Mercury Capture Using Recyclable Magnetosphere from Coal Combustion Fly Ash

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INTRODUCTION

Mercury, as a global threat to human health and environment, has raised worldwide attention in recent years. Coal burning is one of the most significant anthropogenic source of mercury emissions to the atmosphere. Different technologies for Hg$_0$ removal have being investigated, such as catalytic oxidation, and sorbent injection, etc. Among these available technologies, the common limitations are the recovery and recycle of spent sorbent / catalyst, the disposition of mercury containing in the spent sorbent, the high operating cost, etc. It is therefore extremely attractive to develop regenerable magnetic sorbent / catalyst to overcome these limitations.

Several researches have focused on the development and application of magnetic mercury sorbents. Dong et al. published a very comprehensive study on the development of magnetic multi-functional nano composites (MagZ–Ag), which presented excellent mercury capacity and recyclability. Recently, some studies indicated that fly ash can both adsorb and oxidize elemental mercury, and several studies have focused on the influence of magnetospheres present in fly ashes on mercury oxidation. As the by-products in coal combustion, the low-cost magnetospheres will present huge potential application in Hg$_0$ removal. More attractive, because of their magnetism, the spent magnetospheres could be easily separated from fly ash by magnetic separation to recycle after mercury capture. However, the Hg$_0$ removal capacity over different magnetospheres may be significantly varied, which are closely related to their physical properties, chemical composition, and mineral components. Therefore, assessing and improving the Hg$_0$ removal capacity of magnetospheres is essential. The combination of active substance and magnetosphere for mercury removal is a potential cost-efficiency catalyst.

The application of this novel regenerable magnetic catalyst for mercury removal is schematically shown in Figure 1. Magnetospheres were firstly separated from fly ashes to synthesis the catalyst, which was then injected into flue gas to remove mercury. The spent catalyst was then collected by the particulate control devices, and recovered again from fly ash using magnetic separation. The spent sorbent was regenerated and recycled after heat treatment at suitable temperature. A device for the recovery of
mercury was equipped followed the regeneration device, such as Hg condenser. The mercury in the exhaust gas that was desorbed from the catalyst during the regeneration process was condensed and then collected in a container. The exhaust gas with relatively high temperature come back the system together with the catalyst, thus the catalyst could be preheated before the next mercury capture cycle. In this case, the application of this type of magnetospheres catalyst could minimize the secondary mercury pollution from the industrial waste. Our method will provide further insight into the development and application of cost-effective magnetic sorbents for mercury removal from coal combustion flue gas.

In this work, the main objective is to develop a series of recyclable cost-efficiency magnetospheres catalysts. The mercury removal performance as well as the recyclability over these regenerable catalysts were evaluated.

![Figure 1. Schematic of regenerable magnetosphere catalyst for mercury emission control from coal-fired power plants](image)

**EXPERIMENTAL SECTION**

Catalyst preparation

The Co-MF catalysts were prepared by an impregnation and thermal decomposition method using magnetospheres and Co(NO$_3$)$_2$ aqueous solution. The CuCl$_2$–MF catalysts were prepared by impregnation of magnetospheres from fly ash with an aqueous solution of CuCl$_2$·2H$_2$O following the incipient wetness method.

Experimental apparatus and procedures

The Hg$^0$ removal performance as well as the regeneration performance of Co-MF catalysts and CuCl$_2$–MF catalysts were investigated using a laboratory-scale fixed-bed reactor. The simulated flue gas was a mixture of 6% O$_2$, 12% CO$_2$, 1200 ppm SO$_2$, 300
ppm NO, 10 ppm HCl and balanced with N2, with a total flow rate of 1.2 L min⁻¹. The Hg⁰ concentration in the stream was about 85 μg·m⁻³. The Hg⁰ removal efficiency (η) was defined as the following equation:

\[ \eta = \frac{H_{in}^0 - H_{out}^0}{H_{in}^0} \times 100\% \]  

where \( H_{in}^0 \) and \( H_{out}^0 \) represented the instantaneous Hg⁰ concentration in the inlet and outlet of the reactor.

RESULTS AND DISCUSSION

Characterization of Co-MF catalyst

The magnetic property of 5.8% Co-MF catalyst is shown in Figure 2. The catalyst sample presents superparamagnetism because of its minimized coercivity and negligible magnetization hysteresis. This magnetization characteristic ensures that the spent Co-MF catalyst could be easily separated from fly ash mixture using magnetic separation, but will not be aggregated when the external magnetic field was removed.

