

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

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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.

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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: 4NO + 4NH₃ + O₂ → 4N₂ + 6H₂O. 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

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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 steam 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%

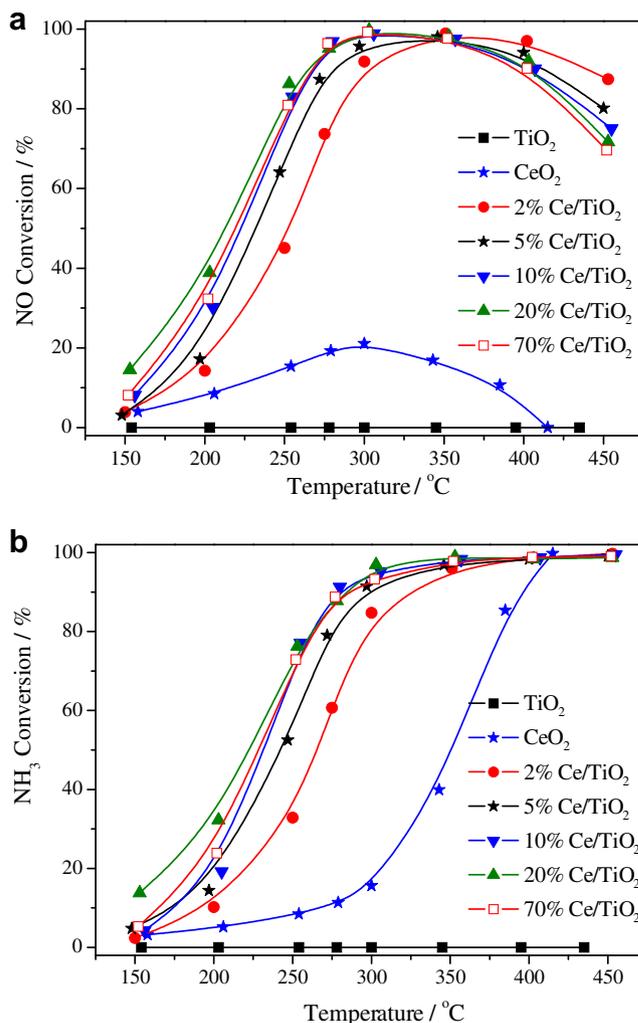


Fig. 1. NO conversion (a) and NH₃ conversion (b) over pure TiO₂, pure CeO₂ and Ce/TiO₂ catalysts with different Ce contents. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, balance N₂, GHSV = 50,000 h⁻¹, total flow rate 500 cm³ min⁻¹.

to 70% lowered the NO conversion at both low and high temperatures. As shown in Fig. 1b, NH₃ was almost completely consumed and there was no considerable slip at high temperatures when the NH₃/NO ratio was 1:1. The decrease of NO conversion at above 350 °C can be ascribed to the unselective ammonia oxidation by O₂, which usually takes place at high temperatures. The remarkable point is that, N₂O, as a potential by-product of the SCR of NO_x, was not detected at any temperature, which indicates that this catalyst showed excellent N₂ selectivity. Since the 20% Ce/TiO₂ catalyst showed the highest activity for NO reduction, all of the Ce/TiO₂ catalysts that appear below have a Ce loading of 20%.

3.2. Effect of GHSV on NO reduction by NH₃ over 20% Ce/TiO₂ catalyst

The influence of the GHSV on the NO conversion was studied by varying the GHSV over the 20% Ce/TiO₂ catalyst. The catalytic activity decreased dramatically with increase of the space velocity from 25,000 h⁻¹ to 100,000 h⁻¹, especially in the temperature range below 300 °C. As shown in Fig. 2, for a GHSV at 25,000 h⁻¹, the NO conversion was greater than 95% in the range 250–375 °C. With a GHSV of 50,000 h⁻¹, 97% NO conversion was obtained at 350 °C. Even with a GHSV as high as 100,000 h⁻¹, the maximum of NO conversion was 94% at 350 °C. These results suggest that the 20% Ce/TiO₂ catalyst is highly effective for NO reduction within a wide range of GHSV.

3.3. Effect of concentration of O₂ on 20% Ce/TiO₂ activity for NO reduction

Previous studies have shown that O₂ plays an important role in the reaction of NO with NH₃ [1]. Accordingly, the effect of O₂ concentration on the catalytic performance was also studied in this work. The NO conversion data

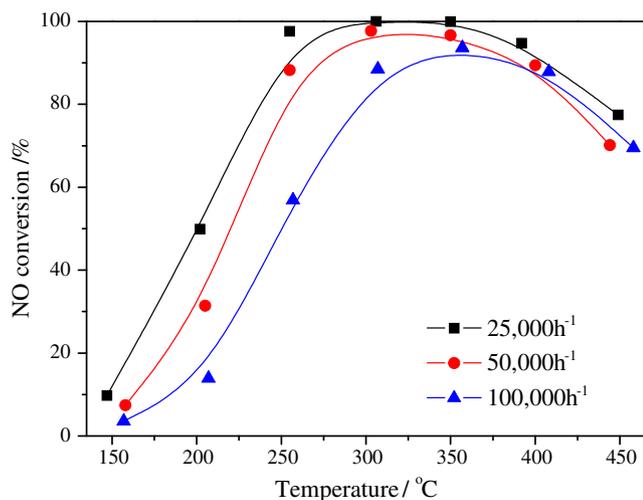


Fig. 2. Influence of GHSV on the catalytic performance over the 20% Ce/TiO₂ catalyst. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, balance N₂, total flow rate 500 cm³ min⁻¹.

