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Photocatalytic oxidation removal of Hg^0 by ternary Ag@AgCl/Ag_2CO_3 hybrid under fluorescent light

Anchao Zhang [a,*], Lixiang Zhang [a], Qifeng Zhu [a], Bingjie Dai [a], Wei Sheng [a], Sheng Su [b], Jun Xiang [b,*]

[a] *School of Mechanical and Power Engineering, Henan Polytechnic University, Jiaozuo 454000, China*
[b] *State Key Laboratory of Coal Combustion, Huazhong University of Science and Technology, Wuhan 430074, China*

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ABSTRACT

Photocatalytic oxidation removal of elemental mercury (Hg^0) by Ag@AgCl/Ag_2CO_3 hybrids was carried out in a wet scrubbing reactor under fluorescent light. The photocatalysts synthesized via a modified coprecipitation method were characterized by using SEM-EDS, HRTEM, N_2 adsorption-desorption, XRD, XPS, DRS, and ESR. Effects of operational parameters on Hg^0 removal, including AgCl content, fluorescent light (FSL) irradiation, pH value, reaction temperature, and flue gas components (O_2, SO_2 and NO) were studied in detail. Furthermore, simultaneous removal of Hg^0 and SO_2 was investigated and the possible mechanism of highly enhanced Hg^0 removal efficiency was proposed. The results showed that AgCl amount, fluorescent light irradiation, reaction temperature, SO_2 and NO had notable impact on Hg^0 removal efficiency. Simultaneous removal efficiencies of 98% for SO_2 and 80% for Hg^0 were obtained by coupling Ag@AgCl(0.3)/Ag_2CO_3 with $Ca(OH)_2$ under FSL. The trapping studies of reactive radicals exhibited that holes (h^+) were one of the main reactive species for Hg^0 removal.

1. Introduction

Mercury has been an issue of great concern among the toxic heavy metals due to its volatility, persistence, and bioaccumulation [1–3]. Coal-fired utility is believed to be the largest anthropogenic mercury emission sources because of the great consumption of coal [4,5]. Elemental mercury vapor (Hg^0), oxidized mercury species (Hg^{2+}), and particulate-bound mercury (Hg^p) are the three primary species existed in coal-burning flue gas [6–8]. Hg^{2+} could be effectively controlled in wet flue gas desulfurization (WFGD) system because of its water solubility, and Hg^p can be captured mostly by electrostatic precipitators (ESP) or fabric filters (FF). However, being the primary component of mercury in flue gas, Hg^0 is hard to be removed from flue gas because of its high volatility and low solubility in water [9]. Thus, mercury removal efficiency could be greatly improved when Hg^0 is converted to its oxidized form [10].

The standard potential of Hg^0/Hg^{2+} redox-pair is reported to be 0.85 V, thus to achieve superior performance of Hg^0 oxidation, the standard oxidizing potential of the oxidants should at least be 1.2–1.3 V [11]. Recently, various advanced oxidation processes (AOPs) using UV/Fenton [10], $K_2S_2O_8/Ag^+/Cu^{2+}$ [11], $KMnO_4$ [12], $NaClO_2$ [13], $H_2O_2/Na_2S_2O_8$ [14], UV/H_2O_2 [15], and $Fe_{2.45}Ti_{0.55}O_4/H_2O_2$ [16] were investigated to remove Hg^0 from flue gas. Moreover, the design and investigation of TiO_2-based photocatalysts on Hg^0 removal are considered more promising owing to the high efficiency and non-secondary pollution [6,17–21]. However, because of the large band gap energy of TiO_2 (3.0 eV for rutile and 3.2 eV for anatase), it can only be reactive under plenty of UV light irradiation, which accounts for merely 4% of the total solar radiation. Furthermore, the existed photocatalytic processes of Hg^0 removal using TiO_2 or TiO_2-based photocatalysts were mainly focused on gaseous phase photocatalytic environment, which is not conducive to simultaneously remove Hg^0 and SO_2 from flue gas. Therefore, the development of advanced Hg^0 removal technology with high efficiency, low pollution and low cost is still necessary and urgent [22].

