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Mercury capture by manganese modified copper oxide

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ABSTRACT

To increase elemental mercury removal efficiency of CuO without HCl gas, the Mn-modified CuO samples were proposed. In this work, four doping ratios of Mn to CuO were fabricated by a hydrothermal synthesis method. The surface morphologies, crystalline structures and chemical states of as-prepared sorbents were characterized by scanning electron microscope (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS), respectively. The results showed that all the Mn-modified samples contained the CuMnO₂ phase with different contents. The Hg⁰ removal experimental results indicated that the Mn-modified CuO sorbents had the higher elemental mercury removal efficiency than pure CuO. The pseudo-first-order kinetic model fitted well to the adsorption experimental data. The CuMnO₂ content in sorbents had a positive effect on mercury capture. We speculated that CuMnO₂ acted as a dominant factor for the mercury removal capacity of Mn-modified CuO sorbents. The high valance Mn oxidized the elemental mercury to oxidized mercury. Moreover, CuO can re-oxidize the low valance Mn to the high valance, resulting in the further increase in Hg⁰ removal efficiency.

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1. Introduction

Mercury control technique has considerably attracted international attention due to its toxicity and persistent bioaccumulation [1,2]. Coal-fired power plant is classified as the greatest anthropogenic source of mercury emission [3]. Mercury exists three forms in coal-fired flue gas: elemental (Hg⁰), oxidized (Hg²⁺), and particle-bound (Hg^p). Among these mercury species, Hg²⁺ and Hg^p are relatively easy to remove from flue gas by using typical air pollution control devices (APCDs), such as ESPs (Electrostatic Precipitators) and wet-FGD (Flue Gas Desulfurization). Elemental mercury (Hg⁰), however, is difficult to be captured, because it is insoluble in water and chemical inertness [4].

Copper, a transition metal, has special catalytic effects for mercury oxidation due to its ability to store/release oxygen via the redox shift between Cu²⁺ and Cu⁺. Previous studies [5–8] showed that CuO or CuCl₂ has very strong mercury capture capacity in HCl gas, because Cu²⁺ can make HCl generate much active Cl which can oxidize mercury. Hence, CuO is regarded as a potential catalyst for Hg⁰ removal under high-concentration HCl environment. However, flue gas from coal-fired power plant in China only has a low concentration of HCl gas. Hence, fabricating an effective catalyst to oxidize mercury in few HCl or no HCl gas becomes very important. Lattice oxygen has been previously suggested as a versatile oxidant

for mercury in a Mars–Maessen mechanism [9], and oxides such as manganese oxide were shown to have good capacities for mercury in various gas streams [10–12]. Many pre-treatments for sorbents were performed to avoid the effect of natural flow of sorbent in order to improve the adsorption capacity [13,14]. The catalyst contained manganese-based oxides also has well performance for mercury removal [15]. Al₂O₃ [16] and TiO₂ [17] were employed as catalyst supports to disperse MnO_x for guaranteeing the high utilization of Mn active sites [11]. Co–MnO_x [18], Ce–MnO_x [10], graphene oxide [19], and some other elements are used to modify MnO_x. Furthermore, manganese oxide also has an enhancing effect on Hg⁰ oxidation in the presence of NO_x [11], some special crystal structure provides a higher catalytic oxidation performance.

In this work, we modified copper oxide by manganese via a hydrothermal synthesis method under different ratios of Mn to Cu elements. The effect of Mn on mercury capture of CuO was evaluated by adsorption experiments.

2. Experimental

2.1. Synthesizing Mn-modified CuO nanoparticles

Typical hydrothermal synthesis method was used to synthesize Mn-modified CuO nanoparticles in this work. For comparison, the pure CuO nanoparticles were also fabricated. Firstly, CuO·3H₂O and MnSO₄·H₂O powders were placed in 30 ml deionized water with magnetic stirring, then 10 ml 2.5 mol/l NaOH was dropped into this solution. After 20 min continuous stirring, the solution

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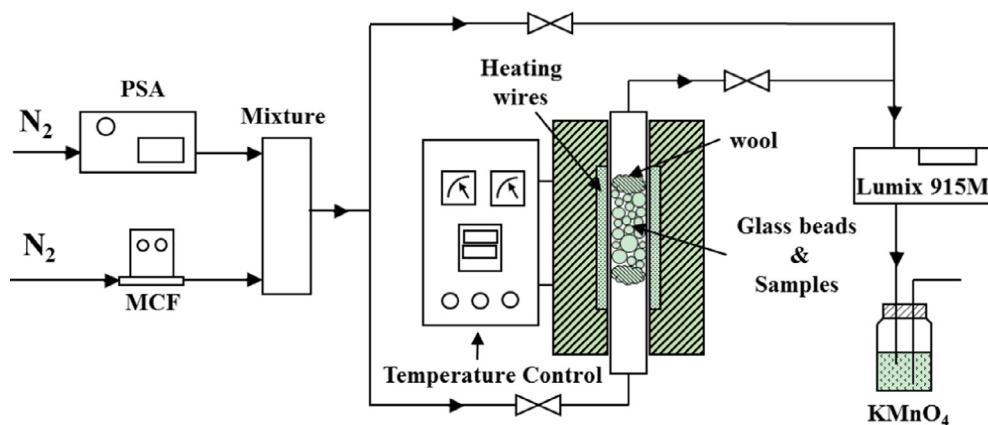


Fig. 1. Schematic diagram of the experimental setup of mercury adsorption.

was warmed at 130 °C for 15 h in an electric oven. Thereafter, the nanoparticles were collected and then washed by deionized water and ethanol for three times. Finally, these nanoparticles were dried at 80 °C for 12 h. Four weigh ratios of $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ to $\text{CuO} \cdot 3\text{H}_2\text{O}$ were designed to 0 wt%, 20 wt%, 40 wt%, and 60 wt%, and the total mass of each sample was set as 500 mg. All the drugs were purchased from Guoyao Chemical Reagent Co. Ltd. All chemicals were analytical grade.