were all collected under the steady state conditions. As shown in Fig. 3, the NO conversion at 300 °C was around 30% over the 20% Ce/TiO₂ catalyst in the absence of O₂. The activity under the steady state in the absence of O₂ is due to the following reaction: 6NO + 4NH₃ → 5N₂ + 6H₂O. The remarkable point is that the NO conversion without O₂ was initially 60%, but then decreased gradually in 10 h to 30% to reach a steady state (shown in the insert graph of Fig. 3). According to the literature [9,19], lattice oxygen usually participates in the reaction between NO and NH₃ in the absence of O₂. Therefore, XPS measurement was performed to determine the surface element state of the Ce/TiO₂ catalyst before and after the testing without O₂ in 10 h (result not shown). In comparison with the fresh sample, the percentage of Ce³⁺ calculated from Ce3d XPS spectra of the sample increases after the testing. However, there is no difference in XPS spectra of Ti2p. Accordingly, we suppose that the decrease of activity is mainly because the lattice oxygen of CeO₂ was continually consumed during this process. When a small concentration of O₂ was added into the stream, the NO conversion sharply increased. However, no obvious change was observed when the O₂ concentration exceeded 0.5%. This indicates that O₂ plays a significant promoting role in the SCR reaction. Gas phase oxygen and adsorbed oxygen species achieved a balanced state when the O₂ concentration reached a particular value (1%). Then the rate of the reaction was of zeroth order with respect to the concentration of O₂.

3.4. Effect of the presence of H₂O and SO₂ on NO reduction by NH₃ over 20% Ce/TiO₂ catalyst

Fig. 4 shows the influence of H₂O and SO₂ on the reaction of NO with NH₃ in the presence of O₂. Before adding

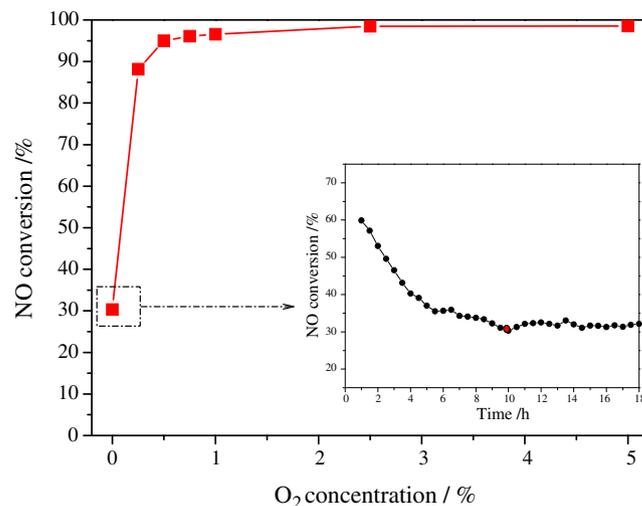


Fig. 3. Effect of O₂ concentration on the NO conversion over the 20% Ce/TiO₂ catalyst at 300 °C. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 0–5%, balance N₂, GHSV = 50,000 h⁻¹, total flow rate 500 cm³ min⁻¹. Insert: NO conversion in the absence of O₂ as a function of time.

H₂O or SO₂, the SCR reaction was stabilized for 2 h at 300 °C. When 3% H₂O was added, there was almost no change of NO conversion in 12 h. When the H₂O concentration increased to 10%, NO conversion was also unchanged in 12 h. This result indicates that the Ce/TiO₂ catalysts are resistant to water vapor at 300 °C. As shown in Fig. 4, when 100 ppm SO₂ was added to the reactants at 300 °C, the NO conversion decreased slowly to about 88%, then gradually recovered to 90% at which point it stabilized. The inhibition by SO₂ becomes a little stronger at high SO₂ concentration of 180 ppm. The results suggest that the Ce/TiO₂ catalyst has sulfur tolerance under our test conditions. The effect of H₂O + SO₂ on the SCR activity of the 20% Ce/TiO₂ catalyst is also illustrated in Fig. 4. The result indicates that when both 3% H₂O and 100 ppm SO₂ were added to the reactants, the NO conversion showed a relatively significant decrease to 85% at 300 °C in 12 h.

