



Synthesis of mercury sorbent including metal oxides with layered carbonates material

Ching-Tsung Yu^{a,*}, Hui-Mei Lin^b, Han-Wen Cheng^a

^a Chemistry Division, Institute of Nuclear Energy Research, Longtan 325, Taiwan

^b Department of Mechanical Engineering, National Central University, Jhongli 320, Taiwan

HIGHLIGHTS

- Mercury sorbents of M–Al–CO₃ (M = Mg²⁺, Zn²⁺, Cu²⁺, and Mn²⁺ ions) were prepared.
- Sorption Hg was tested at 30–400 °C by hydrothermal conditions and fixed-bed reactor.
- Mn/Al predominated the materials with embodiment of Hg compositions that were double that of MnO.
- Elemental mercury sorption on Mn/Al sorbents also exhibited a maximum slope at 300 °C.

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ABSTRACT

Mercury sorbents M–Al–CO₃ were synthesized by coprecipitating M²⁺ and Al³⁺ in an alkaline NaOH/Na₂CO₃ solution, where M²⁺ corresponds to Mg²⁺, Zn²⁺, Cu²⁺, and Mn²⁺ ions. The formation of a layered double hydroxide structure significantly enhanced the surface area of the synthetic materials. Mercury removal tests were conducted under hydrothermal conditions between 30 and 250 °C and in a fixed-bed reactor at 100–400 °C. Energy-dispersive X-ray spectroscopy clearly indicated that the principal elements were embedded in the spent sorbents along with Hg. This analysis showed that Mn/Al predominated the materials with compositions that were double that of MnO, followed by Zn, Mg, and Cu. The mercury sorption curve exhibited a maximum slope at 300 °C for the Mn/Al sorbent. These findings demonstrate the potential of these synthetic sorbents under medium to high temperature conditions.

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1. Introduction

Mercury reduction is a crucial step in achieving sustainable environment and global environmental protection through Hg threat prevention. It is recognized today that approximately 80% of global Hg emissions originate from anthropogenic sources, particularly coal-fired utilities and incinerators [1]. Because of the substantial utilization of carbonaceous fuels for continuous energy development and the high toxicity, volatility, and bioaccumulation of mercury, capturing this heavy metal at a fixed emission point is of great significance to human health. Hg control techniques must be further improved to meet these requirements and advance current global clean air efforts. These Hg mitigation routes involve several technologies [2]. Various analytical scenarios have shown that scrubbing is a promising advanced mercury control technology [3]. Mercury capture-based adsorption methods have

indicated that chemical wet solvents and solid sorbents are major scrubbers that play an important role.

Carbon-based fuel combustion emits three main forms of Hg: Hg^p, Hg²⁺, and Hg⁰. The particulate-bound species Hg^p and their ions (Hg²⁺) are largely removed by typical processes such as electrostatic precipitation and flue gas desulfurization (FGD). The highly volatile and water-insoluble Hg⁰ is currently reduced by activated carbon injection and selective catalytic reduction (SCR) coupled with FGD at ambient temperature [4]. Mercury control at flue gas presents evident drawbacks related to low Hg concentration and diffusion throughout the process. Common sorbents, such as activated carbon, zeolites, and Al₂O₃, readily adsorb Hg at low temperature but their capacity decreases significantly above 100 °C. Therefore, many emerging technologies have adopted cleaner processes that reduce industrial Hg emissions under warm gas conditions. The advanced oxidation process including oxidative compounds such as SO₂/NO [5], H₂S/HCl [6], and halogens [7] could be considered as potentiality for effective removal elemental mercury (Hg⁰). This provides a feasible route for developing metal

* Corresponding author. Tel.: +886 3 4711400.

E-mail address: ctyu@iner.gov.tw (C.-T. Yu).

oxide-based mercury capture agent at elevated temperature conditions.

Capturing Hg close to the initial stages of the combustion process is more effective under elevated temperature conditions than at ambient temperature. Solid sorbents using mixed oxide (MO) nanoparticles exhibit high mercury removal efficiency at 200–450 °C, these sorbents are such as noble metals [8], palladium–alumina [9], CuO [10], and Fe₂O₃/Fe₃O₄ [11,12]. This efficiency can be significantly enhanced by combining the heterogeneous catalytic oxidation of Hg⁰ [13] with preferred adsorptive materials. Successive mercury adsorption and oxidation steps occur on the sorbents, in which the instantaneous electric dipole moment induced by Hg and MO nanoparticles drives the major mechanism by improving electrostatic forces and their interactions. Transition metal oxide-based catalysts are highly attractive sorbents because of their low cost relative to noble metals, high capacity, diversity, and their potential use as low–high temperature SCR catalysts.

