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Fe–Mn–Ce/ceramic powder composite catalyst for highly volatile elemental mercury removal in simulated coal-fired flue gas

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ABSTRACT

The Fe–Mn–Ce/CP catalyst prepared by the incipient-wetness impregnation method was investigated for elemental mercury (Hg^0) removal in simulated coal-fired flue gas. The incorporation of Fe could remarkably enhance the SO_2-resistance of Fe–Mn–Ce/CP catalyst at low temperature, and the existence of water vapor had negative impact on Hg^0 removal efficiency. More than 95% of Hg^0 could be removed at 100 °C under the conditions of 60 ppm HCl, 3% O_2 (*v*/*v*), 5% H_2O (*v*/*v*) and 400 ppm SO_2. Hg-TPD results indicated that Hg^0 adsorption amount decreased after the addition of H_2O or SO_2. The XPS results revealed that the incorporation of Fe could enhance the contents of high valence Mn^{x+} (i.e., Mn^{3+}/Mn^{4+}) and Ce^{3+} species in the composite catalysts, which are favorable for the oxidation process of elemental mercury. The surface characteristics were not the primary factor determining the catalytic activity. Overall, the catalytic performance of the Fe–Mn–Ce/CP catalyst was closely related to the Fe^{3+} state, high ratios of $(Mn^{4+} + Mn^{3+})/Mn^{2+}$ and high content of not fully coordinated cerium species.

Introduction

Mercury is a toxic and persistent pollutant that poses harmful impact on human health and ecology system [1–3]. Coal-fired power plants are recognized as one of the primary anthropogenic source of mercury emission. The effective removal of mercury from the coal-fired power plant flue gas is of great significance [4,5]. Mercury exists in the flue gas mainly in three forms: elemental mercury (Hg^0), oxidized mercury (Hg^{2+}), and particulate bound mercury (Hg^p). The capture of mercury by typical air pollution control devices is depending upon mercury species. Hg^p is usually trapped by ash collection process, such as electrostatic precipitation and fabric filter. Most of water soluble Hg^{2+} can be effectively removed during the process of wet flue-gas desulfurization [1,6–8]. However, Hg^0 is very difficult to be captured by air pollution control devices due to its high volatility and low water solubility [6,9,10].

Lots of technologies have been developed to control the mercury emission from coal-fired power plants, including sorbents-injection, photochemical oxidation and catalytic oxidation [11–17]. The sorbents-injection, such as activated carbon, had not been widely used in the coal-fired power plants due to its high cost and difficulty in recycling [4]. The photochemical oxidation of mercury was difficult to be operated with UV light in the coal-fired power plants [12]. The SCR catalyst, which had been widely used for controlling nitrous oxides emissions in many coal-fired power plants, was found to be capable of oxidizing Hg^0 to Hg^{2+} [18,19]. And catalytic oxidation of Hg^0 in the flue gas was an economical and cost-effective technology. Besides SCR catalyst, many metal oxides had been studied for Hg^0 oxidation, such as Mn, Co, Ce, Cu, and Fe oxides [6,11,20,21]. For instance, the removal efficiency of Hg^0 was up to 90% at about 327 °C with the assistance of 20 ppm HCl over MnO_x/α-alumina catalyst [22]. Remarkably, the activity of $CeO_2–WO_3/TiO_2$ had been extensively investigated and about 95% of Hg^0 can be removed by HCl in the presence of O_2 due to the high active oxygen storage and release capacity of CeO_2 and superior mercury chloridizing ability of HCl [23]. The Mn–Ce/TiO_2

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catalyst was highly active for Hg^0 oxidation at low temperature, but the presence of SO_2 inhibited Hg^0 oxidation greatly. Mn–Fe spinel possessed excellent SO_2 poisoning resistance during the process of mercury removal, while the Hg^0 oxidation ability of related catalysts was very limited [24]. As far as we are concerned, the Fe–Mn–Ce oxide based catalyst was seldom reported in the literature for mercury oxidation.

In this study, the ceramic powder (hereafter, denoted as CP) were used as catalyst support. The ceramic powder was made of kaolin clay that is one type of clays, which is highly abundant and cheap in China [25]. The clays had been used as adsorbents and catalyst supports for the removal of Hg^0 and NO [25,26]. However, the CP had never been used as catalyst supports for the catalytic removal of Hg^0 in flue gas. Compared with the clays, the CP has better thermal stability and conductivity, and also has higher corrosion resistance and better mechanical strength. These characteristics can make the catalysts well adapt the complex environment of flue gas. The Ce/CP, Mn/CP, Mn–Ce/CP and Fe–Mn–Ce/CP catalysts were prepared by incipient-wetness impregnation method with the CP support. The catalytic performances of catalysts were comprehensively studied in the presence of HCl and O_2 in the temperature range of 100–400 °C. The effects of H_2O, SO_2 and HCl concentrations on the activity of Fe–Mn–Ce/CP for mercury oxidation were also investigated.

