The behavior of the manganese-cerium loaded metal-organic framework in elemental mercury and NO removal from flue gas

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HIGHLIGHTS

- The MOF was used as Mn-Ce catalyst support for Hg^0 and NO removal.
- The MOF support exhibited superiority in O$_2$ utilization and storage.
- The ratio of Mn^{3+}/Mn^{4+} remain stable and the ratio of Ce^{3+}/Ce^{4+} decreased during the reaction.

ARTICLE INFO

ABSTRACT

Mn-Ce loaded metal-organic framework (MnCe@MOF) catalyst was obtained by incipient wetness impregnation of MOF with manganese-cerium nitrate. The obtained materials were investigated as potential catalysts for elemental mercury (Hg^0) and NO removal from simulate flue gas and the results indicated that MnCe@MOF exhibited superior activity in comparison with the conventional catalysts Mn-Ce loaded ZrO$_2$, especially at low temperatures (<250 °C). It was established that the crystalline structure of MOF support influenced the catalytic behavior in a complex way. The MOF support played an important role in promoting dispersion of active components, improving the Hg^0 adsorption and enhancing oxygen utilization, which resulted in a desirable catalytic activity. To understand the mechanism of the Mn-Ce catalyst better, dynamic valence state evolution during the Hg^0 oxidation for the active components was investigated. The ratio of Mn^{3+}/Mn^{4+} remained constant during the reaction at various temperatures, indicating the stability of Mn in the catalytic process. However, the ratio of Ce^{3+}/Ce^{4+} gradually decreased with extended periods of reaction time, which most likely lead to the decreased of chemical adsorbed oxygen on the catalyst.

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1. Introduction

Mercury is an important environmental pollutant that aroused worldwide concern due to its persistence, bioaccumulation in the ecosystem and intense neurotoxicity to human [1]. Anthropogenic mercury emissions accounts for approximately 60% of the total atmospheric emissions and combustion of coal is the largest contributor to the anthropogenic sources of mercury emissions [2,3]. _ENREF_2 Mercury in coal combustion flue gas exists in three forms including oxidized mercury (Hg^{2+}), particle-bound mercury (Hg$_p$) and elemental mercury (Hg^0). Among them, Hg^0 accounted for 66–94% of total mercury in flue gas [4]. Hg$_p$ and Hg^{2+} can be effectively removed by particulate control devices and/or wet flue gas desulfurization (WFGD) system [5,6]. However, Hg^0 is very difficult to be captured due to its high volatility and low solubility [7,8]. Catalytic oxidation was proved to be one of the most effective technologies for Hg^0 removal from flue gas [9–15]. By catalytic oxidation, Hg^0 could be translated into Hg^{2+} and captured in the WFGD system. Among various active components for Hg^0 catalytic removal, Mn and Ce based oxides have attracted great interest as catalysts due to their high redox property, oxygen storage capacities and the low temperature activity [17,18].

Many researches proved that loading active components on the support materials could achieve better catalytic performance [19–25]. Metal-organic frameworks (MOFs) are a class of porous, crystalline material constructed from metal cluster nodes and organic ligands. The advantages of high porosities, specific surface areas and versatility of structure made it very attractive in many fields [26], including the removal of Hg^0 and NO from flue gas [27–29].

The use of MOF as support material in catalytic reaction attracted wide attention. Han et al. [30] loaded cobalt on MOF by impregnation, which exhibited an evidently improvement in catalytic performance in comparison with that cobalt oxide or cobalt oxide loaded on silica nanospheres. Henschel et al. [31] incorporated palladium particles into MOF via incipient wetness impregnation and it exhibited higher catalytic activity than that of traditional substrate (activated carbon) supported palladium in hydrogenation reaction.

In pioneering work, Cavka et al. [32] published the synthesis and characterization of the metal-organic framework UiO-67 $(Zr_6O_4(OH)_4(C_{12}H_{10}(CO_2)_2)_6(DMF)_x(H_2O)_y)$, which composed of Zr^{4+} clusters and linear 4,4′-biphenyldicarboxylic acid ligands. UiO-67 was proved as a very promising candidate for a catalyst support due to the highly developed three dimensional pore systems and the high thermal, chemical and mechanical stability [33,34].

In this study, the catalyst with Mn-Ce supported on UiO-67 was prepared by a simple and facile method involving impregnation followed by a heat treatment method. Catalytic activity of the Mn-Ce loaded MOF as well as catalytic mechanisms in Hg^0 oxidation was investigated. Besides, recently studies found that Mn-Ce catalysts could achieve Hg^0 catalytic oxidation as well as selective catalytic reduction (SCR) of NO from flue gas. The simultaneously removing Hg^0 and NO have the benefit of reducing the apparatus volume and operating costs [35]. Therefore, the NO removal efficiency of the catalyst and the mutual influence of the Hg^0 and NO removal were also investigated in this study.

