



Short communication

SO₄²⁻-Mn-Co-Ce supported on TiO₂/SiO₂ with high sulfur durability for low-temperature SCR of NO with NH₃



Lu Qiu, Yun Wang, Dandan Pang, Feng Ouyang*, Changliang Zhang

Environmental Science and Engineering Research Center, Shenzhen Graduate School, Harbin Institute of Technology, Shenzhen 518055, PR China

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ABSTRACT

The catalysts SO₄²⁻-Mn-Co-Ce/TiO₂/SiO₂ were investigated for the low-temperature SCR of NO with NH₃ in the presence of SO₂. An excellent SO₂ durability at low temperature was obtained with the catalyst used TiO₂/SiO₂ as support and modified with SO₄²⁻. The catalyst sulfated with 0.1 mol/L H₂SO₄ solution and then calcined at 300 °C exhibited the best NO_x conversion efficiency of 99.5% at 250 °C in the presence of 50 ppm SO₂. The conversion efficiency did not decrease after repeatedly used for 8 times.

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1. Introduction

The selective catalytic reduction (SCR) of NO_x with ammonia is a superior technology for the removal of NO_x emitted from stationary sources [1]. V₂O₅/TiO₂-based catalysts are the most active and commercially favored catalysts which worked in the temperature range of 300–400 °C [2]. In addition, there has been strong interest in developing low-temperature SCR catalysts operated at the tail end of power plants in order to avoid reheating of the flue gas. Among these catalysts, Mn-contained catalysts, such as Mn/Al₂O₃ [3,4] and Mn-Ce/TiO₂ [5,6], were proved to be highly active for NO_x reduction at low temperatures. The low-temperature SCR catalysts suffered low concentration of residual SO₂ at the tail end of power plants. However, the earlier studies have demonstrated that SO₂ had a more serious poisoning effect on the activity of catalyst at low temperature [7]. The deactivation is due to the formation of thermodynamically stable sulfate phases or deposition of ammonium sulfates on the catalyst surface [8,9], which was regarded as being caused by the reaction of SO₂ with O₂ [9,10]. Kijlstra et al. [4] indicated that the formation of surface MnSO₄ was the main deactivation route over the catalyst Mn/Al₂O₃.

Accordingly, some researchers have proposed various attempts to overcome the SO₂-poisoning problems on SCR catalysts. It was found that the SO₂ resistance of Mn/TiO₂ catalysts could be greatly enhanced with Ce modification [6,8]. In addition, the SCR activity of V₂O₅ loaded on sulfated TiO₂ was increased by the sulfating [11,12]. The research

indicated that promoting role of SO₂ resulted from the increase of surface acidity by sulfate species formed [12–14]. From the research by Kobayashi and Hagi [15], the vanadia loaded on TiO₂-SiO₂ with small amounts of SiO₂ exhibited a significantly lower SO₂ oxidation activity than that on TiO₂. However, it is difficult to realize high SO₂-poisoning resistance at low temperature. Few studies have been performed on TiO₂/SiO₂ composite oxides as support for Mn-contained catalysts which worked at low temperature.

In a previous paper [16], we have reported that the Mn-Co-Ce/TiO₂ catalysts exhibited a remarkable high activity in the temperature range of 150–200 °C. In this study, to improve the SO₂-poisoning resistance of the catalyst, the TiO₂/SiO₂ composite oxides were prepared by sol-gel method as support materials and the Mn-Co-Ce/TiO₂/SiO₂ catalysts were sulfated with H₂SO₄ solution. The activities of the catalysts were tested in repeated temperature programmed reactions between NH₃ and NO in the presence of SO₂. The influences of impregnating SO₄²⁻ concentration and calcination temperature after sulfating on the SCR activity were investigated. The catalysts were characterized by N₂ adsorption-desorption, X-ray diffraction (XRD) and NH₃ temperature-programmed desorption (NH₃-TPD).

2. Experimental

2.1. Catalyst preparation

The support TiO₂/SiO₂ was prepared by sol-gel method. The anhydrous alcohol (10 mL), acetic acid (2 mL) and deionized water (0.5 mL) were mixed under vigorous stirring at room temperature for 20 min to form solution A. In addition, solution B was formed with

* Corresponding author.

