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Removal of elemental mercury from flue gas using wheat straw chars modified by Mn-Ce mixed oxides with ultrasonic-assisted impregnation

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HIGHLIGHTS

- A novel adsorbent of Mn-Ce mixed oxides modified wheat straw char was prepared.
- Ultrasonic-assisted impregnation method was used to prepare the adsorbent.
- Mercury removal performance and mechanism were studied.
- Presence of CeO_2 contributed to the form of Mn/Ce redox cycle.
- Chemical adsorption of Hg^0 played a key role in mercury removal.

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ABSTRACT

In this article, Mn-Ce mixed oxides modified wheat straw chars were prepared by an ultrasonic-assisted impregnation method, and were employed to remove elemental mercury (Hg^0) from flue gas. Thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET) were employed to characterize the physicochemical properties of the catalysts. The effects of ultrasonic-assisted impregnation, Mn/Ce molar ratios, calcination temperatures, Mn-Ce loading values, reaction temperatures and main flue gas components such as SO_2, O_2, NO and H_2O on mercury removal using these catalysts were studied in a fixed bed reactor. The results showed that the catalyst with a Mn/Ce molar ratio of 2/1 exhibited high mercury removal activity at 150 °C. The optimal Mn-Ce loading value and calcination temperature were 0.12 mol/L and 250 °C, respectively. The presence of O_2 and NO obviously promoted Hg^0 removal. Low concentrations of water vapor and SO_2 strengthened Hg^0 removal, but high concentrations of water vapor and SO_2 inhibited Hg^0 removal. Finally, the mercury removal mechanism was also discussed based on experimental results and characterization analysis.

1. Introduction

Mercury is one of the most hazardous pollutants due to its strong toxicity [1]. Coal combustion has been recognized as a major source of anthropogenic mercury emissions. It is estimated that about 30% of the anthropogenic mercury emissions is from coal combustion [2]. There are three forms of mercury from coal-fired flue gas: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}) and particulate bounded mercury (Hg^p). Oxidized mercury (Hg^{2+}) can be easily removed by wet flue gas desulfurization (WFGD) systems. Particulate bounded mercury (Hg^p) can be captured by electrostatic precipitators (ESPs) and fabric filters (FFs) [3]. However, Hg^0 is hard to be removed because of its high volatility and low solubility in water. In order to remove elemental.mercury, many methods have been developed [4]. Activated carbon injection (ACI) is an effective technology for mercury removal, but high cost of this method has limited its application [5]. Therefore, developing economic and effective adsorbents/catalysts has become the research focus in the area of coal-fired flue gas purification.

Wheat straw, a kind of common renewable resource, is highly abundant, and is very cheap in China. Therefore, wheat straw bio-char is considered to be the valuable alternative to activated carbon due to its low costs and extensive sources [6]. However, wheat straw bio-char usually has low catalytic performance for Hg^0 due to the poor surface activity sites [7]. Chemical modification is considered to be a simple and effective way to increase the activity sites on the surface of bio-char, and to improve mercury adsorption capacity. The related research on halogens (Cl, Br and I) or sulfur modified biomass chars for mercury removal has

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been widely reported and has made significant progress [8,9]. Nevertheless, several deficiencies such as narrow reaction temperature range and potential secondary contamination of the modified reagents restricted their application and development [6,10,11].

Manganese oxides (MnO_x) have been widely investigated as the low-temperature SCR catalysts due to its high activity [12]. The Mn-based catalysts such as MnO_x/Al_2O_3 [13] and MnO_x/TiO_2 [14] also have been used for gaseous mercury capture. Zeng et al. [15] reported that MnO_x-based catalysts had good mercury removal capacity. Li et al. [16] reported that the presence of MnO_x greatly enhanced mercury removal. However, when SO_2 existed in flue gas, the mercury removal capacity of these catalysts often obviously reduced. In recent years, cerium oxides have been given great attention because of its superior activity, high oxygen storage capacity, abundant oxygen vacancies and unique couple Ce^{3+}/Ce^{4+} [17–21].

Zhao et al. [22] indicated that cerium oxide exhibited strong SO_2 resistance in Hg^0 capture due to its surface sulfation. In addition, Ce-based catalysts also exhibited good resistance to water vapor [23,24]. Based on these advantages, Mn-Ce mixed oxides are considered as the promising catalysts due to the strong oxidizing capacity and stability. It has been also reported that Mn-Ce mixed oxides exhibited excellent catalytic performance because of the synergy between manganese oxides and cerium oxides [25]. Li et al. [26] investigated that TiO_2 supported Mn-Ce mixed oxide had high mercury removal performance. Xie et al. [27] indicated that commercial columnar activated coke modified by Mn-Ce mixed oxides also exhibited high catalytic activity for Hg^0 from flue gas. However, so far, the research on Hg^0 capture using low temperature catalysts, Mn-Ce mixed oxides modified wheat straw chars, have rarely been reported. Wheat straw chars may become a kind of potential alternative to AC and TiO_2 due to the wide sources and low costs (especially it is a kind of renewable resource). According to the results in this article, the highest average mercury removal efficiency of Mn-Ce/wheat straw chars is up to 94.1%, showing that the novel catalysts have good mercury removal performance. Besides, some results [26,28,29] showed that ultrasound treatment could obviously improve the activity and surface characteristics of catalysts/ adsorbents.

