



Full Length Article

Influence of textures, oxygen-containing functional groups and metal species on SO₂ and NO removal over Ce-Mn/NACFang Ning-Jie^a, Guo Jia-Xiu^{a,b,*}, Shu Song^a, Li Jian-Jun^{a,b}, Chu Ying-Hao^{a,b}^a College of Architecture and Environment, Sichuan University, Chengdu 610065, China^b National Engineering Research Center for Flue Gas Desulfurization, Chengdu 610065, China

ARTICLE INFO

Article history:

Received 13 February 2017

Received in revised form 6 April 2017

Accepted 8 April 2017

Available online 21 April 2017

Keywords:

Activated carbon

Manganese

Cerium

Desulfurization

Denitration

ABSTRACT

A series of Ce and Mn bimetal modified activated carbon were prepared by excessive impregnation method. The removal of SO₂ or NO was carried out at a fixed bed reactor under a simulated flue gas. The results showed that Ce(1)-Mn/NAC exhibits excellent SO₂ removal capacity at 80 °C with breakthrough sulfur capacity of 113 mg/g, and Ce(7)-Mn/NAC displays a good NO removal capacity and maintains 100% removal efficiency in the range of 130–220 °C. The specific surface area and pore volume decline first and then increase with the increase of Ce loadings, and the pore sizes of samples center at 0.4–4 nm. C=O and O=C–O groups are favorable for SO₂ oxidation, and C–O can promote the oxidation of SO₂ and NO. The –OH groups can promote the adsorption and oxidation of SO₂ and NO, but the ways that they acted are different. Mn₂O₃, Mn₃O₄, Ce₂O₃ and CeO₂ are observed in fresh samples, but MnO₂ and Ce₂(SO₄)₃ are detected and Ce₂O₃ disappears after desulfurization. MnO₂ appears after denitration when Ce loading amount is small, but it disappears gradually with the increase of Ce loadings. CeO₂ gradually decreases while Ce₂O₃ is increasing after denitration, indicating that CeO₂ can convert into Ce₂O₃ in NO removal process.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

The emission of SO₂ and NO_x from burning of fossil fuels has brought many environmental problems, such as haze, acid rain and photo-chemical smog. Separate removal of SO₂ or NO_x has been widely studied. For example, activated carbon/coke can be used to remove SO₂ from flue gas [1]. Selective catalytic reduction (SCR) with NH₃ has been mainly applied for NO removal at high temperature (350–420 °C) over V₂O₅–WO₃(MoO₃)/TiO₂ [2]. Many measures have been considered to improve the removal ability of SO₂ and NO. Liu et al. [3] have found that Fe modified activated carbon shows excellent removal ability of SO₂. When rare earth oxides are loaded onto the activated semi-coke surface, a high NO conversion is obtained at low temperature [4]. However, separate control of SO₂ and NO results in high operational costs. Catalyst deactivation and NH₃ escape will seriously affect the life time and catalytic ability of catalysts. So, simultaneous removal of SO₂ and NO has caught great interesting, including the electron beam with ammonia (EBA), the pulse corona-induced plasma chemical process

(PPCP), the activated coke (AC) methods. Regretfully, when catalyst is installed at upstream of dust control and desulfurization, these technologies do not fundamentally solve the catalyst poisoning because of dust and SO₂ with high concentration. Therefore, separate deSO₂/NO_x at low temperature in one device will be promising and gradually gets more attention.