E-mail address: ouyangfh@hit.edu.cn (F. Ouyang).

dissolution of 5 mL tetrabutyl titanate into 13 mL anhydrous alcohol. Solution A was added dropwise into solution B with vigorous stirring for 2 h to get homogeneous transparent sol, and then 2.0 g silica gel of 60–100 mesh was added into the sol with agitation for 1 h. The amount of TiO₂ content by weight was 36 wt.%. The resulted gelatinous solution transformed to gel after aging at room temperature for 24 h and then dried at 80 °C for 12 h. The solid was crushed and calcined at 500 °C in air for 2 h.

The Mn–Co–Ce/TiO₂/SiO₂ catalysts were synthesized by wet impregnation method using above prepared TiO₂/SiO₂ as support materials. The aqueous solution of Mn, Co and Ce nitrates were used as precursors. A certain amount of TiO₂/SiO₂ support was added into the solution. The mixed solution was stirred for 1 h and left at room temperature for 24 h. Subsequently, the samples were dried at 110 °C for 12 h, followed by calcination at 500 °C in air for 3 h. The contents of Mn, Co and Ce oxides were 5 wt.%, 2 wt.% and 1 wt.%, respectively. Finally, the above prepared catalysts were impregnated with aqueous sulfuric acid (0.10, 0.15, 0.25 mol/L, respectively). After impregnation, the mixtures were dried at 100 °C and then calcined at 300, 400 or 500 °C for 2 h to obtain SO₄²⁻ Mn–Co–Ce/TiO₂/SiO₂ powders, denoted as SO₄²⁻ MnCoCe/T/S.

For comparison, the Mn–Co–Ce/TiO₂ catalyst was prepared by co-impregnation method using TiO₂ P25 as support, denoted as MnCoCe/T. The preparation conditions were same with the preparation of MnCoCe/T/S catalyst.

2.2. Catalyst characterization

Specific surface areas of the samples were determined using a BELSORP-mini II (Ankersmid, Holland), through nitrogen adsorption at liquid nitrogen temperature after standard evacuation at 300 °C for 3 h.

The crystalline phases of the catalysts were determined by X-ray diffractometer (RIGAKU, D/Max 2500PC, Japan) in the 2θ angle range of 10–80° using Cu Kα radiation combined with nickel filter.

The NH₃ temperature programmed desorption (NH₃-TPD) measurements were carried out with 0.05 g samples at a total flow rate of 40 mL/min. Before the TPD measurements, the catalysts were pretreated in a flow of He at 300 °C for 1 h and subsequently cooled to 100 °C. The samples were then treated with 10% NH₃/He for 1 h and purged with He for 1 h. Subsequently, the TPD runs were carried out from 100 °C to 450 °C at a heating rate of 15 °C/min. The online gas chromatograph (GC6890, China) with a TCD detector was used to monitoring the desorbed ammonia.

2.3. Activity measurement

The catalytic activity tests were carried out in a fixed bed quartz reactor (inner diameter 8 mm) containing 0.15 g catalyst (60–100 mesh) with a gas hourly space velocity (GHSV) of 40,000 h⁻¹. The reaction conditions were as follows: 320 ppm NO, 320 ppm NH₃, 5 vol.% O₂, and 50, 90 or 150 ppm SO₂ in Ar. A thermocouple and a PID-regulation system (Bachy, CKW-2200) were used to control the reactor temperature. After saturated adsorption of the gas components over the catalysts at room temperature, the reaction was carried out in the temperature range of 100–350 °C at a heating rate of 1 °C/min. In the repeated reaction tests, the temperature programmed reactions were repeated run without catalyst activation. The concentrations of NO, NO₂ and NO_x in the outlet streams of the reactor were monitored using an online nitrogen oxides analyzer (Ecotech EC9841B, Australia).

