



## Full Length Article

# A novel catalyst CuO-ZrO<sub>2</sub> doped on Cl<sup>-</sup> activated bio-char for Hg<sup>0</sup> removal in a broad temperature range



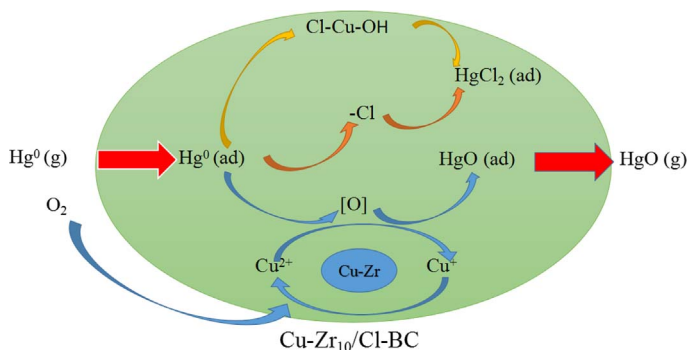
Le Tang<sup>a,b</sup>, Caiting Li<sup>a,b,\*</sup>, Lingkui Zhao<sup>a,b,c</sup>, Lei Gao<sup>a,b</sup>, Xueyu Du<sup>a,b</sup>, Jiawen Zeng<sup>a,b</sup>, Jie Zhang<sup>a,b</sup>, Guangming Zeng<sup>a,b</sup>

<sup>a</sup> College of Environment Science and Engineering, Hunan University, Changsha 410082, PR China

<sup>b</sup> Key Laboratory of Environmental Biology and Pollution Control (Hunan University), Ministry of Education, Changsha 410082, PR China

<sup>c</sup> College of Environmental Science and Resources, Xiangtan University, Xiangtan 411105, PR China

## GRAPHICAL ABSTRACT



## ARTICLE INFO

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## ABSTRACT

To obtain a new low-cost catalyst that possesses well Hg<sup>0</sup> removal activity in a broad temperature range, a series of Cu-Zr<sub>x</sub>/Cl-BC catalysts were synthesized with the application of bio-char which was activated by NH<sub>4</sub>Cl. CuO-ZrO<sub>2</sub> as the active component largely improved Hg<sup>0</sup> removal activity of the catalysts. The catalysts were characterized by SEM-EDX, BET, XRD, H<sub>2</sub>-TPR, XPS and FT-IR. When the CuO-ZrO<sub>2</sub> loading value was 10%, Cu-Zr<sub>10</sub>/Cl-BC reached the best Hg<sup>0</sup> removal efficiency (98.87%) at 120 °C and maintained over 80% until 240 °C. O<sub>2</sub> was of benefit to Hg<sup>0</sup> removal process especially at high temperature because it could regenerate the lattice oxygen which participated in the removal reaction. In addition, Hg<sup>0</sup> removal was mainly determined by adsorption at low temperature and the function of oxidation increased at high temperature. The characterization results indicated that the superior performance of Cu-Zr<sub>10</sub>/Cl-BC might be ascribed to lower crystallinity, stronger redox ability and better texture properties which resulted from the interaction of CuO and ZrO<sub>2</sub>. The mechanism for Hg<sup>0</sup> removal over Cu-Zr<sub>10</sub>/Cl-BC was also proposed on the basis of above studies.

## 1. Introduction

As one of air pollutants of coal combustion in coal-fired power plants, elemental mercury (Hg<sup>0</sup>) has attracted a great deal of concern

due to its toxicity, volatility and bio-accumulation [1,2]. It is hard to remove cleanly and will leave bad effects on both human and the environment [3]. The US Environmental Protection Agency issued the national standard Final Mercury and Air Toxic Standards for the control

\* Corresponding author at: College of Environment Science and Engineering, Hunan University, Changsha 410082, PR China.  
E-mail address: [ctli@hnu.edu.cn](mailto:ctli@hnu.edu.cn) (C. Li).

of mercury, acid gases and other harmful air contaminants on April, 19, 2012 [4]. Mercury and its compounds were limited to  $0.03 \text{ mg/m}^3$  by the Ministry of Environmental Protection of China (MEPC) [5]. Therefore, a series of measures have been taken to investigate and handle  $\text{Hg}^0$  emission issues.