Recently, Mn oxides, as active components, can highly disperse on an inert carrier with a large surface to remove SO₂ and NO_x because of labile oxygen atoms [5]. Activated carbon (AC) materials have attracted much attention due to huge surface area, rich pore structure and oxygen-containing functional groups on the carbon surface [3]. AC can selectively adsorb SO₂ and NO_x and achieve a high performance even at low concentrations [6]. When Mn oxides loaded onto the carbon materials, they can improve SO₂ removal ability [7,8] and exhibit better NH₃-SCR activity at low temperature and a more extensive operating temperature window [7]. However, they easily lose activity because NH₃ can react with SO₂ to form ammonium sulfates in the presence of O₂ and H₂O and deposits on the catalyst surface [8]. Therefore, further efforts must be carried out to improve SO₂ resistance of SCR catalysts. Ceria (CeO₂), as an oxygen storage material, can store/release oxygen during the redox process due to the Ce⁴⁺ ↔ Ce³⁺ as well as the transfer of electrons, ions and oxygen [9,10]. Ceria-based materials

* Corresponding author at: College of Architecture and Environment, Sichuan University, Chengdu 610065, China.

E-mail address: guojiaxiu@scu.edu.cn (J.-X. Guo).

are commonly used as catalysts and promoters in several heterogeneous reactions [11,12]. Some studies have shown that Ce–W catalyst exhibits high catalytic performance of NO [13] and CeO₂ shows good SO₂ resistance during NH₃–SCR process [14]. In order to obtain better performance of denitration, Mn and Ce are simultaneously loaded on TiO₂ to remove NO_x. They achieve a 92% conversion of NO at 120 °C [15], and their interactions are critical for sulfur resistance [16]. The sulfur-resistant behavior is improved remarkably because of Ce doping [17]. When AC is used as carrier to load Mn and Ce, NO conversion maintains at 99% in the range of 120–250 °C and the synergistic effects of Mn and Ce improve greatly the catalytic ability of NO comparing to single metal oxides [18]. However, to the best of our knowledge, there are few reports for the removal of SO₂ by Ce and Mn bimetal modified AC, and the main role of Ce and Mn in desulfurization and denitration is scarce. Therefore, this work is to explore the removal capacity of SO₂ or NO on Ce and Mn bimetal modified AC treated by nitric acid. The influence factors on catalytic ability are also discussed when catalyst bed temperatures are only changed, including oxygen-containing functional groups, the adsorption diameter of gas molecules and metal oxides species. The main role of Ce and Mn in desulfurization and denitration is also involved. The results will significantly improve the SO₂ and NO removal technology in flue gas.

In this paper, manganese oxides and cerium oxides with different Ce/Mn ratios were impregnated on AC treated by nitric acid. The physical and chemical properties of samples were characterized by N₂ adsorption/desorption isotherms, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) before and after SO₂ and NO removal.

2. Experimental

2.1. Pretreatment of activated carbon

All samples were prepared by impregnation method. All chemicals used in this work were analytic reagent (AR). The original activated carbon, purchasing from Henan Changge Chemical Co., Ltd., China, was ground and sieved to 10–20 mesh. These carbons were immersed in distilled water and boiled in an electric furnace for 30 min. After that, the sample was filtered and washed in distilled water until the washing liquid became neutral. The sample was dried in an oven at 105 °C for 12 h, and the washed carbon was named as AC. The washed AC was completely immersed into 39 wt% HNO₃ solution and heated at 60 °C for 2 h in water bath. Then, the sample was filtered and washed with distilled water until the washing liquid became neutral. Finally, the sample treated by HNO₃ was dried in an oven at 105 °C for 12 h and denoted as NAC.

2.2. Catalyst preparation

Manganese nitrate and cerium nitrate were used as precursors. The NAC was completely immersed into manganese nitrate solution with an appropriate concentration to achieve 5 wt% Mn loading. During the impregnation, the mixture was stirred constantly for 30 min and placed stillly for 12 h. The solution was heated at 60 °C with stirring until the liquid was totally eliminated. The sample was dried at 110 °C for 12 h and then calcined at 650 °C for 3 h in pure N₂ atmosphere. The obtained sample was named as Mn(5)/NAC. The obtained sample was immersed into the Ce(NO₃)₃ solution with different cerium concentration to achieve 1, 3, 5, 7 and 9 wt% Ce loading and calcined at 450 °C in a pure N₂ atmosphere for 3 h. The other treatment process is the same as the Mn(5)/NAC. They were

labeled as Ce(1)-Mn/NAC, Ce(3)-Mn/NAC, Ce(5)-Mn/NAC, Ce(7)-Mn/NAC and Ce(9)-Mn/NAC. As a comparative sample, 5 wt% Ce loaded on NAC was prepared and named as Ce(5)/NAC.

