Simultaneous removal of NO and Hg^0 from simulated flue gas over CoO_x-CeO_2 loaded biomass activated carbon derived from maize straw at low temperatures

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HIGHLIGHTS

- Manufacturing maize straw derived BAC obtains the unit of environmental and economic benefits.
- 15%$Co_{0.4}Ce_{0.6}$/BAC exhibited superior performance for simultaneous removal of NO and Hg^0.
- The interaction between NO reduction and Hg^0 oxidation was investigated.
- The mechanisms of simultaneous removal of NO and Hg^0 were systematically proposed.

GRAPHICAL ABSTRACT
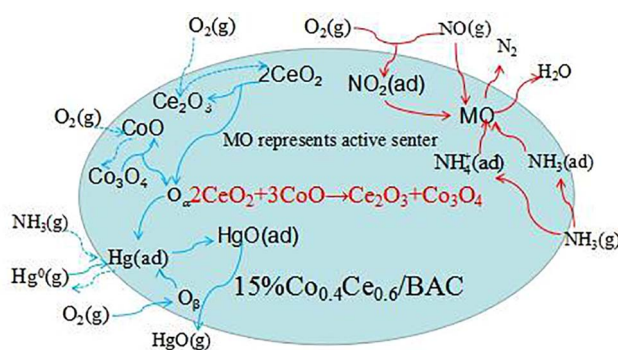
ABSTRACT

To rationally utilize agricultural wastes and expediently simultaneous control of elemental mercury (Hg^0) and NO, a series of CoO_x-CeO_2 loaded maize straw derived biomass activated carbon (CoCe/BAC) samples were applied for simultaneous NO and Hg^0 removal. These samples' physicochemical characteristics were characterized by BET, SEM, XRD, NH_3-TPD, H_2-TPR, XPS and FTIR. 15%$Co_{0.4}Ce_{0.6}$/BAC yielded prominent Hg^0 removal efficiency (96.8%) and superior NO removal efficiency (84.7%) at 230 °C. The separate or synchronous deactivation effects of 400 ppm SO_2 and 5%H_2O were detected. The interaction between NO removal and Hg^0 removal was investigated, the results demonstrated that abundant Hg^0 exhibited very slightly inhibitory effect on NO removal, and NH_3 negatively affected Hg^0 removal, whereas NO mildly boosted Hg^0 removal in presence of O_2. The characterization analyses indicated the excellent performance of 15%$Co_{0.4}Ce_{0.6}$/BAC could be ascribed to its better texture properties, lower crystallinity and stronger redox ability. Besides, a synergetic effect appeared between cobalt oxide and cerium oxide, resulting in generating more Ce^{3+} and Co^{3+} to induce more anionic defects and produce more active oxygen and oxygen vacancies. The removal mechanisms of NO and Hg^0 were systematically investigated, and NO reduction reactions were mainly assigned to the Langmuir-Hinshlwood mechanism while both adsorption and Hg^0 oxidation contributed to Hg^0 removal. Meanwhile, Hg^0 oxidation corresponded to the Mars-Masson mechanism prevailed gradually with the increase of reaction time.

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1. Introduction

Coal-fired power plant, as the major contribution of worldwide energy demand, has become one of leading anthropogenic atmosphere pollutant emission sources [1–3]. Thereinto, nitrogen oxides (NO_x) and elemental mercury (Hg^0) are deemed to be two significant atmosphere pollutants and have aroused widespread concern. NO_x is considered as an incentive for numerous environmental problems, such as regional acid smog, zone depletion and photochemical smog [3]. Hg^0 is a global threat to the environment and human health because of its volatility, toxicity, persistence and bioaccumulation [2,3]. Consequently, more and more national laws and regulations have been implemented to restrict NO_x and Hg^0 emissions [4,5]. For example, some strict regulations aiming to achieve ultra low emission in coal-fired power plants are put forward in China, in which the emission concentrations of NO_x and Hg^0 are limited to $5\,mg/m^3$ and $0.002\,mg/m^3$, respectively [5].

Therefore, enormous technologies have been developed to reduce NO_x or Hg^0 emissions from coal-fired power plants to meet these laws and regulations [2,4–6]. Among them, selective catalytic reduction (SCR) of NO_x with NH_3 is regarded as one widely applied technique due to its excellent performance, while activated carbon injection (ACI) for Hg removal has been a mature technology [2,7]. However, the ACI technology suffers from many shortcomings such as the low capture efficiency at high temperature, potential secondary pollution caused by spent sorbents and high operating cost due to the tremendous consumption of activated carbon (AC) [8,9]. Moreover, traditionally separate NO_x and Hg^0 control technology faced several bottlenecks including large footprint requirement, high equipment and operation investment [10]. Hence, it is easy to consider whether or not to utilize the denitration catalyst for Hg^0 removal, but researches demonstrated the most widely engaged denitrification catalysts (V_2O_5-WO_3(MoO_3)/TiO_2) were not effective enough for Hg^0 conversion in the flue gas burnt the low chlorine coal [4,6]. Furthermore, to avoid deactivation and reduce reaction costs, the SCR system was required to be loaded downstream of the particulate collector where the temperature was lower than the narrow active temperature window of the for-mentioned SCR catalyst [6,11]. Considering these handicaps, the development of novel appropriate catalysts for simultaneous removal NO_x and Hg^0 at low temperature is of significantly practical interest.

