

Selective catalytic reduction of NO by NH₃ over a Ce/TiO₂ catalyst

Wenqing Xu, Yunbo Yu, Changbin Zhang, Hong He*

State Key Laboratory of Environmental Chemistry and Ecotoxicology, Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

Received 7 August 2007; received in revised form 10 December 2007; accepted 17 December 2007
Available online 31 December 2007

Abstract

Samples of cerium supported on titania with different Ce loadings have been prepared by an impregnation method and tested for the selective catalytic reduction of NO by NH₃ in the presence of excess oxygen. The catalysts with 5% Ce and above had high activity in the temperature range 275–400 °C at a space velocity of 50,000 h⁻¹. All the catalysts showed an excellent selectivity to N₂ and high tolerance to SO₂ and H₂O under our test conditions.

© 2007 Elsevier B.V. All rights reserved.

Keywords: SCR; Ce/TiO₂; NO_x; NH₃; Sulfur dioxide; Water vapour

1. Introduction

Emissions of nitrogen oxides (NO_x) in fuel combustion from stationary and mobile sources cause a variety of environmentally harmful effects such as acid rain and urban smog; they also contribute to the greenhouse effect. The selective catalytic reduction (SCR) of NO_x using ammonia or urea is a well-proven technique for NO_x removal from stationary power stations and diesel engines [1–5]. The general reaction is: $4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}$. Commercial catalysts for the above reaction are based on V₂O₅–WO₃–TiO₂ or V₂O₅–MoO₃–TiO₂ [6,7]. However, many other transition metal oxide based systems such as Mn/TiO₂ [8], Fe/TiO₂ [9], Cu/TiO₂ [10] and Cr/TiO₂ [11] have also been extensively studied and found to be highly effective. In these studies, TiO₂-anatase has been most widely used as the support material for the SCR catalysts, because TiO₂ is only partially and reversibly sulfated on its surface when the SCR reaction takes place in the presence of SO₂ [12].

The use of cerium oxide as an additive in the three way catalyst has generated great interest in the properties of this

oxide [13,14]. The wide application of cerium oxide either as a promoter or as an active catalyst is due to its unique redox and acid–base properties. Labile oxygen vacancies and bulk oxygen species with relatively high mobility are easily formed during the redox shift between Ce³⁺ and Ce⁴⁺ under oxidizing and reducing conditions, respectively [15]. Long and Yang studied the performance of cerium oxide catalysts supported on Fe-ZSM-5 [16] and Fe-Ti-PILC [17] for the SCR of NO with NH₃ and concluded that cerium oxide enhanced the oxidation of NO to NO₂, resulting in an improvement of activity. Their group also reported a novel MnO_x–CeO₂ [18] catalyst which was highly active for the SCR of NO with NH₃ at low temperature. Ito et al. [19] found that cerium-exchanged mordenite was active and highly selective for the NO_x reduction in a wide temperature range (250–560 °C).

As stated above, TiO₂ is commonly used as a support during the SCR of NO by NH₃ because of its excellent sulfur tolerance. Cerium oxide is a suitable candidate for NO reduction by NH₃ based on its unique redox properties. However, there have been few reports that have focused on the reduction of NO by NH₃ over Ce/TiO₂ until our present work, in which we have studied the activities of a series of Ce/TiO₂ catalysts for this reaction. The results show that Ce/TiO₂ is highly effective for NO reduction in

* Corresponding author. Tel.: +86 10 62849123; fax: +86 10 62923563.
E-mail address: honghe@rcees.ac.cn (H. He).

the temperature range 275–400 °C and yields 100% N₂ selectivity.

2. Experimental

2.1. Catalyst preparation

The Ce/TiO₂ catalysts were prepared by an impregnation method using an anatase type TiO₂ (Shanghai Huijing Co.) and an aqueous solution of cerium nitrate. After impregnation, the excess water was removed in a rotary evaporator at 80 °C. The samples were first dried at 110 °C for 12 h followed by calcination at 500 °C in air for 3 h. The weight ratio of Ce is measured with respect to the support TiO₂. Pure TiO₂ was prepared through a densification process. The mixture of TiO₂ and deionized water was dried and also calcined at 500 °C in air for 3 h. Pure CeO₂ was prepared by direct decomposition of Ce(N-O₃)₃ · 6H₂O which was calcined at 500 °C in air for 3 h.

2.2. Characterization of catalysts

The nitrogen adsorption–desorption isotherms were obtained at –196 °C over the whole range of relative pressures, using a Quantasorb-18 automatic equipment (Quanta Chrome Instrument Co.). Specific areas were computed from these isotherms by applying the Brunauer–Emmett–Teller (BET) method.

The samples were characterized by X-ray diffractometry using a computerized Rigaku D/max-RB Diffractometer (Japan, Cu K α radiation, 0.154056 nm). Scans were taken over a 2 θ range of 10–90° at a speed of 4° min⁻¹.