The NO_x conversion is defined as follows:

$$\text{NO}_x \text{ conversion (\%)} = \frac{(\text{NO}_{\text{in}} + \text{NO}_{2,\text{in}}) - (\text{NO}_{\text{out}} + \text{NO}_{2,\text{out}})}{\text{NO}_{\text{in}} + \text{NO}_{2,\text{in}}} \times 100. \quad (1)$$

3. Results and discussion

3.1. Influence of TiO₂/SiO₂ support and sulfating on catalytic activity

To investigate the influence of TiO₂/SiO₂ support and SO₄²⁻ modification on improvement of SO₂ durability for these catalysts, the catalytic activities for NO_x conversion over the MnCoCe/T, MnCoCe/T/S and SO₄²⁻ MnCoCe/T/S were tested. These results are shown in Fig. 1. For the MnCoCe/T, the NO_x conversion efficiency increased with the reaction temperature rising, reached the top NO_x conversion of 90.2% at 350 °C. However, for the catalyst MnCoCe/T/S, the NO_x conversion efficiency below 250 °C was higher than that of the catalyst used TiO₂ as support. The top NO_x conversion was 95.7% at 190 °C, and then decreased with the increasing temperature. The result indicates that using TiO₂/SiO₂ composite oxide as support is beneficial to the SCR reaction in the presence of 50 ppm SO₂.

The influence of sulfuric acid concentration in the starting materials on catalytic activity for NO_x conversion over the SO₄²⁻ MnCoCe/T/S catalysts was studied by varying the concentration of H₂SO₄ solution from 0.10 to 0.25 mol/L. The results are presented in Fig. 1. After sulfating, these catalysts were calcined at 300 °C. The results showed that these catalysts modified with 0.10, 0.15 and 0.25 mol/L SO₄²⁻ reached top NO_x conversions of 99.5%, 99.0% and 99.1% at 250 °C, 270 °C and 310 °C, respectively. Sulfating with SO₄²⁻ can increase the NO_x conversion in the presence of SO₂ and shift the reaction window toward higher temperatures. The reaction window in this paper was defined as the reaction temperature range above 90% of NO_x conversion. The results indicate that the concentration of impregnated aqueous SO₄²⁻ mainly influences the position of reaction window, but not the top NO_x conversion. The catalyst SO₄²⁻ MnCoCe/T/S impregnated with 0.1 mol/L H₂SO₄ solution showed the best activity for NO_x conversion.

3.2. Influence of calcination temperature on catalytic activity

The influence of calcination temperature after sulfating on NO_x conversion over the SO₄²⁻ MnCoCe/T/S catalysts is presented in Fig. 2. Before sulfating, these catalysts were all calcined at 500 °C. As shown in Fig. 2, the catalytic activity for NO_x conversion decreased with the sulfating calcination temperature increasing from 300 to 500 °C. The catalyst calcined at 300 °C after sulfating showed the top NO_x conversion of

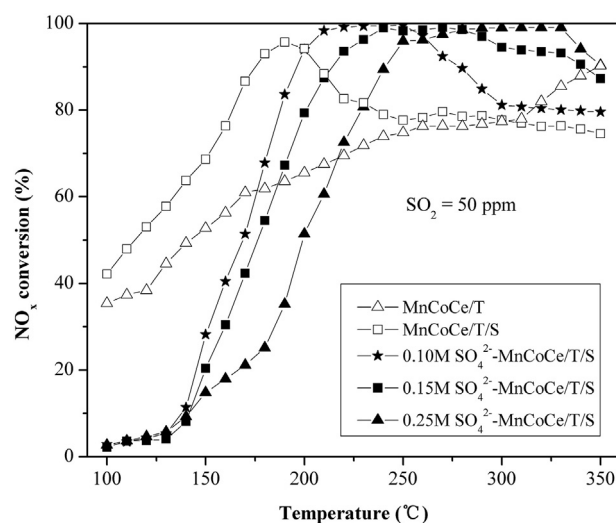


Fig. 1. NO_x conversion over the MnCoCe/T, MnCoCe/T/S and SO₄²⁻ MnCoCe/T/S catalysts treated with different concentrations of H₂SO₄ solution. Reaction conditions: 320 ppm NO, 320 ppm NH₃, 50 ppm SO₂, 5% O₂ and balance Ar. GHSV = 40,000 h⁻¹.

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