2. Experimental section

2.1. Preparation of the catalysts

All of the reagents were purchased from Beijing J&K Co., Ltd. (Beijing, China). The synthesis of UiO-67 was performed according to the previous report by Zhu et al. [36]. The Mn-Ce loaded catalyst was synthesized via incipient wetness impregnation of UiO-67 using $Ce(NO_3)_2$ and $Mn(NO_3)_2$ as precursor diluted in ethanol. 0.32 mL of $Ce(NO_3)_2$ and 0.32 mL of $Mn(NO_3)_2$ (50 wt% solution in H_2O) were added to 20 mL ethanol to obtain manganese solution (the mass ratio of Mn/Ce = 1 and the Mn and Ce loading were both 5 wt% in the preparation procedure). 1.5 g of MOF was impregnated with the solution under vigorous stirring at room temperature for 3 h, at 60 °C for 3 h and at 80 °C for 2 h. The solid sample was then dried in oven at 60 °C for 12 h and then heated at 300 °C for 5 h to achieve Mn-Ce impregnated MOF, which was denoted as MnCe@MOF. Mn-Ce impregnated ZrO_2 was obtained by impregnated 1.5 g ZrO_2 with cerium and manganese ethanolic solution. The following procedures were same as the preparation of MnCe@MOF and the obtained material was denoted as MnCe@ZrO$_2$.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were recorded over the range of 5–80° (2θ) on a Bruker AXS GmbH X-ray diffractometer (Bruker D8 FOCUS, Germany) with Cu Kα radiation. The textural characteristics of the samples were determined by N_2 adsorption at −196 °C on an ASAP 2020/Tristar 3000 system (Micromeritics, America). The specific surface areas were calculated using the BET method, and the specific pore volumes were calculated by the BJH method. The concentrations of active species in the catalysts were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Varian Inc.) The morphologies of the catalysts were investigated by Scanning Electron Microscope-Energy Dispersive Spectrometer (SEM-EDS) (Phenom-World BV, Netherlands).

2.3. Catalytic performance

The activities of catalysts for Hg^0 and NO removal were tested with a bench scale catalytic activity test system (Fig. 1). Simulated flue gas was introduced into a quartz reactor, where catalyst loaded. The simulated flue gas contained NO, NH_3 with N_2 as carrier gas, the O_2 concentration in the experimental system was set as 5% of the total simulate flue gas. The components of the simulated flue gas were ~35 μg/m³ Hg^0, 500 ppm NO, 500 ppm NH_3 balanced N_2. The total flow rate of the flue gas in Hg^0 removal experiment was set as 1500 mL/min based on the Hg^0 analytical instrument requirement, the GHSV was 225,000 h^{-1} in section 3.2.1. The GHSV was set as 450,000 h^{-1} in section 3.2.3 for better understanding the contrast performance in the experiment. In the NO removal experiment, the total flow rate of the flue gas was ~450 mL/min. With the same equal volumes of catalyst in Hg^0 removal experiment, the GHSV in NO removal was 67,500 h^{-1}.

As shown in Fig. 1, when "a-b" air holes of the valve were connected, the flue gas bypassed the reactor and the inlet Hg^0 or NO concentration was measured. When "a-c" air holes of the valve were connected, the flue gas pass through the adsorbent and the outlet Hg^0 or NO concentration was measured. The Hg^0 and NO removal efficiency (defined as η) were calculated on the basis of gases concentrations in the inlet and outlet as Eq. (1). The Hg^0 concentrations at the inlet and outlet of the reactor were measured by H11-QM201H mercury monitoring system (Mercury VM-3000, mercury instruments, China). The NO concentration was monitored respectively by a Flue Gas Analyzer (KM900, Kane 100 international limited, UK).

$$\eta = (C_{in} - C_{out})/C_{in} \times 100\% \tag{1}$$

where C_{in} and C_{out} represent the Hg^0 or NO concentration at the inlet and outlet of the reactor, respectively.

3. Results and discussion

3.1. Characterization of the catalysts

Crystal structures of the catalysts were characterized using XRD analysis and the results are shown in Fig. 2. The XRD pattern of undoped MOF could be well indexed to UiO-67 with an octahedrons crystalline structure [36]. The XRD pattern of the impregnated MnCe@MOF catalyst showed no apparent loss of crystallinity, revealing the integrity of the MOF matrix. Zirconium oxide with monoclinic structure was observed in the XRD patterns of ZrO_2 and MnCe@ZrO$_2$ according to the JCPDS 37-148. However, no visible diffractions of manganese and cerium species were observed in the XRD patterns of MnCe@MOF and MnCe@ZrO$_2$, which might be due to the Mn-Ce oxides are non-crystal or the sizes of metal oxides were below the detection limit of the technique [30].

The texture properties and atom concentrations of the materials were analyzed by N_2 adsorption and ICP-OES, and the results were listed in Table 1. The data showed that MOF possessed the highest BET specific surface area of 1376.95 m² g^{-1}. After the loading of Mn-Ce species, the Mn-Ce oxide particles deposited in the pores of MOF and partial blocked the cages of the frameworks, leading to slightly decreased BET surface area and pore volume. However, a large BET surface area of 1015.13 m² g^{-1} was still obtained for MnCe@MOF due to the well preservation of the octahedral crystalline structure of the material. A support material with a high surface area could endow the catalysts with high dispersion of active components. The developed porous structure was expected to facilitate gas molecules contact and adsorbed on catalyst, therefore benefit for the catalytic reaction [37].