

## Short communication

# SO<sub>4</sub><sup>2-</sup>-Mn-Co-Ce supported on TiO<sub>2</sub>/SiO<sub>2</sub> with high sulfur durability for low-temperature SCR of NO with NH<sub>3</sub>



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## ABSTRACT

The catalysts SO<sub>4</sub><sup>2-</sup>-Mn-Co-Ce/TiO<sub>2</sub>/SiO<sub>2</sub> were investigated for the low-temperature SCR of NO with NH<sub>3</sub> in the presence of SO<sub>2</sub>. An excellent SO<sub>2</sub> durability at low temperature was obtained with the catalyst used TiO<sub>2</sub>/SiO<sub>2</sub> as support and modified with SO<sub>4</sub><sup>2-</sup>. The catalyst sulfated with 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution and then calcined at 300 °C exhibited the best NO<sub>x</sub> conversion efficiency of 99.5% at 250 °C in the presence of 50 ppm SO<sub>2</sub>. 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<sub>x</sub> with ammonia is a superior technology for the removal of NO<sub>x</sub> emitted from stationary sources [1]. V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub>-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/Al<sub>2</sub>O<sub>3</sub> [3,4] and Mn-Ce/TiO<sub>2</sub> [5,6], were proved to be highly active for NO<sub>x</sub> reduction at low temperatures. The low-temperature SCR catalysts suffered low concentration of residual SO<sub>2</sub> at the tail end of power plants. However, the earlier studies have demonstrated that SO<sub>2</sub> 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 SO<sub>2</sub> with O<sub>2</sub> [9,10]. Kijlstra et al. [4] indicated that the formation of surface MnSO<sub>4</sub> was the main deactivation route over the catalyst Mn/Al<sub>2</sub>O<sub>3</sub>.

Accordingly, some researchers have proposed various attempts to overcome the SO<sub>2</sub>-poisoning problems on SCR catalysts. It was found that the SO<sub>2</sub> resistance of Mn/TiO<sub>2</sub> catalysts could be greatly enhanced with Ce modification [6,8]. In addition, the SCR activity of V<sub>2</sub>O<sub>5</sub> loaded on sulfated TiO<sub>2</sub> was increased by the sulfating [11,12]. The research

indicated that promoting role of SO<sub>2</sub> 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 TiO<sub>2</sub>-SiO<sub>2</sub> with small amounts of SiO<sub>2</sub> exhibited a significantly lower SO<sub>2</sub> oxidation activity than that on TiO<sub>2</sub>. However, it is difficult to realize high SO<sub>2</sub>-poisoning resistance at low temperature. Few studies have been performed on TiO<sub>2</sub>/SiO<sub>2</sub> 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/TiO<sub>2</sub> catalysts exhibited a remarkable high activity in the temperature range of 150–200 °C. In this study, to improve the SO<sub>2</sub>-poisoning resistance of the catalyst, the TiO<sub>2</sub>/SiO<sub>2</sub> composite oxides were prepared by sol-gel method as support materials and the Mn-Co-Ce/TiO<sub>2</sub>/SiO<sub>2</sub> catalysts were sulfated with H<sub>2</sub>SO<sub>4</sub> solution. The activities of the catalysts were tested in repeated temperature programmed reactions between NH<sub>3</sub> and NO in the presence of SO<sub>2</sub>. The influences of impregnating SO<sub>4</sub><sup>2-</sup> concentration and calcination temperature after sulfating on the SCR activity were investigated. The catalysts were characterized by N<sub>2</sub> adsorption-desorption, X-ray diffraction (XRD) and NH<sub>3</sub> temperature-programmed desorption (NH<sub>3</sub>-TPD).

## 2. Experimental

## 2.1. Catalyst preparation

The support TiO<sub>2</sub>/SiO<sub>2</sub> 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

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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 TiO<sub>2</sub> 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/TiO<sub>2</sub>/SiO<sub>2</sub> catalysts were synthesized by wet impregnation method using above prepared TiO<sub>2</sub>/SiO<sub>2</sub> as support materials. The aqueous solution of Mn, Co and Ce nitrates were used as precursors. A certain amount of TiO<sub>2</sub>/SiO<sub>2</sub> 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 SO<sub>4</sub><sup>2-</sup> Mn–Co–Ce/TiO<sub>2</sub>/SiO<sub>2</sub> powders, denoted as SO<sub>4</sub><sup>2-</sup> MnCoCe/T/S.