To date, in the field of wastewater treatment, researchers designed many kinds of novel visible-light-responsive catalysts to improve their visible-light activity, such as Ag-based photocatalysts [23–26] and Bi-based photocatalysts [27,28] and so on. Among various photocatalysts, Ag_2CO_3 has been recognized as one of the most promising photocatalysts for higher degradation of various organic dyes [29,30]. But it is often confronted with a poor stability in photocatalytic process due to the photochemical corrosion [31]. Ag_2CO_3 material was usually decorated by halide to improve its stability [23–25,29]. Mehraj et al. [24] and Xu et al. [25] noticed that the photocatalytic performance of AgX/Ag_2CO_3 ($X = $ Cl, Br, I) can be greatly enhanced owing to the effective separation of photogenerated carriers. Yao et al. [23] confirmed that $\bullet O_2^-$ and holes (h^+) were the two primary reactive free radicals during the photocatalysis degradation of methylene blue over Ag_2CO_3/Ag/AgCl composite. Moreover, an interesting phenomenon which has

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* Corresponding authors.
E-mail addresses: anchaozhang@126.com (A. Zhang), xiangjun@mail.hust.edu.cn (J. Xiang).

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been used for the preparation of highly effective visible light responsive photocatalyst is the surface plasmon resonance (SPR) effect induced by noble metal nanoparticles [23]. In particular, metallic silver nanoparticles (Ag^0 NPs) exhibiting SPR effect have been employed on silver halides to extend the visible light absorption of the photocatalysts [32, 33]. Hu et al. [33] verified that Ag^0 NPs could serve as a sinker for photogenerated charge carriers, promoting the separation of charge to enhance the photocatalytic activity due to its SPR effect. In the photocatalysis of semiconductor under visible light, lots of reactive radicals such as $\bullet O_2^-$, •OH, and h^+ were produced, which might be able to greatly oxidize Hg^0 due to their strong oxidation abilities. Therefore, it is feasible to synthesize a silver-based photocatalyst with suitable matching band potentials for effective removal of Hg^0. Furthermore, since visible light accounts for 43% of the incoming solar radiation, it's promising to remove Hg^0 using efficient visible-light-responsive photocatalyst. Unfortunately, the mechanism of Hg^0 removal by a novel silver-based photocatalyst has remained unclear because of a big difference between gas phase pollutant and liquid pollutant [16,34,35].

Based on the above analysis, to make full use of sunlight, a series of plasmonic Ag-enhanced AgCl and Ag_2CO_3 hybrids (hereafter designated as $Ag@AgCl/Ag_2CO_3$) was fabricated using a facile coprecipitation method. To realize the simultaneous removal of Hg^0 and SO_2, the photocatalytic oxidation process was carried out in a photocatalytic gas-liquid reactor. The experimental results indicated that Hg^0 and SO_2 can be effectively removed by coupling $Ag@AgCl/Ag_2CO_3$ with $Ca(OH)_2$ under fluorescent light. According to the characterization and experimental results, a corresponding mechanism for enhanced Hg^0 removal performance was elucidated in detail.

2. Experimental

2.1. Preparation of photocatalyst

The $Ag@AgCl(X)/Ag_2CO_3$ ($X = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1$) hybrids were prepared via a facile coprecipitation method and the molar ratio X of $AgCl/Ag_2CO_3$ was regulated by altering the amount of added hydrochloric acid (HCl). Typically, firstly, 9.86 g of $AgNO_3$ and 3.08 g of Na_2CO_3 were dissolved in 300 mL and 150 mL of deionized water to obtain $AgNO_3$ and Na_2CO_3 aqueous solutions, respectively, then 0.5 mL of hydrochloric acid (HCl, wt. 36%) was dropwise added into the Na_2CO_3 aqueous solution. Secondly, the $NaCl/Na_2CO_3$ mixed solution slowly poured into the above $AgNO_3$ solution under vigorous stirring for about 20 min. Thirdly, the above reaction product was incubated at 60 °C under continuous stirring for 10 min, subsequently 5 mL ethylene glycol (EG) was dropwise introduced to generate some amount of metallic Ag (Ag^0) and kept at 60 °C for another 25 min [36]. At last, after placed 24 h, the suspension was washed with distilled water for 3– 5 times, and then dried at 60 °C for 24 h. The final product was designated as $Ag@AgCl(0.1)/Ag_2CO_3$ photocatalyst. Other different molar ratios of $AgCl/Ag_2CO_3$ hybrids were synthesized in the similar manner by varying the contents of HCl or/and EG. They were named as Ag_2CO_3, $Ag@Ag_2CO_3$, $Ag@AgCl(0.3)/Ag_2CO_3$, $Ag@AgCl(0.5)/Ag_2CO_3$, $Ag@AgCl(0.7)/Ag_2CO_3$, $Ag@AgCl(0.9)/Ag_2CO_3$ and Ag@AgCl.