2.3. Activity test

The catalytic reaction was carried out in a fixed-bed quartz flow reactor at atmospheric pressure. The reactor was a 6 mm i.d. quartz tube with a thermocouple placed at the outside wall of the reactor to control the temperature of the furnace. About 0.6 ml of catalyst (20–40 mesh) was used in all the experiments. The reactor was heated by a temperature-controlled furnace. The feed gases consisting of 500 ppm NO, 500 ppm NH₃, 5 vol.% O₂, 100 or 180 ppm SO₂ (when used), 3 or 10 vol.% H₂O (when used) in N₂ were adjusted by mass flow controllers and introduced into the reactor with a total flow rate of 500 cm³ min⁻¹, yielding a gas hourly space velocity (GHSV) of 50,000 h⁻¹. Different space velocities were obtained by changing the volume of catalyst used. Water was supplied with a micro-pump into the gas stream and vaporized by a coiled heater at the inlet of the reactor. Analysis of the concentrations of NO, NO₂, N₂O and NH₃ was carried out using an on-line NEXUS 670-FTIR spectrophotometer equipped with a gas cell of volume 0.2 dm³. The reaction system was kept for 1 h at each reaction temperature to reach a steady state before the analysis of the product was performed.

3. Results and discussion

3.1. Activity tests for NO reduction by NH₃ over Ce/TiO₂ catalysts

Fig. 1a shows the NO conversions at various temperatures for the SCR of NO by NH₃ over Ce/TiO₂ catalysts with different Ce loadings, pure TiO₂ and CeO₂. There was no conversion of NO over pure TiO₂. Pure CeO₂ showed slight activity and 20% NO conversion was obtained when the temperature reached 300 °C. It should be noted that the addition of 2% Ce caused a significant enhancement of the catalytic activity. Increasing the Ce loading from 2% to 20% further enhanced the NO conversion in the low temperature range (150–350 °C) and the temperature showing the maximum NO conversion shifted towards lower temperatures. For 20% Ce/TiO₂, NO conversion was greater than 92% in a wide temperature range (275–400 °C). Further increase of the Ce loading from 20%

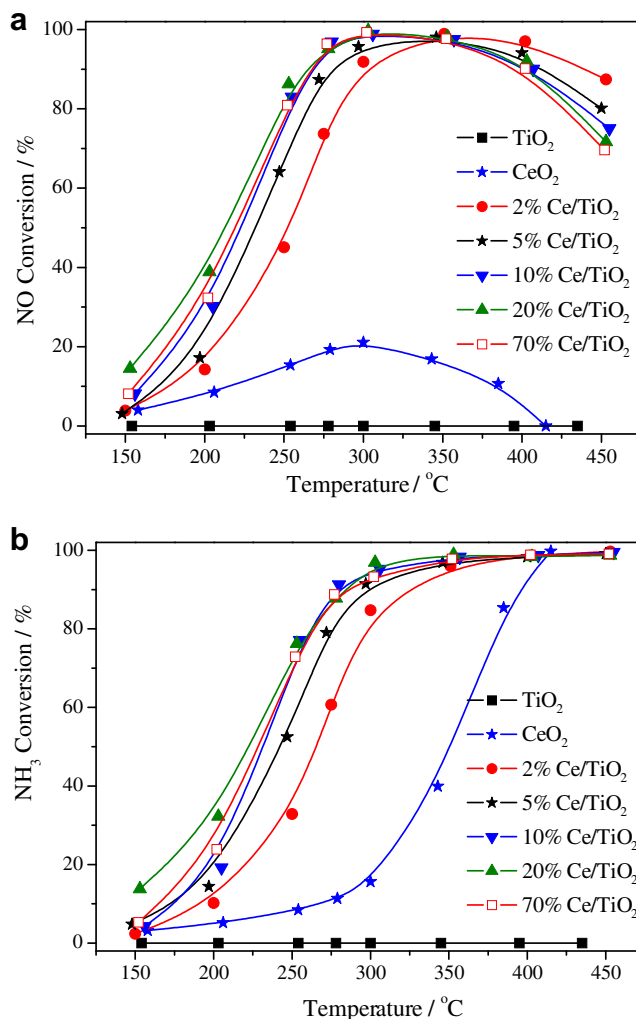


Fig. 1. NO conversion (a) and NH₃ conversion (b) over pure TiO₂, pure CeO₂ and Ce/TiO₂ catalysts with different Ce contents. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, balance N₂, GHSV = 50,000 h⁻¹, total flow rate 500 cm³ min⁻¹.

Download English Version:

<https://daneshyari.com/en/article/52172>

Download Persian Version:

<https://daneshyari.com/article/52172>

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