This study describes the preparation and characterization of Hg sorbents and investigates their sorption capacity under hydrothermal conditions and in a fixed-bed reactor. The sorbents consisted of double hydroxides involving divalent (Mg²⁺, Zn²⁺, Cu²⁺, and Mn²⁺) and trivalent ions (Al³⁺) as well as anions (CO₃²⁻, OH⁻), providing a simple way to develop mercury removal materials via changing adsorbent structures [14] and with dual catalyst and absorbent functions. In these materials, the transition metals embedded in a porous support, such as M–Al–CO₃, act as oxidants and exhibit excellent sintering resistance [15,16]. Mercury capture may involve a catalytic oxidation assisted by attractive electrostatic forces in gas–solid reaction. The detail mechanism of this process will be investigated in the future.

2. Experimental

2.1. Preparation of Hg sorbents

Magnesium nitrate (Mg(NO₃)₂), copper nitrate (Cu(NO₃)₂), zinc nitrate (Zn(NO₃)₂), manganese nitrate (Mn(NO₃)₂), aluminum nitrate (Al(NO₃)₃), sodium carbonate (Na₂CO₃), and sodium hydroxide (NaOH) were purchased from Merck Inc., Germany.

The sorbents were synthesized by coprecipitation of M²⁺ (M = Mg²⁺, Zn²⁺, Cu²⁺, or Mn²⁺) and Al³⁺ ions under alkaline conditions. An acidic solution with M²⁺/Al molar ratio of 7:1 was prepared and stirred into a 0.1 M Na₂CO₃/1.6 M NaOH alkaline solution to form a pH 10 slurry. This slurry was subjected to vacuum filtration and the collected precipitate was dried overnight at 110 °C. The obtained M–Al–CO₃ powders were calcined at 200 °C to produce the sorbents.

The surface area, morphology, crystallinity, and elemental composition of the synthetic sorbents were determined using BET

surface area analysis (Quantachrome NOVA 4200), scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDX, JEOL S4800), and inductively coupled plasma (ICP) analysis (PE-ULTIMA2, Perkin), respectively.

2.2. Hg sorption experiment

Table 1 lists the test parameters for the capture of Hg²⁺ and Hg⁰ using the synthetic sorbents under hydrothermal conditions and in a fixed-bed reactor. The experiment device figure of fixed-bed reactor is showed in Fig. 1.

Test Hg²⁺ solutions (C₀ = 0.1–10 ppm) were prepared from 1000 ppm aqueous Hg(NO₃)₂ (Merck Inc, Germany). For the sorption tests, sorbents (0.1 g) and Hg²⁺ solution (100 mL) were loaded in a stirred reactor (Parr Instrument Company, USA) equipped with a temperature control ranging between 30 and 250 °C for 1 h. The mixture was cooled overnight before filtration. The residue (spent powder) was dried and characterized. The residual Hg(II) concentration (C_e) was determined by analyzing the filtrate by atomic fluorescence spectroscopy (PSA Millennium, USA). The mercury removal capacity (μg/g) was calculated using the difference between initial (C₀) and equilibrium (C_e) concentrations and the sorbent weight.

Alternatively, the performance of the Hg sorbent was assessed using a temperature-programmable fixed-bed reactor linked to an Hg generator, a temperature controller set at 100–400 °C, and an online Hg analyzer. Hg vapor was stably generated at a rate of



Fig. 1. Test rig of Hg removal system. (1: Adsorbent/furnace; 2: Hg vapor generator; 3: temperature controller; 4: Hg analyzer; 5: purge gas system.)

Table 1

Test factors of Hg capture in hydrothermal conditions and fixed-bed reactor.

Conditions	Hg sorbents	Hydrothermal	Fixed-bed reactor
Sorbent weight (g)	M–Al–CO ₃ , M ²⁺ = Mg ²⁺ , Zn ²⁺ , Cu ²⁺ , and Mn ²⁺ ions	0.1	1.0
Gas flow (L/min)		–	1.0
Adsorption temperature (°C)		200	300
Hg ²⁺ concentration (ppm)		0.1, 10	–
Hg ⁰ concentration (μg/m ³)		–	389.2
GHSV ^a (h ⁻¹)		–	23,715
Hg capacity (μg/g)	Mg/Al	4660	0.68
	Zn/Al	4890	157.59
	Cu/Al	3070	256.57
	Mn/Al	7870	294.88

^a GHSV = Gas hourly space velocity (h⁻¹).

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