The crystal form of cobalt species loading on the carrier was studied using XRD, as shown in Figure 3. Except for two weak peak of Co₃O₄, no other obvious crystallite patterns of cobalt species were observed. This implied that Co₃O₄ probably existed amorphous state in isolation because of the small surface area (0.28m²/g) of carrier, with several percent loading (5.8%).

Mercury removal performance of Co-MF catalyst

Effect of loading value

As shown in Figure 4, the Hg⁰ removal efficiency increased from 15.1% to 94.7% along with the increase of loading value from 0 to 5.8%, indicating that Co₃O₄ significantly enhanced the Hg⁰ removal activity over original magnetospheres. However, when the loading value was above 5.8%, the Hg⁰ removal efficiency decreased with the increase
of the Co₃O₄ loading content. In particularly, with a loading value of 10.2%, the Hg⁰ removal efficiency decreased to 75.5%. The loading value significantly affected the dispersion degree of cobalt oxide on the catalyst surface, which will be responsible for the Hg⁰ removal capacity. Therefore, when the loading value exceeded a critical point, the Hg⁰ removal capacity decreased.

Regeneration performance

As shown in Figure 5, similar Hg⁰ removal capacity over fresh and regenerated catalyst was observed. To further evaluate the effect of extended thermal treatment on Hg⁰ removal capacity, the 5th oxidation - regeneration cycle were studied following continuous thermal treatment for 20 h at 400 °C, where is the equivalent of 10 oxidation - regeneration cycles in theory. As shown, repeated oxidation - regeneration cycles did not result in any significant reduction of mercury removal capacity over Co-MF catalyst. This implied that the spent Co-MF could be effectively regenerated by thermally treatment at 400 °C for 2h, and the catalyst did not undergo obvious variation after regeneration. Because of its magnetism and reusability, the Co-MF catalyst makes it economically viable, since the spent catalyst could be easily separated from fly ash mixture by magnetic separation to regenerate and reuse.

Characterization of CuCl₂–MF catalyst

As shown in Figure 6, the binding energies of 934.8 ev and 955.1 ev corresponding to Cu 2p3/2 and Cu 2p1/2 is assigned to Cu²⁺ in CuCl₂ 13, along with the satellite spike at 938.3–945.8 eV assignable to Cu²⁺ 14. Little Cu⁺ in CuCl was also observed with the binding energies at 932.4 and 952.2 eV, which are attributable to Cu 2p3/2 and Cu 2p1/2 levels of Cu⁺ species 13,14. The occurrence of Cu⁺ was attributed to the reduction of Cu²⁺ in the high–vacuum environment during the XPS measurement 15.
Hg\textsuperscript{0} removal performance of CuCl\textsubscript{2}−MF catalyst

Effect of loading value

As shown in Figure 7, raw magnetospheres present poor Hg\textsuperscript{0} removal performance, while supporting with CuCl\textsubscript{2} significantly enhanced their activity. The $\eta_T$ increased from 15.1% to 90.6% when the CuCl\textsubscript{2} loading value changed from 0% to 9%. The total mercury efficiency $\eta_T$ was primarily determined by the adsorption efficiency $\eta_{ads}$ within the reaction proceed. However, at low Cu loading, the enhancement of Hg\textsuperscript{0} removal efficiency was slight, implying that there are little active adsorption sites for Hg\textsuperscript{0} at low Cu loading. When the Cu loading was lower than 9%, the $\eta_{ads}$ increased with the increasing Cu loading. The $\eta_{oxi}$ of different tested samples are nearly constant at about 10%. Superabundant CuCl\textsubscript{2} loading would not increase the active adsorption and oxidation sites for Hg\textsuperscript{0}. In contrast, the excess loading value would decrease the dispersion degree of CuCl\textsubscript{2} on the catalyst surface as well as the surface area.

Regeneration performance

Repeated oxidation-regeneration cycles were carried out after regenerated at 400 °C and thereafter pretreated by HCl and O\textsubscript{2}. As shown in Figure 8, the Hg\textsuperscript{0} oxidation performance did not vary apparently comparing with the fresh catalyst after 4 cycles. This implied that the catalyst did not undergo significant variation after regeneration, and the spent CuCl\textsubscript{2}-MF can be effectively regenerated. To further evaluate the effect of extended thermal treatment on Hg\textsuperscript{0} oxidation performance, the 4\textsuperscript{th} oxidation - regeneration cycle were studied following 20 h of continuous thermal treatment at 400 °C. This is the equivalent of 10 oxidation - regeneration cycles in theory, where a cumulative 20 h heat treatment was carried out. The results showed that the Hg\textsuperscript{0} oxidation capacity remained constant over successive cycles. Therefore, the regeneration method proposed above is successfully applied to the regeneration of spent CuCl\textsubscript{2}-MF.
REFERENCES