2.2. Evaluation of photocatalytic activity

The schematic diagram of the experimental setup is shown in Fig. 1, which included three main subsystems: a flue gas supply system, a detection system, and a photocatalytic oxidation system. The baseline gases (BL) contained 6% O_2, 12% CO_2, and balance N_2 coupled with SO_2 (when used) or/and NO (when used) were employed as simulated flue gas. A U-tube and mercury permeation tube (VICI Metronics, USA) were placed into a thermostatic water-bath to maintain a constant Hg^0 permeation rate. The reaction system consisted of a gas reactor (vol. 2000 mL, i.d. 100 mm), a magnetic rotor, a water bath with magnetic stirring, a quartz glass tube, a fluorescent light (YDN11-π.RR, 220 V, 11 W, Color temperature: 6500 K, Luminous flux: 750 lm, 35 × 25 × 235 mm, Foshan Electrical and Lighting Co., Ltd., China) with a wavelength range of 400–700 nm, and a circulating cooling device that was used to take away the heat generated by fluorescent light irradiation. The measuring system was composed of a flue gas analyzer (Kane International Limited, U.K.) and a mercury analyzer (VM-3000, Mercury Instruments GmbH, Germany). One bottle of $SnCl_2$ solution (10 wt%) was employed to investigate the mercury speciation in gas phase out of removal device. To protect the detection cell of mercury analyzer, a low temperature tank (−10 °C) and a bottle of NaOH solution (20 wt%) were employed to condense water vapor carried out by simulated flue gases from reaction system and absorb other acid gases, respectively.

During the experiment, about 1.5 L/min of simulated flue gas and an initial Hg^0 concentration (C_{in}) of about 55.0 μg/m³ were used. The reaction solution was made by mixing 0.80 g photocatalyst with 1 L deionized water. To clearly understand the influence of different experimental

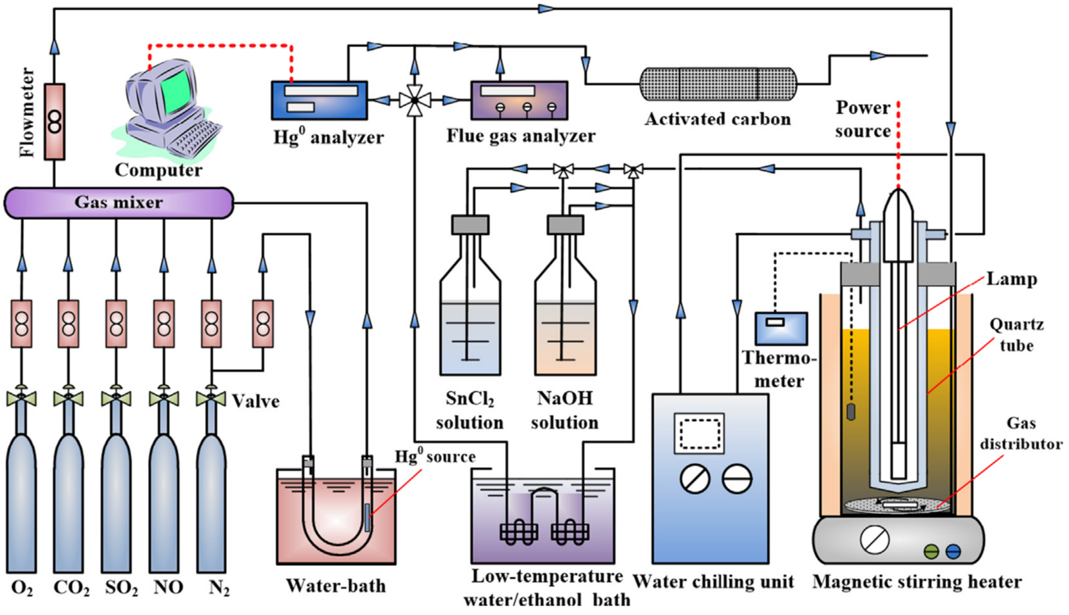

Fig. 1. Schematic diagram of the experimental setup.