



## Full Length Article

# Simultaneous removal of NO and Hg<sup>0</sup> using Fe and Co co-doped Mn-Ce/TiO<sub>2</sub> catalysts



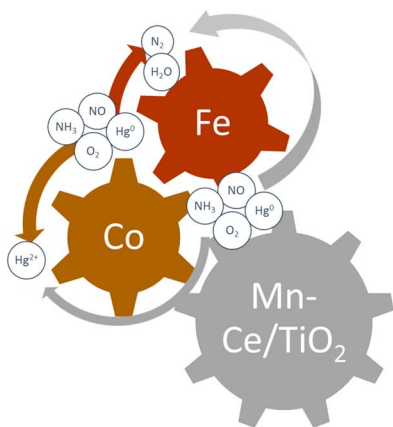
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## GRAPHICAL ABSTRACT



## ARTICLE INFO

**Keywords:**

Simultaneous removal  
Nitric oxide  
Elemental mercury  
Fe–Co

## ABSTRACT

Fe and Co co-doped Mn-Ce/TiO<sub>2</sub> (MCT) catalysts were investigated for the simultaneous removal of nitric oxide (NO) and elemental mercury (Hg<sup>0</sup>) at reaction temperature lower than 200 °C. The catalysts were characterized by Brunauer–Emmett–Teller (BET), temperature program reduction (TPR), scanning electron microscope (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) analysis. The experimental results showed that the co-doped 2Fe4Co-MCT catalyst exhibited better performance for the simultaneous removal of NO and Hg<sup>0</sup> compared to Fe or Co doped catalysts. This could be due to higher BET surface area and better redox property of 2Fe4Co-MCT catalyst. In addition, we propose that chemisorbed O<sub>2</sub> played a dominant role in selective catalytic reduction (SCR) of NO while lattice O<sub>2</sub> played a key role in Hg<sup>0</sup> oxidation. The results also indicate that the introduction of Fe species enhanced the activity of SCR, whereas the introduction of Co species enhanced the oxidation of Hg<sup>0</sup>. The synergistic effect of Fe and Co species in the 2Fe4Co-MCT catalyst are also suggested to be an important mechanism for simultaneously removing NO and Hg<sup>0</sup>.

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## 1. Introduction

Mercury emitted from coal-fired power plants, cement kiln and solid waste incineration units normally has three forms: 1) elemental mercury ( $\text{Hg}^0$ ), 2) Oxidized mercury ( $\text{Hg}^{2+}$ ) and 3) Particle-bond mercury ( $\text{Hg}^p$ ) [1,2].  $\text{Hg}^p$  can be easily removed by dust removal systems such as electrostatic precipitator or bag-type dust remover.  $\text{Hg}^{2+}$  is soluble in water and can be easily captured by wet flue gas desulfurization (WFGD) scrubber. However,  $\text{Hg}^0$  is volatile and insoluble in water. Common air pollution control devices (APCDs) is normally used to remove mercury. The overall efficiency of mercury removal in APCDs ranges from 43.8% to 94.9%, depending on the form of mercury and the operating conditions [3]. To meet the increasingly strict environmental standards of mercury control, it is necessary to develop an enhanced or supplementary process to increase the removal of mercury.