2.3. Activity evaluation

SO₂ or NO removal testing was carried out at a fixed-bed reactor under atmosphere pressure for all samples. The inner diameter of the reactor is 18 mm. For SO₂ removal testing, 8 g samples were filled into the reactor, and the filling height was 70 mm. The simulated flue gas contained 2700 ppm SO₂, 10% O₂, 10% water vapor and N₂ as the balance. These gases were fully mixed in the mixing bottle before entering the reactor. The gas flow rate was 800 mL/min. The reaction temperature was 80 °C. The gas hourly space velocity (GHSV) was 2700 h⁻¹. NaOH solution was used to absorb the SO₂ in the tail gas. When the concentration of outlet SO₂ reaches 200 ppm, it could be considered as breakthrough. Breakthrough sulfur capacity is usually defined as the accumulated quantity of SO₂ removal per unit mass of catalyst at breakthrough point. The corresponding working time is regarded as the breakthrough time. Breakthrough capacity of each sample is calculated from the SO₂ inlet concentration, working time, flow rate and mass of sample. The concentration of SO₂, and O₂ in the stimulated gas before and after the reactor were analyzed on-line by Gasboard 3000 gas analyzer (Wuhan Cubic Optoelectronics Co., Ltd. Wuhan, China).

For NO removal testing, 3.5 g samples were filled into the reactor, and the filling height was 28 mm. The simulated flue gas mixture contained 530 ppm NO, 530 ppm NH₃, 5% O₂ and N₂ as the balance. The total flow rate was 600 mL/min, corresponding to a GHSV of 5000 h⁻¹. The simulated gas was fully mixed in the mixing bottle. The range of reaction temperature was from 80 to 220 °C, and at each temperature point, it was maintained for half an hour. When the reaction proceeded steadily at each temperature point, the data of outlet NO concentration were collected. The NO_x in tail gas was absorbed by NaOH solution. The concentration of NO and O₂ in the stimulated gas before and after the reactor were analyzed on-line by Gasboard 3000 gas analyzer (Wuhan Cubic Optoelectronics Co., Ltd. Wuhan, China).

The removal efficiency (%) of NO is obtained by analyzing the NO inlet and outlet concentration as the following formula:

$$\text{NO removal efficiency}(\%) = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\%$$

2.4. Catalyst characterization

N₂ adsorption–desorption isotherms of the samples at –196 °C were measured on AUTOSORB-IQ adsorption apparatus (Quantachrome Instruments, USA) and high purity N₂ was used as adsorbate. Prior to analysis, each sample was outgassed at 250 °C and 10⁻⁵ torr for 6 h. The adsorption isotherms were used to calculate the surface area (S_{BET}) of each sample using the Brunauer–Emmett–Teller equation in the range of P/P₀ from 0.05 to 0.35. The total pore volume (V_{total}) was calculated corresponding to the nitrogen adsorption amount at P/P₀ = 0.95. The micropore volume (V_{micro}) and pore size distribution were calculated by Dubinin–Radushkevich (D–R) equation and Horvath–Kawazoe (H–K) model, respectively [19].

Crystal structure of the samples was detected by a powder X-ray diffraction on a DX-2700 diffractometer (Dandong Haoyuan Instrument Co., Ltd., China) using Cu K α radiation ($\lambda = 0.15418$ nm) and operating at 40 kV and 30 mA. The samples were scanned in the range of 2 θ from 10° to 80° with the step of 0.03°. The crystalline phases were identified by comparing the

Download English Version:

<https://daneshyari.com/en/article/6474575>

Download Persian Version:

<https://daneshyari.com/article/6474575>

[Daneshyari.com](https://daneshyari.com)