Up to now, many methods have been studied to remove  $\text{Hg}^0$  in the flue gas. Wet flue gas desulfurization (WFGD) is regarded as a good method for the  $\text{SO}_2$  removal, it also be used to remove  $\text{Hg}^{2+}$  after the oxidation of  $\text{Hg}^0$  in the industry. But, the re-emission of mercury during the WFGD is a serious problem [6]. Activated carbon injection (ACI) has been recognized as the mainly commercialized technology to dispose  $\text{Hg}^0$  at the temperature window of  $100\text{--}200^\circ\text{C}$  [7], and activated carbons modified by sulfur, chloride and metal oxide ( $\text{CuO}$ ,  $\text{MnO}_2$ ,  $\text{V}_2\text{O}_5$ ) were widely used [8,9]. However, the main problems related to ACI include the large consumption and low utilization rate, which might increase the cost immensely [10]. Therefore, it is important to develop a new material with low cost and high activity to replace the commercial activated carbon. Bio-char (denoted as BC below) has received considerable attention for  $\text{Hg}^0$  removal due to its characteristics of going green, environmental protection and low-cost [11,12]. It could be obtained by pyrolysis of various biomass which are from cheaper source, including bamboo, corn cob, sawdust and so on [5]. It is well known that pine nut has become popular among Chinese family as one of the nut food. In order to improve economics of the material, pine nut shell might be suitable and cheap source for BC as the raw material for  $\text{Hg}^0$  removal. However, the original pyrolysis products of bio-char were not effective enough for  $\text{Hg}^0$  removal [13]. Hence, how to enhance the  $\text{Hg}^0$  removal efficiency of bio-char is becoming popular. Recently, the literature reported that impregnated Cl element could greatly help activated carbon adsorbing  $\text{Hg}^0$  in the flue gas [14]. For example, Li et al. [15] have indicated that the bio-char (prepared by both microwave and 5 wt%  $\text{NH}_4\text{Cl}$  loading) was a cost-effective  $\text{Hg}^0$ -capture sorbent. Tan et al. [16] have suggested that  $\text{ZnCl}_2$  modified bamboo charcoals had excellent adsorption activity of elemental mercury. Nevertheless, new problem came out that the efficient temperature of halogen activated bio-char often existed at lower temperature window ( $60\text{--}100^\circ\text{C}$ ) [15,17]. Therefore, developing a novel low cost catalyst which not only possess excellent  $\text{Hg}^0$  removal efficiency at low temperature but also can maintain well activity at higher temperature is desirable.

It is worth noting that  $\text{CuO}$  has been demonstrated to have high oxidation activity for  $\text{NO}_x$  and  $\text{SO}_x$  [18]. In addition, many types of doped Cu based catalysts with excellent  $\text{Hg}^0$  removal catalytic activity have also been investigated [19,20]. For instance, Wang et al. [21] have studied the oxidation of  $\text{Hg}^0$  by  $\text{CuO-MnO}_2\text{-Fe}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ , which indicated that the active  $\text{Cu}^{2+}$  phase participated in the reaction and be reduced to  $\text{Cu}^+$ .  $\text{Cu}^{2+}$  could enhance SCR performance and mercury removal efficiency over  $\text{CeO}_2\text{-CuO}$  catalyst [22]. Interestingly, most of researches have been focusing on the effect of  $\text{ZrO}_2$  combined with another metal oxide for mercury removal. The reason was that  $\text{ZrO}_2$  additive could essentially benefit the catalysts performance with high temperature durability [23]. Li et al. [24] have deduced that the synergetic effect between Ce and Zr might result in the high  $\text{Hg}^0$  catalytic oxidation efficiency of  $\text{CeO}_2(\text{ZrO}_2)/\text{TiO}_2$ . Xie et al. [25] developed a novel regenerable sorbent based on Zr-Mn binary metal oxides, and proved that Zr significantly improved the sorbent's mercury removal capacity at  $75\text{--}200^\circ\text{C}$ . Unfortunately, comparatively fewer investigations of  $\text{CuO-ZrO}_2$  doped on  $\text{Cl}^-$  activated bio-char for  $\text{Hg}^0$  removal have been reported.

Herein, the purpose of this study was to investigate the performance and mechanism of  $\text{CuO-ZrO}_2$  doped on  $\text{Cl}^-$  activated bio-char for  $\text{Hg}^0$  removal in simulated flue gas at  $60\text{--}270^\circ\text{C}$ , and the effect of  $\text{CuO-ZrO}_2$  doped on  $\text{Hg}^0$  removal was evaluated. The role of flue gas components ( $\text{O}_2$ ,  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{H}_2\text{O}$ ) in the  $\text{Hg}^0$  removal was also examined. Besides, SEM-EDX, BET, XRD,  $\text{H}_2$ -TPR, XPS and FTIR were used to characterize the physicochemical properties of catalysts and to discuss the reaction mechanism.

## 2. Materials and methods

### 2.1. Preparation of catalysts

10 g pine nut shell used as the original material was crushed and sieved to  $80\text{--}100$  mesh, and became about 4 g BC after calcination in an electric tube furnace at  $600^\circ\text{C}$  for 2 h under  $\text{N}_2$  atmosphere. Then, the requisite amount of  $\text{NH}_4\text{Cl}$  was dissolved in deionized water with 1 h vigorous stirring to form 5% (mass fraction)  $\text{NH}_4\text{Cl}$  solution. A certain amount of BC ( $\text{BC}/\text{NH}_4\text{Cl}$  solution = 1 g:20 ml) was added to the solution with vigorous stirring for 4 h, after aging for 12 h, the mixture was dried in an electric blast drying oven at  $90^\circ\text{C}$  for 24 h. The obtained  $\text{NH}_4\text{Cl}$ -biochar support was denoted as Cl-BC.