There are two key approaches to enhance the removal of mercury from flue gas. The first method is to absorb mercury using adsorbents. The other method is to oxidize  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  which can then be captured by downstream WFGD. The injection of powder carbon materials has been commercially applied for the removal of mercury from flue gas. To enhance the chemisorption of  $\text{Hg}^0$  on the surface of carbon-based adsorbents, various reagents have been used to modify these carbonaceous adsorbents. For example, activated carbons were treated by acids including  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$  or  $\text{HClO}_4$  to enhance the removal of  $\text{Hg}^0$ , due to the formation of oxygen-containing (C-O) or chlorine-containing groups (C-Cl) on the surface of the adsorbents [4]. Various kinds of chlorides such as  $\text{ZnCl}_2$  [5–8],  $\text{FeCl}_3$  [7] and  $\text{NH}_4\text{Cl}$  [8] were used as predecessors to modify carbonaceous adsorbents to improve the efficiency of mercury removal. The chemisorption between carbonaceous materials and  $\text{Hg}^0$  was enhanced after the modification of adsorbent such as sulfur treatment [9] and the addition of  $\text{CeO}_2$  [7,10]. However, using sorbent to remove  $\text{Hg}^0$  has some drawbacks [11]: 1) a large amount of sorbent is required for the adsorption of  $\text{Hg}^0$  indicating the high cost of sorbent use; 2) the disposal challenges of the exhaust sorbents mixed with fly ash.

In flue gas, the oxidation of  $\text{Hg}^0$  to  $\text{Hg}^{2+}$  could be obtained using oxidants such as a mixture of urea and  $\text{KMnO}_4$  solution [12],  $\text{NaClO}_2$  solution [13–15],  $\text{H}_2\text{O}_2$  solution [16,17],  $\text{K}_2\text{FeO}_4$  [18], and Fenton reagent [19,20]. However, the corrosive nature of the oxidants limits the deployment of such technology, even though the direct oxidation of  $\text{Hg}^0$  using oxidants has higher removal efficiency. Therefore, the oxidation of  $\text{Hg}^0$  by catalyst seems to be a preferable alternative because it has a low secondary pollution.

$\text{CePO}_4$  catalyst was employed to capture elemental mercury and showed much better performance in  $\text{Hg}^0$  removal compared with a commercial SCR catalyst [21]. The  $\text{CePO}_4$  catalyst promoted the formation of nitrogen dioxide ( $\text{NO}_2$ ) from NO oxidation. And  $\text{NO}_2$  was effective to react with  $\text{Hg}^0$  ad-species (e.g.,  $\text{Hg}_2\text{O}$ ) [21].  $\text{LaMnO}_3$  perovskite oxide was chosen to remove  $\text{Hg}^0$ . The results indicated that mercury primarily existed as  $\text{Hg-O}$ , and the used  $\text{LaMnO}_3$  catalyst can be regenerated using thermal desorption [22].  $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$  have been investigated to oxidize  $\text{Hg}^0$  at low temperature of 100–200 °C [23]. Due to the low cost and the excellent performance for mercury oxidation,  $\text{TiO}_2$ -supported catalysts have been widely investigated to remove mercury including molybdenum (Mo) and ruthenium (Ru) modified  $\text{V}_2\text{O}_5\text{-WO}_3/\text{TiO}_2$  [24], Ce-doped  $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2$  [25], nanosized  $\text{V}_2\text{O}_5/\text{TiO}_2$  [26] and  $\text{MnO}_x\text{-CeO}_2/\text{TiO}_2$  [27,28].

In addition, more strict regulations are applied to reduce the emission of other pollutants (e.g.,  $\text{NO}_x$ ) in coal-fired power plants. At the moment, medium temperature selective catalytic reduction (SCR, around 350 °C) is commercially available for the removal of  $\text{NO}_x$  in coal-fired power plants. However, the installation of medium temperature SCR system needs a large space which should be located before the removal of particulate matter. Installing low temperature SCR system (less than 200 °C) could solve the problem, as the SCR catalyst is unlikely to be deactivated compared with the catalyst for medium-

temperature SCR. Therefore, the simultaneous removal of NO and  $\text{Hg}^0$  by the oxidation at low temperature SCR system employing various catalysts has been proposed and investigated [29,30].

In terms of low temperature SCR, MnOx based catalyst has been widely studied [31–33]. Ji et al. [34] found that  $\text{MnO}_x/\text{TiO}_2$  catalyst could achieve high efficiency for the removal of NO at low temperature. Similarly,  $\text{CeO}_2$  has a large capacity of oxygen storage and has been extensively used as a catalyst for low temperature SCR [35,36]. Our previous study showed that Ce was an efficient promoter in low temperature SCR [37]. Additionally, interactions between  $\text{CeO}_2$  and MnOx were found to be crucial to improve SCR performance as reported by Qi et al. [38].