Materials and methods

Catalyst preparation

All chemicals were purchased from Aladdin Company (Shanghai, China). The kaolin clay was calcined in air at about 1250 °C for 10 h to gain the ceramic. The ceramic crushed into CP, which was dried and used as the support. The loading of each metal element was set to be 1.0 wt% for all catalysts. Typically, 8.0 g of CP carriers were impregnated into 10 mL of single or mixture metal nitrate precursor aqueous solutions (i.e., 0.5206 g $Mn(NO_3)_2$, 0.2480 g $Ce(NO_3)_2{\cdot}6H_2O$ and 0.5771 g $Fe(NO_3)_2{\cdot}9H_2O$). The obtained powders were firstly dried overnight at room temperature, and then dried at 80 °C for 12 h to remove the residual water. Afterward, the dried materials were calcined in air at 500 °C (2 °C/min) for 5 h to gain the final catalysts and they were sieved to 20–40 mesh particles, which were denoted as Mn/CP, Ce/CP, Mn–Ce/CP and Fe–Mn–Ce/CP, respectively.

Catalyst characterization

Powder X-ray diffraction (PXRD) patterns were obtained at room temperature with an X'PertProMPD diffractometer (X'Pert Pro, PANalytical B.V., Holand) using Cu Kα radiation ray in the range of 10–80° (scanning rate of 4°/min). BET surface area was determined by N_2 adsorption at 77 K using Automatic Micropore and Chemisorption Analyzer (ASAP 2020M + C, Micromeritics, USA). The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure (P/P_0) of *ca.* 0.99. XPS analyses were tested on an X-ray photoelectron spectrometer (ESCALAB250, Thermo Scientific, USA) with aluminum Kα radiation to analysis the chemical nature of surface elements.

The experiment of Hg temperature-programmed desorption (Hg-TPD) was carried out on Quantachrome ChemBET-3000TPR-TPD instrument (Quantachrome, USA), and the detailed experiment procedures can be found elsewhere [23]. The experiments consisted of four stages: (1) N_2 swept 0.10 g of Fe–Mn–Ce/CP catalyst in a quartz reactor at 500 °C for 2 h; (2) the catalyst adsorbed about 320 $\mu g/m^3$ Hg^0 (with/without H_2O or SO_2) in N_2 atmosphere for 24 h at 23 or 115 °C until the mercury concentrations were equal in the inlet and outlet of reactor; (3) the N_2 (500 mL/min for 5 h) stream removed the physical adsorbed mercury on the catalyst; (4) TPD measurements were carried out from 23 or 115 to 500 °C at a heating rate of 10 °C/min using N_2 as the carrier gas (500 mL/min), and the concentration of Hg^0 was continuously recorded by Lumex RA 915+ mercury analyzer.

Catalytic activity test

A schematic diagram of the system is shown in Fig. 1. The system consists of a Dynacal Hg^0 permeation device (VICI Metronics), a packed-bed reactor, an online mercury analyzer, and a data acquisition system. The flue gas was generated by a cylinder gas with the desired concentration, and the flow rate was controlled by mass flow controller (MFC). Hg^0 vapor was generated from the Hg^0 permeation unit (placed in a water bath at 40 °C) with a flow of pure N_2. The Hg^0 vapor and mixing gases passed through the gas mixer and then entered the tube reactor together. Both the gas mixer and reactor were made of quartz and kept at the desired temperature by the E-type temperature controller.

In each experiment, 1.0 g of catalyst was filled in the reactor, and the total gas flow rate was maintained as 1.0 L/min. The catalyst was first exposed to the flue gas that contained 41–43 $\mu g/m^3$ Hg^0, 3% O_2 (*v*/*v*) and N_2 (balance gas) for four days, until the Hg^0 breakthrough in the outlet gas reached at least 98% of inlet Hg^0 concentration. This was followed by the tests on catalytic activity in the presence of 20 ppm HCl at different temperatures. The effects of SO_2 (400 ppm), H_2O (5% (*v*/*v*)), and HCl concentrations (20–100 ppm) on Hg^0 removal were further tested. The Hg^0 concentration was measured by Lumex RA 915+ mercury analyzer when the outlet of the Hg^0 reached equilibrium during the process of catalytic oxidation. The mercury removal efficiency over the catalysts was estimated according to Eq. (1):

$$\text{Mercury removal efficiency} = \frac{Hg^0_{in} - Hg^0_{out}}{Hg^0_{in}} \times 100\% \qquad (1)$$

where, $Hg^0{}_{in}$ is the inlet Hg^0 concentration, and $Hg^0{}_{out}$ is the outlet Hg^0 concentration.

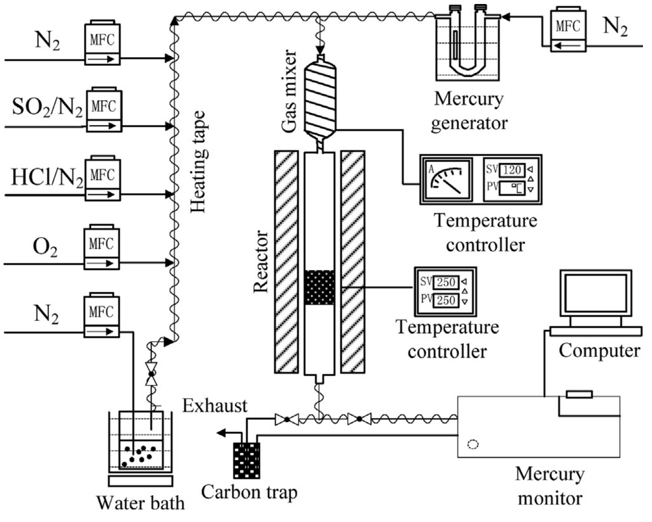

Fig. 1. Schematic diagram of experimental setup.