A series of catalysts were synthesized using impregnation method. The molar ratio of  $\text{CuO}$  and  $\text{ZrO}_2$  was set as 1:1. Typically, 0.286 g  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  and 0.382 g  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  were dissolved in 10 ml deionized water (support/deionized water = 1 g:5 ml). After stirring 1 h, the mixed solution was impregnated on 2 g Cl-BC support and stirred for 4 h. Subsequently, the mixture was aged for another 12 h. Then, the mixture was dried in an electric blast drying oven at  $105^\circ\text{C}$  for 24 h and finally calcined in an electric tube furnace at  $450^\circ\text{C}$  for 4 h at a heating rate of  $5^\circ\text{C}/\text{min}$  under  $\text{N}_2$  atmosphere. The obtained catalyst was denoted as  $\text{Cu-Zr}_{12}/\text{Cl-BC}$ , and another  $\text{Cu-Zr}_x/\text{Cl-BC}$  materials were also prepared by the same steps with different consumption of  $\text{Cu}(\text{NO}_3)_2\cdot 3\text{H}_2\text{O}$  and  $\text{ZrOCl}_2\cdot 8\text{H}_2\text{O}$  (where x represented the mass percentage of  $\text{CuO-ZrO}_2$  to Cl-BC ( $x = 2, 4, 6, 8, 10, 12$ ), Cu represented  $\text{CuO}$  and Zr symbolized  $\text{ZrO}_2$ ).

Besides, to understand the effect of each element on mercury removal,  $\text{Cu-Zr}/\text{BC}$ ,  $\text{Cu}/\text{Cl-BC}$  and  $\text{Zr}/\text{Cl-BC}$  were prepared with the same processes which have the corresponding element blank.

### 2.2. Characterization of catalysts

The catalyst microstructure and morphology were observed by scanning electron microscopy (SEM) (Quanta FEG 250, USA). Every image of catalysts was magnified to  $10,000\times$ . Energy Dispersive X-ray Analysis (EDX) was used to analyze the elementary composition of each catalyst.

Micromeritics Tristar II 3020 analyzer (Micromeritics Instrument Crop, USA) was used to analyze the Brunauer-Emmett-Teller (BET) surface area, pore volume and average pore diameter of catalysts from  $\text{N}_2$  adsorption isotherm.

The X-ray diffraction was used to determine the crystalline phases of catalysts, which carried out on a Rigaku D/Max 2500 (Rigaku Corporation, JPN). And the patterns were obtained in the  $2\theta$  range from  $10$  to  $80^\circ$  with  $\text{Cu K}\alpha$  radiation.

The Temperature-programmed reduction of  $\text{H}_2$  ( $\text{H}_2$ -TPR) was measured on TP-5080 automated chemisorption analyzer (Xian quan Tianjing China).

X-ray photoelectron spectroscopy was measured by a K-Alpha 1063 system (Thermo Fisher Scientific, UK) with an Al  $\text{K}\alpha$  X-ray source. The binding energy was corrected by C1s at 284.6 eV.

The Fourier Transform Infrared Spectroscopy (FT-IR) was conducted on IRAffinity-1 (Shimadzu, Japan). Prior to each test, every sample was treated at  $250^\circ\text{C}$  under pure  $\text{N}_2$  for 1 h to remove adsorbed species on the surface and cooled to room temperature. The FT-IR experiments were conducted immediately after each reaction, and the reaction conditions were as follows:  $\text{NH}_3 + \text{O}_2$  (500 ppm  $\text{NH}_3$ , 6%  $\text{O}_2/\text{N}_2$ ),  $\text{SO}_2 + \text{O}_2$  (400 ppm  $\text{SO}_2$ , 6%  $\text{O}_2/\text{N}_2$ ),  $\text{NH}_3 + \text{NO} + \text{O}_2$  (500 ppm  $\text{NH}_3 + 500$  ppm  $\text{NO}$ , 6%  $\text{O}_2/\text{N}_2$ ),  $\text{H}_2\text{O} + \text{O}_2$  (8 vol%  $\text{H}_2\text{O}$ , 6%  $\text{O}_2/\text{N}_2$ ). The total gas flow was 500 ml/min.

### 2.3. Test of catalytic performance

The experimental setup for evaluating the  $\text{Hg}^0$  removal is shown in Fig. S1.  $\text{Cu-Zr}_x/\text{Cl-BC}$  catalysts were tested in a fixed bed continuous

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