Therefore, a catalyst containing Mn, Ce and  $\text{TiO}_2$  seems to be effective for the simultaneous removal of  $\text{NO}_x$  and  $\text{Hg}^0$ . In addition, Fe and Co have been widely examined as active sites for SCR process. Qi et al. [39] found that the addition of iron oxide not only increased the NO conversion but also increased the resistance to  $\text{H}_2\text{O}$  and  $\text{SO}_2$ . Shen et al. [40] also reported that the doping of iron enhanced the dispersion of Mn and Ce on the surface of the catalyst. The presence of  $\text{Fe}^{3+}$  active sites could promote the oxidation of NO to  $\text{NO}_2$  by  $\text{O}_2$  resulting in an improvement of  $\text{NO}_x$  reduction in the  $\text{NH}_3$ -SCR process [41]. The formation of Co-Mn oxides was found to be important in SCR process [42,43]. In addition, Co oxides have been reported to efficiently absorb active oxygen by generating oxygen vacancy derived from the conversion of  $\text{Co}^{3+}/\text{Co}^{2+}$  [25,44]. The addition of Co into nanoporous nickel phosphate has been reported to enhance the catalytic efficiency of  $\text{NO}_x$  reduction [45,46]. However, to the best of our knowledge, the co-doping of Fe and Co in Mn-Ce/ $\text{TiO}_2$  catalyst for the simultaneous removal of NO and mercury has not been reported in literature. In this study, a series of Mn-Ce/ $\text{TiO}_2$  catalysts modified with Fe and Co have been investigated aiming to enhance the simultaneous removal of NO and  $\text{Hg}^0$  at low temperature.

## 2. Experimental

### 2.1. Catalyst preparation

All catalysts were prepared by wet impregnation method. An appropriate proportion of precursors (the nitrate of Mn, Ce, Fe and Co) were dissolved in excess deionized water and a corresponding amount of  $\text{TiO}_2$  was added to the solution. The molar ratio of (Fe + Co):Mn:Ce: $\text{TiO}_2$  was 0.075:0.12:0.024:1. The total moles of Fe and Co were kept constant while Fe/Co ratios were changed. The precursors were mixed using a water bath with continuous stirring at 80 °C. The samples were then dried in an oven at 120 °C overnight and then calcined in an electric furnace at 500 °C for 4 h. The catalysts were ground and sieved to granules (40–80 mesh) for further characterizations and experimental uses. Mn-Ce/ $\text{TiO}_2$  catalyst is indicated as MCT. MCT catalyst with Fe addition is assigned as 6Fe-MCT. In addition, MCT catalyst with Co addition is assigned as 6Co-MCT. And 2Fe4Co-MCT indicates the MCT catalyst having a Fe/Co molar ratio of 2:4.

### 2.2. Catalytic activity test

The catalytic activities were carried out in a fixed-bed reactor as shown in Fig. 1. The flue gases including NO,  $\text{NH}_3$ ,  $\text{O}_2$  and  $\text{N}_2$  were obtained from the compressed gas tanks and were adjusted by mass flow controllers (MFC). A mercury permeation tube (VICI Metronics Inc., USA) (“U” type tube) was used to provide a uniform and stable release of elemental mercury vapor by the carrier gas. The “U” type tube was dipped into a water bath. The concentration of  $\text{Hg}^0$  entering the reactor was controlled by regulating the temperature of the water bath and the flow rate of the carrier gas. All gases were converged and blended in a mixer first and then fed to the reactor. NaOH solution was used to remove the residual NO and  $\text{NH}_3$ , while a silica gel was used to eliminate the effect of water vapor. The total gas flow rate was

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