In order to describe clearly and easily, all the samples were denoted as Samples I–IV, respectively. The as-fabricated samples were characterized by scanning electron microscope (SEM) (Phillips XL-30 FEG/NEW), X-ray diffraction (XRD) (Bruker D8 Advance, Germany), and X-ray photoelectron spectroscopy (XPS) (PHI 5000C ESCA System).

2.2. Adsorption tests

Fig. 1 shows the schematic of the adsorption setup. The high pure nitrogen gas with a flow of 200 ml/min passed through mercury generating device (PSA 10.536 SIR GALAHAD II, UK) to carry the Hg^0 vapor and then mixed the other N_2 gas with the flow of 600 ml/min in the mixture. The Hg^0 inlet concentration was controlled around $50 \mu\text{g}/\text{m}^3$. Then, the mixed gas flowed through the fixed-bed reactor where the sample was placed in an adsorption quartz tube with 6 mm inner diameter. The temperature was set at 120 °C, which was equal to the temperature of flue gas emitted from coal-fired power plant. The Hg^0 vapor concentration was measured by a mercury analyzer (Lumix 915M). The remaining gas was absorbed by KMnO_4 solution. Finally, it should point out that, in a real flue gas containing SO_2 , SO_3 , NO , and NO_2 , there is the possibility of sorbent poisoning through formation of manganese sulfates or nitrates [9,20], and this will be examined in future work.

Here, Hg^0 removal efficiency (η) was used to evaluate the mercury capture capacity of sample, which was calculated by the following formula:

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

Where Hg_{in}^0 and Hg_{out}^0 represent the mercury concentrations at the inlet and outlet of the fixed-bed reactor, respectively.

3. Results and discussion

The surface morphologies of the samples, as shown in Fig. 2, were characterized by SEM. Fig. 2(a) indicated that Sample I had a nanosheet structure and the average thickness was 50–60 nm.

For the Mn-modified CuO , the nanosheet particles became smaller with increase of Mn weight ratio, as shown in Fig. 2(b)–(d). Additionally, Fig. 2(d) suggested that when the $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ weight ratio increases to 60%, the original nanosheet changed to the cubic nanoparticles.

Fig. 3 showed the XRD pattern of each sample. For Sample I, the XRD curve was readily indexed to the phase of tenorite (JCPDS card No. 72-0629). As compared to Sample I, Sample II generated two small peaks of crednerite (JCPDS card No. 75-1010), indicating that manganese mixed into CuO structure. Thus the new component CuMnO_2 was formed and coexisted with CuO . For Sample III, all peaks were consistent with the phase of crednerite. This suggested that a relative highly pure CuMnO_2 was fabricated. Sample IV had many phases and became a mixed material, including CuO , MnO_2 , CuMnO_2 , and $\text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4$. MnO_2 growth indicated that elemental Mn concentration reached to a saturated level to modify copper oxide. Furthermore, the phase of copper oxide formed again, although its XRD peak was very small. Thus, high Mn concentration was not beneficial for fabricating pure CuMnO_2 . The XRD patterns showed that the CuMnO_2 content of Sample IV was considerably larger than that of Sample II, indicating that the Mn concentration plays a crucial role in fabricating CuMnO_2 .

Fig. 4 showed the Hg^0 removal efficiency of each examined sample. The measured data showed that all the Mn-modified CuO samples had the higher Hg^0 removal efficiencies than pure CuO . The average Hg^0 removal efficiencies of Samples I–IV were 14.86%, 20.05%, 72.46%, and 60.15% after 3 h adsorption time, indicating that manganese is favorable for the mercury removal due to its strong oxidizing ability. However, the manganese content considerably affected the mercury capture. The highest Hg^0 removal efficiency was Sample III, rather than Sample IV that had the highest manganese content. Hence, some components maybe determine the enhanced mercury capture. As mentioned above, the XRD patterns indicated that Sample III had the highest pure CuMnO_2 . Meanwhile, Samples II and IV also contained the relatively low content of CuMnO_2 component. The results indicated that the higher content of CuMnO_2 the catalysts had, the higher mercury removal efficiency they had. Hence, we speculated that the CuMnO_2 would play a vital role on the improvement of the Hg^0 removal efficiency for Mn-modified CuO sorbent.

The Lagergren pseudo-first-order [21] and Lagergren pseudo-second-order [22] models were widely used in estimation of adsorption kinetics. The pseudo-first-order model is described as:

$$\frac{dC}{dt} = -K_1(C_m - C_s) \quad (2)$$

Where K_1 is the constant of speed rate of first-order model (h^{-1}), C_m (mg/g) is the amount of mercury adsorption at equi-

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