury monitoring system (Qing'an Co. LTD, China). The mass of the sorbent used in the test was 200 mg of 2Br-UiO-66, 260 mg of Br-UiO-66 or 320 mg of UiO-66 (with the bulk volume of 1 mL), and the gas flow rate corresponded to a gas hourly space velocity (GHSV) of approximately 50 000 h^{-1}.

2.3. Bromine leaching procedure

The bromine leaching procedure was carried out according to the method reported by Bisson et al. [11]. 50 mg of dry sorbent was mixed with 30 mL of ultrapure water in a 50 mL polypropylene centrifuge tube. The mixture was agitated in an orbital shaker-water