Up to date, CeO_2 has been successfully widely used in a variety of heterogeneous reactions as an effective catalyst, a promoter, a support or active ingredient for NO reduction and Hg^0 oxidation respectively because of its large oxygen storage capacity and unique redox couple Ce^{4+}/Ce^{3+} [4,12–14]. It was known that the combination of CeO_2 with other metal oxides such as MnO_x, CuO and La_2O_3 could produce synergistic effect, which was conducive to the promotion of NO reduction and Hg^0 oxidation [4,6,15,16]. Zhang et al. [17] studied hollow porous $Mn_xCo_{3-x}O_4$ nanocages $deNO_x$ catalyst and found it had excellent low temperature activity and good SO_2 resistance. Due to the synergistic effect of high oxygen storage-release ceria and active Co species, Co_3O_4–CeO_2 composite catalyst, Co_3O_4/CeO_2 catalyst and CoO_x-CeO_2 loaded activated coke sorbent-catalyst had been reported to yield superior performance for VOCs oxidation [18,19], CO oxidation [20] and Hg^0 oxidation [14], respectively. However, to the authors' knowledge, systematic researches with respect to CoO_x and CeO_2 as active ingredients for NO_x and Hg^0 simultaneous removal are rarely reported.

In addition, activation carbon (AC) is considered as the most widely employed sorbent and the carrier of catalysts due to its large surface areas, favorable pore size and flexible working conditions [6,14,21]. Traditional ACs are usually derived from relatively expensive and nonrenewable raw materials such as bituminous coal and wood. At the same time, as a big agricultural country, China faces the challenges from the dispose of billions of tons of renewable agriculture straws every year. Since most of them cannot receive reasonable utilization and be open burning, thus engendering great harms to the environment [22]. Therefore, it is much monetary and environmentally friendly

incentive for manufacturing biomass activated carbon (BAC) derived from annually renewable agriculture wastes. Thus, biomass activated carbons (BAC) derived from agriculture wastes have become a new concern due to significant practical interest [23,24]. Nevertheless, these BACs are mainly used for waste water treatment [23], and only limited applications on gas purification [24]. Notably, some meaningful researches related to bio-chars from various straws have emerged for mercury removal by adsorption or catalytic oxidation [25,26]. However, as we know, ideal adsorbents/catalysts should possess excellent surface area, these bio-chars often own unimpressive BET surface areas (about $200\,m^2/g$). In this work, BACs from maize straw prepared by $ZnCl_2$ activation have severalfold BET surface areas (543–$1029\,m^2/g$), which are more propitious to adsorption and catalytic reactions. CoO_x and CeO_2 supported on the carrier of BAC by the impregnation method were investigated for NO and Hg^0 simultaneous removal.

2. Experimental

2.1. Preparation of samples

Maize straws were collected from the rural areas of Xinyang city, Henan province, PR China. The raw material was first rinsed with deionized water and dried at $105\,°C$ overnight, crushed and sieved for standby application. Then the resulted particles (RP) were impregnated into $ZnCl_2$ solution at calculated quantity (the mass ratio of activating agent ($ZnCl_2$) and RP of 1, which was chosen based on our preliminary experiments) for 24 h at ambient temperature. After that, the obtained materials were dried at $105\,°C$ overnight, and subsequently they were activated in a tube-type electronic heating furnace at $750\,°C$ for 2 h under N_2. After activation, the obtained materials were washed several times by 5 M HNO_3 and then bathed with deionized water until the pH of cleaning water reached approximately 7. Subsequently, the product was dried and sieved, thus obtaining the carrier of BAC.

The catalysts were prepared by impregnation method using foregoing BAC as the carrier and cobalt nitrate or cerium nitrate as the precursors of active ingredients. Calculated amounts of BACs were impregnated in corresponding precursors solutions for 24 h. Afterwards, these impregnated samples were dried at $105\,°C$ for 18 h and then calcined at $550\,°C$ for 4.5 h under N_2 atmosphere. Thus XCo_yCe_{1-y}/BAC catalyst was obtained, where X represented the mass percentage of metal oxides of the $Co_y Ce_{1-y}/BAC$ samples while y referred to the molar ratio of Co in metal oxides, similarly, 1-y referred to the molar ratio of Ce in metal oxides. Moreover, for comparison, XCo/BAC and XCe/BAC were synthesized by the same method.

2.2. Sample characterization

Pore characteristics including average pore diameter, total pore volume and Brunauer–Emmett–Teller (BET) surface area of different samples were acquired by N_2 adsorption with an automatic Micromeritics ASAP2460 volumetric sorption analyzer (Micromeritics Instrument Corp., USA).

The microstructure and morphology of different samples were measured by Scanning electron microscopy (SEM) using Nova Nano SEM 230 (USA).

X-ray diffraction (XRD) measurements of different samples were carried out on a Rigaku Smartlab (3KW) system (Japan) with Cu-Ka radiation (40 kV, 30 mA) in the 2θ range from $10°$ to $90°$.

H_2-temperature programmed reduction (H_2-TPR) and ammonia-temperature programmed desorption (NH_3-TPD) were conducted on a TP-5080 automatic chemical adsorption instrument (Tianjin Xianquan, China).

X-ray photoelectron spectroscopy (XPS) was performed using a K-Alpha 1063 X-ray photoelectron spectrometer with 72 W Al Kα radiation (Thermo Fisher Scientific, USA).

Fourier transform infrared spectroscopy (FTIR) was conducted on a