The above situation drives us to try to develop the novel catalysts, Mn-Ce mixed oxides modified wheat straw chars, using an ultrasonic-assisted impregnation method, and to study the removal performance of mercury from flue gas. The physicochemical properties of the catalysts were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), scanning electron microscopy (SEM) and Brunauer-Emmett-Teller (BET). The effects of ultrasonic-assisted impregnation, Mn/Ce molar ratios, calcination temperatures, Mn-Ce loading values, reaction temperatures and flue gas components (e.g. SO_2, O_2, NO and H_2O) on Hg^0 removal efficiency were studied. The mercury removal mechanism was also discussed based on experimental results and characterization analysis. These results will provide some important theoretical guidance for the application of the catalysts and this mercury removal technology.

2. Experimental

2.1. Preparation of catalysts

Wheat straw collected from Xuzhou of Jiangsu province, China, was dried, milled and sieved to retain the particles in a 50 Chinese mesh (<300 μm). These raw wheat straw particles were pyrolyzed at 600 °C for 20 min under the protection of N_2 (250 mL/min). The pyrolyzed sample (wheat straw bio-char) was denoted as WS. In this work, Mn-Ce catalysts were prepared by wet impregnation method enhanced by ultrasonic (ultrasounic-assisted impregnation) [30]. The preparation process of Mn-Ce catalysts is as follows: a certain amount of cerium nitrate, manganese nitrate and 120 mL deionized water were completely mixed in a beaker. Then 5 g WS was added into the mixed solution. The containing-WS mixed solution was stirred for 60 min at 40 °C, and then was further processed using ultrasonic for 40 min at 40 °C. After the ultrasonic treatment, the containing-WS mixed solution was first filtered, and then was dried at 90 °C for 4 h. The obtained dry solid sample was calcined at required temperature for 30 min in static air. The catalyst was denoted as MnCex(y)/WSUz, where x represents the total molar concentration (mol/L) of manganese nitrate and cerium nitrate in the above impregnation solution, y represents the molar ratio of Mn/Ce, z represents the calcination temperature (°C), and U represents ultrasounic-assisted impregnation (e.g. MnCe0.12(2/1)/WSU250). The ultrasonic-free sample was denoted as MnCex(y)/WSz. The Mn/Ce molar ratios of the prepared samples were 1:2, 1:1, 2:1, 3:1, respectively. The Mn/Ce loading values (total molar concentrations) of the prepared samples are 0 mol/L, 0.06 mol/L, 0.12 mol/L and 0.18 mol/L, respectively. The calcination temperatures were 230 °C, 250 °C and 270 °C, respectively.

2.2. Characterization of catalysts

The proximate and ultimate analysis of wheat straw were determined by Flash 2000 (Thermo Fisher, USA). Thermogravimetric analysis (TGA) was measured by STA6000 (PerkinElmer, USA). The BET surface area of the samples was determined by N_2 adsorption on a Micromeritics Tristar Ⅱ 3020 analyzer (Micromeritics Instrument Crop., USA). The SEM photographs were obtained by the Scanning Electron Microscopy (JSM-7500F). In order to determine the dispersivity and crystallinity of samples, X-ray diffraction (XRD) measurements were performed in MiniFlex600 powder diffractometer (Rigaku, Japan). In order to study the change of the element valence of Mn-Ce mixed oxides, X-ray photoelectron spectroscopy (XPS) analysis was carried out using a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher, USA).

2.3. Experimental setup and procedure

The experimental installation is shown in Fig. 1. It mainly includes four parts: (I) A simulated flue gas system with four gas cylinders (1–4), six flowmeters (5–10), a gas mixer (11), a Hg^0 vapor permeation device (12–13) (VICI Metronics, USA) and a generator of water vapor (14–15); (II) A temperature adjusting system with two thermostat water baths (13, 15), a thermostat drying oven (16) and a heating tape (18); (III) A reaction system with a quartz fixed bed reactor (17) (inner diameter of 35 mm; length of 50 mm) and a silicone cover; (IV) A sample detection and tail gas treatment device, including a mercury analyzer (19) (QM201H, Suzhou Qingan Instrument Co., Ltd, China), a flue gas analyzer (20) (MRU-VARIOPLUS, Germany) and an exhaust gas treatment pipe (21).

The flow rates of individual flue gas components were regulated by the flowmeters. The total flow rate of flue gas was maintained at 800 mL/min, corresponding to a gas hourly space velocity (GHSV) of 10,000 h^{-1}. $O_2/NO/SO_2/N_2$ simulated flue gas was produced by O_2, SO_2, NO, N_2 cylinders. Water vapor was generated by the generator of water vapor. Hg^0 was generated by the Hg^0 vapor permeation device (a N_2 flow of 100 mL/min was used to carry the mercury vapor from the Hg^0 vapor permeation device). All flue gas components were mixed in gas mixer. In order to prevent the condensation of water vapor and mercury vapor, all of the gas lines were heated to 50 °C by a heating tape. The inlet concentrations of NO, SO_2 and O_2 were measured using flue gas analyzer (MRU-VARIOPLUS, Germany). The inlet concentrations of Hg^0 were mea-