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Full Length Article

Experimental and theoretical studies for the mechanism of mercury oxidation over chlorine and cupric impregnated activated carbon

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ABSTRACT

Experimental and theoretical studies were conducted to investigate the roles of cupric and chloride in $CuCl_2$ impregnated activated carbon for mercury removal. Solution impregnating was used to add cupric, chlorine and copper chloride on activated carbon respectively. Experiment results show that combination of chlorine and cupric possesses stable and high efficiency in mercury removal. In $CuCl_2$ impregnated activated carbon, besides chlorine existence promotes the mercury oxidation and adsorption, dispersed cupric could accelerate the process and provide adsorption sites for oxidated mercury. Theoretical calculations based on density functional theory (DFT) were carried out to elucidate the mechanism of mercury adsorption and oxidation. Models of CuO and $CuCl_2$ doped on monolayer graphene were established to simulate the sorbents surfaces. There is a weak physisorption for Hg adsorption on CuO doped sorbent, but for $CuCl_2$ doped sorbent, it could oxidate mercury and generated $HgCl_2$ with the energy barrier of 121.83 kJ/mol. More than that, the correlation between $CuCl_2$ doped sorbent and CuO doped sorbent pretreated with HCl has been graphene reflected in simulation results. Experimental and theoretical results both evidenced that the cooperation of chlorine and cupric is favorable to remove mercury.

1. Introduction

Mercury contamination has caught great attention because of the bioaccumulation and damage to human [1]. Compared with the natural mercury release, anthropogenic mercury emission has caused many problems. As the Minamata Convention coming into effect, reducing mercury emission becomes a world-wide errand. Chinese mercury emission accounts for about 40% of world emission annually and the coal-combustion power plants is the main source of mercury emission in China. The State Environmental Protection Administration of China (SEPA) has put forward strict rules to control the mercury emission in thermal power plants. These power plants are mandated to cut down the amount of mercury release under the emission standard of 0.03 mg/m^3 in exhaust gas. Effective techniques and methods are demanded in dealing with the mercury in flue gas. Mercury removal greatly depends on its species in the post-combustion flue gases. Compared to the typical air pollution control devices (APCDs), catalytic oxidation and sorbent inject are useful ways to convert Hg^0 to Hg^{2+} and Hg^p [2]. For this purpose, activated carbon inject (ACI), which is a mature technology, has been widely used [3]. Considering the high cost and low efficiency of activated carbon are hindrances in industrial application, exploring economical and effective sorbents will satisfy the industrial demand.

It has been reported that using metals or metal-oxides to replace activated carbon seems to be a good way. Metals and metal-oxides are proved to have excellent capability to oxidate and adsorb mercury in many researches [4–6], but the high efficiency cannot offset the price. On the other hand, chemical modification can improve the removal efficiency and enlarge the adsorption capacity of activated carbon in capturing mercury. Impregnated with halogen, sulfur or acid will increase the groups and active sites on the surface of activated carbon [7–9].

Many researchers have found that the combination of metal and halogen provides oxidative factors as well as Hg^{2+} adsorption sites [10–12]. Chlorine in metal chlorides is the oxidant of mercury oxidation and metal existence will accelerate the process. Through the various researches about metal halide modified sorbents, it was found that $CuCl_2$ enhanced the sorbents' performance greatly in oxidation and adsorption of Hg^0 [13–15]. Joo-Youp Lee and Sang-Sup Lee et al. [16–18] have intensively studied the $CuCl_2$ doped on diverse substrates

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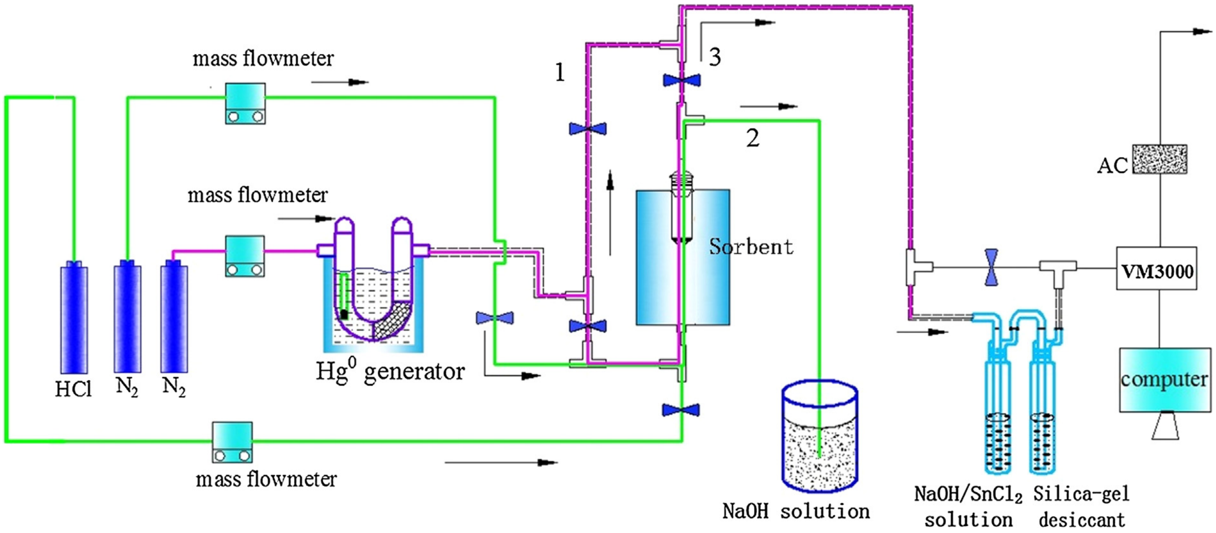

Fig. 1. The schematic diagram of experimental system.

