



Full Length Article

Catalytic oxidation of Hg⁰ in flue gas over Ce modified TiO₂ supported Co-Mn catalysts: Characterization, the effect of gas composition and co-benefit of NO conversion



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HIGHLIGHTS

- Co_xMn₅/TiCe_y catalysts exhibited good capacity of catalytic oxidation of Hg⁰ and NO.
- Ce species existed mainly in amorphous phase.
- Co promoted the generation of Mn₂O₃ but obstructed the dispersion of MnOx.
- Multiple redox couples and surface oxygen species contributed to Hg⁰ and NO oxidation.
- O₂ promoted the oxidation activity but SO₂ generally suppressed it.

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ABSTRACT

A series of Ce modified TiO₂ supported Co-Mn catalysts (Co_xMn₅/TiCe_y) prepared by sol-gel method and impregnation method were evaluated for simultaneous catalytic oxidation of Hg⁰ and NO in the simulated flue gas. Results showed that the catalysts exhibited good capacity of simultaneous catalytic oxidation of Hg⁰ (around 70%) and NO (around 40%) at 300 °C using a simulated flue gas (Hg⁰, NO, SO₂, O₂, H₂O and balanced N₂). These catalysts were investigated in detail by means of N₂ adsorption-desorption, XRD, Raman spectroscopy, TEM and XPS. The characterization results indicated that physical characteristics of catalysts were not the main contributor for Hg⁰ and NO oxidation. Ce species existed mainly in amorphous phase. The addition of CeOx might lead to a migration of Co and Mn species from bulk to surface. The addition of Co could promote the generation of Mn₂O₃ but obstruct the dispersion of MnOx on the surface of catalyst. An appropriate increasing loading amount of CoOx or CeOx would be preferable for the improvement of activity performance. The presence of Co³⁺/Co²⁺, Mn⁴⁺/Mn³⁺ and Ce⁴⁺/Ce³⁺ redox couples as well as surface oxygen species contributed to the Hg⁰ and NO oxidation. A possible synergetic effect Among Co, Mn and Ce species might improve the activity further. Furthermore, an increased oxygen concentration could facilitate the Hg⁰ and NO oxidation. NO was observed to promote Hg⁰ oxidation with the presence of O₂. SO₂ led to a certain decrease of Hg⁰ oxidation efficiency due to the competitive adsorption-H₂O had a slightly inhibitory impact on Hg⁰ oxidation. Moreover, NO oxidation was more susceptible to SO₂ than Hg⁰ oxidation over the catalyst.

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1. Introduction

Due to its persistent and serious toxicity to ecosystem and humanity, mercury emitted from coal-fired power plants, which accounts for a significant fraction of the anthropogenic emissions, has attracted increasing attentions [1]. Through the coal combus-

tion process, mercury generally speciates to three forms: elemental mercury (Hg⁰), oxidized mercury (Hg²⁺) and particulate-bound mercury (Hg^p) [2,3]. Oxidized mercury can be easily captured by the flue gas desulfurization systems due to its high solubility in water. Particulate control devices such as electrostatic precipitators and fabric filters could effectively collect most of the particulate-bound mercury. However, the control of gaseous elemental mercury from coal-fired power plants becomes a thorny issue because of its high equilibrium vapor pressure and low solubility in water.

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Removal of this contaminant in compliance with the environmental emission standard is necessary and many efforts have been made to explore an effective control method especially for Hg⁰ removing (e.g. supported noble metals, activated carbon injection, modified fly ash) [4–8]. However, many of these approaches have shown certain limitations such as high cost and limited availability with respect to their potential for practical applications. Due to its co-benefit of promoting mercury oxidation removal in the process of NO_x reduction, the approach of removing mercury over selective catalytic reduction (SCR) catalysts has been extensively researched over the past few years. Nevertheless, according to the results of many field and pilot tests [9–11], the oxidation efficiency of Hg⁰ by SCR process is generally not as high as expected resulting from two inevitable limiting factors. First of all, the injection of a large amount of ammonia could severely inhibit the gas-solid interface reaction between Hg⁰ and SCR catalysts (competitive relationship between DeNO_x reaction and mercury oxidation). Secondly, the conventional SCR catalysts are not effective enough for Hg⁰ oxidation in the absence of HCl (the dependence on chlorine). The chlorine content of feed-coal in China is low (63–318 mg/kg) [12,13]. Substitution of NH₃ with NH₄Cl in order to increase the HCl content in flue gas is obviously uneconomical.

In addition to HCl, O₂ is also an important oxidant for mercury removal. Alternatively, using O₂ in flue gas to oxidize elemental mercury is a relatively simple and economic method. Moreover, NO and SO₂ in flue gas could be partially transformed into NO₂ and SO₃ separately over a metal oxide catalyst with the aid of O₂ [14], which might be also beneficial to the mercury oxidation [25,51]. Thus, a combined oxidation of Hg⁰ and NO over catalysts could not only enhance the mercury oxidation but also promote the removal of NO, since Hg²⁺ and NO₂ could be both easily captured by wet flue gas desulfurization systems (WFGDs). Based on this line of thinking, the problem of poor mercury oxidation efficiency mentioned above could be resolved by setting the oxidation process of Hg⁰ at the downstream of SCR process and simultaneously achieve the removal of NO not consumed by SCR process. In this way, mercury could be oxidized into easily captured Hg²⁺ without the influence of NH₃ and dependence on chlorine as the main oxidants involved are oxygen sometimes together with NO and SO₂.