For comparison, the Mn–Co–Ce/TiO<sub>2</sub> catalyst was prepared by co-impregnation method using TiO<sub>2</sub> 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 NH<sub>3</sub> temperature programmed desorption (NH<sub>3</sub>-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% NH<sub>3</sub>/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<sup>-1</sup>. The reaction conditions were as follows: 320 ppm NO, 320 ppm NH<sub>3</sub>, 5 vol.% O<sub>2</sub>, and 50, 90 or 150 ppm SO<sub>2</sub> 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, NO<sub>2</sub> and NO<sub>x</sub> in the outlet streams of the reactor were monitored using an online nitrogen oxides analyzer (Ecotech EC9841B, Australia).

The NO<sub>x</sub> 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 TiO<sub>2</sub>/SiO<sub>2</sub> support and sulfating on catalytic activity

To investigate the influence of TiO<sub>2</sub>/SiO<sub>2</sub> support and SO<sub>4</sub><sup>2-</sup> modification on improvement of SO<sub>2</sub> durability for these catalysts, the catalytic activities for NO<sub>x</sub> conversion over the MnCoCe/T, MnCoCe/T/S and SO<sub>4</sub><sup>2-</sup> MnCoCe/T/S were tested. These results are shown in Fig. 1. For the MnCoCe/T, the NO<sub>x</sub> conversion efficiency increased with the reaction temperature rising, reached the top NO<sub>x</sub> conversion of 90.2% at 350 °C. However, for the catalyst MnCoCe/T/S, the NO<sub>x</sub> conversion efficiency below 250 °C was higher than that of the catalyst used TiO<sub>2</sub> as support. The top NO<sub>x</sub> conversion was 95.7% at 190 °C, and then decreased with the increasing temperature. The result indicates that using TiO<sub>2</sub>/SiO<sub>2</sub> composite oxide as support is beneficial to the SCR reaction in the presence of 50 ppm SO<sub>2</sub>.

The influence of sulfuric acid concentration in the starting materials on catalytic activity for NO<sub>x</sub> conversion over the SO<sub>4</sub><sup>2-</sup> MnCoCe/T/S catalysts was studied by varying the concentration of H<sub>2</sub>SO<sub>4</sub> 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 SO<sub>4</sub><sup>2-</sup> reached top NO<sub>x</sub> conversions of 99.5%, 99.0% and 99.1% at 250 °C, 270 °C and 310 °C, respectively. Sulfating with SO<sub>4</sub><sup>2-</sup> can increase the NO<sub>x</sub> conversion in the presence of SO<sub>2</sub> 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<sub>x</sub> conversion. The results indicate that the concentration of impregnated aqueous SO<sub>4</sub><sup>2-</sup> mainly influences the position of reaction window, but not the top NO<sub>x</sub> conversion. The catalyst SO<sub>4</sub><sup>2-</sup> MnCoCe/T/S impregnated with 0.1 mol/L H<sub>2</sub>SO<sub>4</sub> solution showed the best activity for NO<sub>x</sub> conversion.

### 3.2. Influence of calcination temperature on catalytic activity

The influence of calcination temperature after sulfating on NO<sub>x</sub> conversion over the SO<sub>4</sub><sup>2-</sup> 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<sub>x</sub> 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<sub>x</sub> conversion of

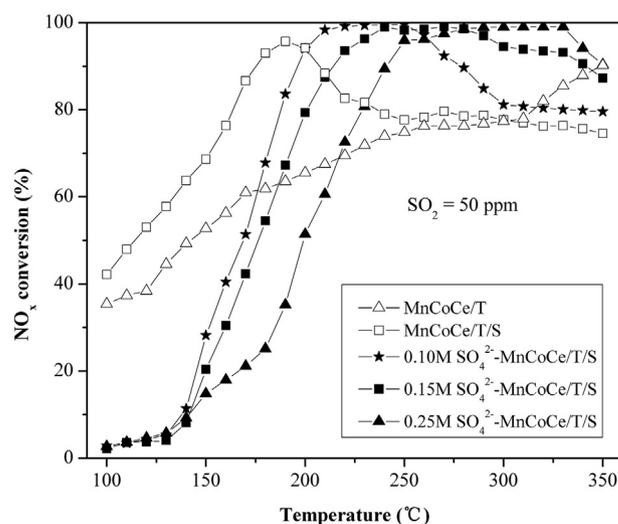


Fig. 1. NO<sub>x</sub> conversion over the MnCoCe/T, MnCoCe/T/S and SO<sub>4</sub><sup>2-</sup> MnCoCe/T/S catalysts treated with different concentrations of H<sub>2</sub>SO<sub>4</sub> solution. Reaction conditions: 320 ppm NO, 320 ppm NH<sub>3</sub>, 50 ppm SO<sub>2</sub>, 5% O<sub>2</sub> and balance Ar. GHSV = 40,000 h<sup>-1</sup>.

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