3.5. Characterizations of catalysts

3.5.1. XRD

The X-ray powder diffraction patterns of the Ce/TiO₂ catalysts with different Ce loadings are shown in Fig. 5. All the reflections provide typical diffraction patterns for the TiO₂ anatase phase (PDF-ICDD 21-1272) and the cubic CeO₂ structure (PDF-ICDD 34-0394). No cubic CeO₂ phase was observed at low Ce loadings (<20%). This demonstrates that cerium existed as a highly dispersed or amorphous surface species. As the Ce loading increased from 20% to 70%, the diffraction line of CeO₂ became apparent and grew sharper. Meanwhile, the diffraction lines of TiO₂ kept broadening. These results suggest that the crystallites of TiO₂ became smaller and the CeO₂ crystallites were formed and slowly growing, as also shown in Table 1.

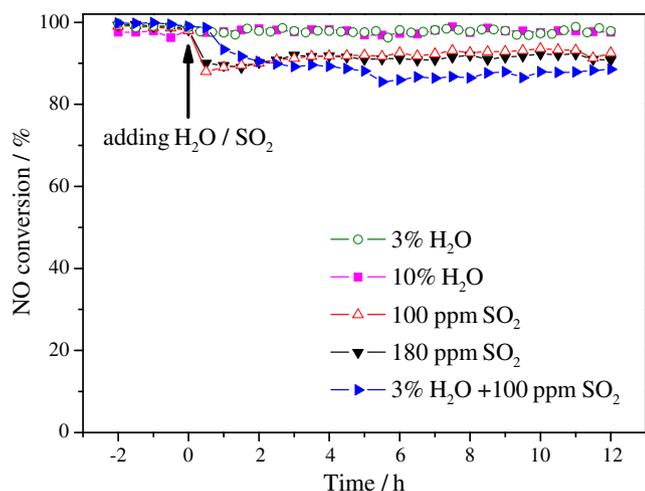


Fig. 4. Effect of H₂O and SO₂ on the NO conversion over the 20% Ce/TiO₂ catalyst at 300 °C. Reaction conditions: NO 500 ppm, NH₃ 500 ppm, O₂ 5%, H₂O 3% or 10%, SO₂ 100 or 180 ppm, balance N₂, GHSV = 50,000 h⁻¹, total flow rate 500 cm³ min⁻¹.

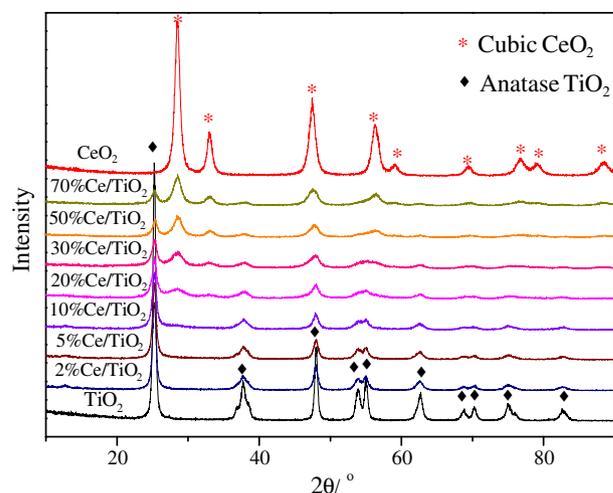


Fig. 5. XRD profiles of Ce/TiO₂ catalysts with different Ce contents.

Table 1

Specific surface area and crystallite size of the catalysts

Samples	BET surface area (m ² g ⁻¹)	TiO ₂ crystallite size (nm)	CeO ₂ crystallite size (nm)
Pure CeO ₂	90.5	–	11.9
Pure TiO ₂	108.1	19.9	–
2% Ce/TiO ₂	102.0	15.4	–
5% Ce/TiO ₂	104.6	15.4	–
10% Ce/TiO ₂	123.0	13.5	–
20% Ce/TiO ₂	128.6	13.2	9.2
30% Ce/TiO ₂	111.7	11.4	10.0
50% Ce/TiO ₂	82.6	11.3	10.6
70% Ce/TiO ₂	78.7	10.3	11.0

3.5.2. BET

The specific surface areas of the Ce/TiO₂ catalysts are summarized in Table 1. It is clear that as the Ce content increases from 2% to 20%, the surface area increases because some cerium can inhibit the agglomeration of the TiO₂ crystallites. However, the surface area decreased as the Ce content increased from 20% to 70%. This was ascribed to the growing of CeO₂ crystallites. The 20% Ce/TiO₂ catalyst that showed the best SCR activity has the largest surface area in this series, which suggests that the appropriate cerium loading can help to maintain a stable structure. This finding indicates that the BET area is one of the main reasons for the different catalytic activities of the Ce/TiO₂ catalysts with different Ce contents.

4. Conclusion

On the basis of the above results, it can be concluded that the Ce/TiO₂ catalyst is highly active and selective for the catalytic reduction of NO to N₂ by NH₃ in the presence of excess oxygen. H₂O and SO₂ have slight influence on the catalytic activity under our test conditions. Characterization results indicate that the catalytic activity is related to the specific surface area of the catalyst. In future work,

the interaction between Ce and Ti and the reaction mechanisms are worthy of detailed investigation.

Acknowledgements

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