(such as AC, clay) in different ways. $CuCl_2$ impregnated sorbents have shown the strong ability to oxidate mercury in complex conditions even at the temperature of 300 °C. What's more, Moon Hyeon Kima and Sung-Won Ham et al. [13] have found that $CuCl_2/TiO_2$ catalysts could reduce Hg^0 and NO at the same time. Also many researches proclaimed that $CuCl_2$ showed excellent anti-sulfur performance when it was used for removing gas element mercury at high concentration of SO_2 [19]. $CuCl_2$ sorbents are potential to meet the application requirements of wide range temperature and multiple flue gas components.

Among these substrates, carbon substrate can effectively adsorb oxidated mercury while other non-carbon substrates seem to be less effective. Modifying carbon substrates with $CuCl_2$ will cut down metal consumption and highlight the superior physical characteristics of carbon, which also can prevent the escape of adsorbed mercury. The high efficient and low cost are both benefit for the application of industry. It has been declared that Cu has great activity in mercury removal in the forms of copper metal or cupric oxide [20], but the effect of dispersed copper on activated carbon has not been stated clearly. It is essential to have an insight into the evolution of mercury oxidation and adsorption on the Cu modified carbon. Additionally, in our previous research, we discovered that HCl in the flue gas has vital function in mercury removal when ferric existed [21]. Similarly, the mechanism of mercury oxidation is needed to be elucidated when cupric and chlorine both exist over the carbon surface. Carbon substrates like biological coke and coal char have been used for mercury removal because of the easy access, while the oxygen functional groups in biological coke and sulfur content in coal char have impact on mercury oxidation and adsorption [22]. In order to reduce the impact of these impurities on mercury oxidation and adsorption, the commercial activated carbon with high purity was chosen as the substrate, which has good physical properties and is suitable for mechanism research.

To clarify the role of chlorine and cupric effect on mercury oxidation, activated carbon based sorbents impregnated with KCl, $Cu(NO_3)_2$ and $CuCl_2$ were synthesized to represent chlorine, cupric and coexistence respectively. Brunauer-Emmett-Teller (BET) was conducted to measure surface properties after the modification. Furthermore, for searching the interaction between cupric and chlorine, the effects of cupric on mercury oxidation with or without chlorine have been discussed. Temperature programmed decomposition desorption (TPDD) were carried out to determine the mercury species on sorbents surface, which helps to the understanding about the formation and adsorption of mercury species. X-ray photoelectron spectroscopy (XPS) was used to detect key element states varies during the reactions. In addition, the model of CuO and $CuCl_2$ embedded activated carbon had been built to elucidate the mercury oxidation mechanism based on the density functional theory (DFT).

2. Experiment and apparatus

2.1. Sorbent preparation

The powder activated carbon (AC, Sinopharm Chemical Reagent Co.,Ltd) was washed to remove the ultrafine particles and dried at 105 °C overnight. To keep the same concentration of chlorine and cupric, 0.2 mol/L $CuCl_2$, 0.2 mol/L $Cu(NO_3)_2$, 0.4 mol/L KCl (reagents are all from Sinopharm Chemical Reagent Co., Ltd, analytically pure) solutions were prepared respectively. 2 g AC was added into each 50 ml solution. After the ultrasonic oscillation for 30 min and maintaining at 25 °C for 6 h, samples were filtered and dried at 105 °C for 12 h. With the completion of these steps, sorbents were kept dry and marked as Cu—AC—Cl, Cu—AC, AC—Cl. For examining the effect of Cu load content, a series of sorbents treated with different concentrations of $CuCl_2$ solution were prepared in the same way. The added solution concentrations were set as 0.05 mol/L, 0.5 mol/L and 1 mol/L and the series of sorbent were marked as xCu—AC—Cl (x represents the concentration of solution, such as 0.05Cu—AC—Cl means the sorbent impregnated by 0.05 mol/L $CuCl_2$ solution).

A pretreated adsorbent was obtained to figure out the probable relevance between Cu and Cl, which is obtained by treating Cu—AC in the following way: under the flow of 30 ppm HCl in N_2 at 150 °C for 2 h and flushed with pure N_2, 50 mg Cu—AC was treated each time in the following apparatus. The pretreated sorbent was signed as HCl/Cu—AC.

2.2. Apparatus and procedure

As shown in Fig. 1, the experiment system contains four parts: gas feeding, Hg^0 generation (Dynacal, VICI Metronics), reaction furnace and Hg^0 online monitor (VM3000, Mercury Instruments, Germany). The pipes were installed by teflon tube enwrapped with heating tape to avoid mercury condensation. Total inlet gas flow was controlled at 1.2 L/min with 45 ± 1 μg/m^3 Hg^0 and 50 mg sorbent was put in the quartz tube for each experiment. Various experiments were designed to figure out the probable reaction paths among Cu, Cl and Hg^0 and each experiment lasted for 2 h. The real time Hg^0 removal efficiency and total removal efficiency are defined asη_1 and η_2:

$$\eta_1 = \frac{C_{in}-C_{out}}{C_{in}} \times 100\% \tag{1}$$