From this background, it is clear that searching for a suitable catalyst which not only has higher Hg⁰ removal efficiency but also can promote the NO removal from the flue gas is of great necessity. Among the extensively researched catalysts, the manganese-based and cobalt-based catalysts were thought to be one of the best candidates for Hg⁰ oxidation or NO oxidation such as MnO_x or Co₃O₄ supported by alumina, titania, zirconia and ceria [15–21]. Moreover, the Ce modified TiO₂ carrier has been widely studied due to its significant oxygen storage capacity originated from cerium redox shift and good resistance to water vapor as well as SO₂ [22,23]. Ce containing catalysts could facilitate the NO oxidation [24], which might correspondingly lead to a positive effect on mercury oxidation [25]. To the authors' knowledge, the related research on cobalt manganese oxides supported on Ce modified TiO₂ carriers for simultaneous catalytic oxidation of Hg⁰ and NO has rarely been reported in the literatures.

Therefore, the main objective of the present work is to perform an experimental study to investigate the performance of Ce modified TiO₂ supported Co-Mn catalysts (Co_xMn₅/TiCe_y) for catalytic oxidation of Hg⁰ in the absence of HCl and its co-benefit of NO conversion. The characterization of catalysts and essential analysis was conducted to illuminate the structural and textural properties of Co_xMn₅/TiCe_y catalysts using methods such as N₂ adsorption-desorption, XRD, Raman spectroscopy, TEM and XPS. The roles of flue gas components (O₂, NO, SO₂, H₂O) in Hg⁰ oxidation and NO oxidation were further investigated. It can provide some basic

insights into the adaption of Ce modified TiO₂ supported Co-Mn catalysts for simultaneous catalytic oxidation of Hg⁰ and NO in flue gas. Mercury and NO oxidation may involve a catalytic oxidation assisted by multiple redox couples and surface oxygen species (chemisorbed oxygen and lattice oxygen) over the catalyst. The mechanism in detail over the present catalytic system will be studied in the future.

2. Experimental

2.1. Catalyst synthesis

The Ce modified TiO₂ (Ti-Ce composites) was prepared by sol-gel method. Typically as follows: 3.15 g Ce(NO₃)₃·6H₂O, 90 ml anhydrous ethanol and 4.5 ml deionized water were mixed to attain A solution; 22 ml titanate was added into anhydrous 88 ml ethanol under stirring to attain B solution; then A solution was drop-wisely added into B solution under continuous stirring (meantime some acetic acid added). The obtained mixed solution was kept statically at 25 °C for 36 h and then dried at 85 °C for 24 h. The resultant solid was calcined under flow air at 500 °C for 4 h to obtain Ce modified TiO₂ which was denoted as TiCe_y (the CeO₂/(CeO₂ + TiO₂) mass ratio = y%, y = 10, 20, 30).

The Co-Mn loaded catalysts were synthesized by impregnation method with a Mn loading of 5 wt.% and Co loading of x wt.% (x = 5, 8, 12, 15). TiCe_y was impregnated with an aqueous solution of the desired amount of manganese acetate and cobalt nitrate under stirring. Then the mixture was exposed to an ultrasonic bath for 1 h, dried at 100 °C for 15 h and subsequently calcined at 500 °C for 3 h in air. The obtained catalyst was denoted as Co_xMn₅/TiCe_y.

2.2. Catalyst characterization

The specific surface areas (BET method) of different catalysts were tested by using nitrogen physisorption at liquid nitrogen temperature (ASAP2020, Micromeritics Inc.). The pore size and pore volume of the samples were calculated by Barrett-Joyner-Halenda (BJH) method. X-ray diffraction measurements were carried out with a diffractometer (D/MX-III A, Rigaku, Japan) by using Cu K α radiation. The scanning range was from 20° to 80° (2 θ) with a step size of 0.019° and step time of 13.125 s. The Raman spectra were collected on a laser Raman spectrometer (INVIA, RENISHAW, UK) with an He/Ne ion laser beam (λ = 633 nm). The morphologies and structures of the selective sample were investigated by using a JEM-2100 field emission transmission electron microscope (TEM). X-ray photoelectron spectroscopy measurements (ESCALAB 250Xi, Thermo Fisher) were used to determine the binding energies of Co 2p, Mn 2p, Ti 2p, Ce 3d, O 1s and Hg 4f with Al K α (h ν = 1486.6 eV). The C 1s line at 284.6 eV was taken as a reference for the binding energy calibration.

2.3. Catalyst activity measurement

The catalytic oxidation of Hg⁰ and NO was performed in a fixed-bed system. 0.5 g of catalysts were filled in the reactor after being pretreated at 200 °C for 1 h in N₂ stream to remove the absorbed water vapor and other impurities. The reactor was a quartz tube (i. d. 10 mm), which was wrapped in a tubular electric furnace with a temperature controlling program. A mercury permeation tube (HE-SR, VICI Metronics, USA) was used as the source of elemental mercury, which was placed in an oil bath with a temperature of 60 °C. Mercury vapor was carried by N₂ and mixed thoroughly with other gases in a buffer tank before entering the reactor. Hg⁰ concentration in the system was controlled at about 30 μ g/m³. Water vapor was generated from a heated water bubbler. The reactant gas

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