



Full Length Article

The promoted performance of CeO₂ catalyst for NH₃-SCR reaction by NH₃ treatment

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ABSTRACT

In this study, NH₃ treatment of CeO₂ was found to significantly enhance its NH₃-SCR performance. The NH₃-treated CeO₂ was characterized by BET, XRD, TPR and XPS. The obtained results revealed the excellent SCR activity and stability of CeO₂ catalyst treated by NH₃ should be originated from the dropped crystallinity, better reducibility, along with the production of more Ce³⁺ and surface adsorbed oxygen. Furthermore, *in situ* DRIFT study has been carried out and the results indicated that the Langmuir-Hinshelwood (L-H) mechanism could be applied for explaining the SCR reaction route over CeO₂-N.

1. Introduction

NOx, which is mainly generated during the combustion process of coal, has posed many significant problems to the environment, such as acid rain [1,2]. For NOx abatement, selective catalytic reduction (SCR) process in coal-burning power plant has become the mainstream of de-NOx techniques [3]. V₂O₅-WO₃(MoO₃)/TiO₂, which is the most commercialized catalyst, possesses high de-NOx performance in 300–400 °C [2,4,5]. However, some evitable drawbacks of this catalyst such as the narrow temperature window, the poisonous V species, and the effective conversion from SO₂ to SO₃ make it unacceptable for future application [6–9]. In response, seeking green and effective SCR catalyst without V species has attracted much attention than before.

Ce-based SCR catalyst is considered as one of the best candidates because it shines in the aspects of oxygen storage ability and redox performance [10,11]. Gao et al. [12] indicated that the synthetic method had a crucial impact on the catalytic ability of Ce/TiO₂ catalyst. It is generally known that pure CeO₂ only shows poor SCR performance. Moreover, the modification of Ce-based catalyst with transition metals seems to be credible for increasing its SCR performance [13,14]. In addition, Ce-based catalyst treated by some acidic or reducing gas such as SO₂, CO, HF and H₂ has also been proved to be effective for obtaining better catalytic performance [15–18]. It is well known that NH₃ is a typical reducing gas, however, the performance of SCR catalyst treated by NH₃ has not been reported. In this study, it was found that NH₃

treatment could effectively improve the catalytic ability and stability of ceria. The promotion mechanism would be further studied by several characterization methods.

2. Experimental

2.1. Catalyst preparation

The fresh CeO₂ is the thermal decomposition product of Ce(NO₃)₂, which was decomposed at 500 °C in air for 5 h. The NH₃-treated CeO₂ was prepared by putting the fresh CeO₂ in 600 ppm NH₃/Ar at 500 °C for 5 h. For convenience, the NH₃-treated sample was named as CeO₂-N. The corresponding samples after the activity test from 100 to 400 °C were named as CeO₂-used-1 and CeO₂-N-used-1. The prepared samples after the stability test were labeled as CeO₂-used-2 and CeO₂-N-used-2 respectively.

2.2. Catalyst characterization

In order to measure the specific surface area of CeO₂, CeO₂-N, CeO₂-used-1, CeO₂-N-used-1, CeO₂-used-2 and CeO₂-N-used-2, N₂ adsorption/desorption measurement was performed on a Quantachrome Autosorb-iQ-AG instrument. The Brunauer–Emmett–Teller (BET) method was applied to calculate the specific surface area and the Barrett–Joyner–Halenda (BJH) method was used to evaluate the pore

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size distribution.

CeO₂, CeO₂-N, CeO₂-used-1, CeO₂-N-used-1, CeO₂-used-2 and CeO₂-N-used-2 were characterized by X-ray diffraction (XRD) to determine their crystal phases (Bruker D8 Advance, Cu K α radiation). The scattering angle range for data collection was 10–80°, and the step size was 0.02°.

H₂-TPR analysis performed on a chemisorption analyzer (Quantachrome Autosorb-iQ-C) was used to investigate the redox behavior of CeO₂, CeO₂-N, CeO₂-used-1, CeO₂-N-used-1, CeO₂-used-2 and CeO₂-N-used-2. A thermal conductivity detector (TCD) was used to monitor the signal of H₂.

The atomic states of surface elements on CeO₂, CeO₂-N, CeO₂-used-1, CeO₂-N-used-1, CeO₂-used-2 and CeO₂-N-used-2 were detected by X-ray photoelectron spectroscopy (XPS) analysis (Thermo ESCALAB 250, Al K α X-ray, $h\nu = 1486.6$ eV). The binding energy shift was calibrated based on C 1s level (284.8 eV). And an X-ray energy dispersive spectroscopy (EDS) connected with a JEM 2100F TEM system was used for determining the bulk atomic concentrations.

The *in situ* DRIFT experiments were performed on an FTIR spectrometer (Nicolet iS50) with an MCT detector and the spectra record was performed by accumulating of 100 scans with a 4 cm⁻¹ resolution. First of all, the sample was heated at 400 °C for 2.5 h under nitrogen and then decreased to 50 °C. The background DRIFT spectra were recorded at different temperature and were automatically subtracted from the sample spectrum. The reaction conditions were as follows: 300 mL/min total flowrate, 600 ppm of NH₃, or/and 600 ppm of NO + 5% of O₂, and N₂ balance.

2.3. Catalytic activity test

The SCR activity was measured in a fixed-bed reactor (i.d. = 8 mm) with 0.55 cm³ sample (80–100 mesh). 600 ppm NO, 600 ppm NH₃, 5% O₂ and balance Ar were contained in the simulated flue gas. The flow rate of the simulated flue gas was set as 1 L/min, leading to a GHSV value of 108,000 h⁻¹. An FTIR spectrometer (Thermo Nicolet iS 50), as an uninterrupted real-time dynamic survey measurement was applied to monitor the concentrations of NO, NO₂, N₂O and NH₃. The NO_x conversion and N₂ selectivity values were evaluated by the following formulas:

$$\text{NO}_x \text{ conversion} = \frac{[\text{NO}_x]_{\text{in}} - [\text{NO}_x]_{\text{out}}}{[\text{NO}_x]_{\text{in}}} \times 100\% \quad (1)$$

$$\text{N}_2 \text{ selectivity} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}}}{[\text{NO}_x]_{\text{in}} + [\text{NH}_3]_{\text{in}} - [\text{NO}_x]_{\text{out}} - [\text{NH}_3]_{\text{out}}} \right) \times 100\% \quad (2)$$

3. Results and discussion

3.1. Catalytic performance

The SCR catalytic abilities of CeO₂ and CeO₂-N ranging from 100 to 400 °C are depicted in Fig. 1. In the preset temperature range, pure CeO₂ exhibits bad SCR activity of no more than 55%. It is remarkable that NH₃ treatment could effectively enhance its SCR performance. The activity of CeO₂-N is over 80% in 195–336 °C. The observed activity drop above 300 °C over the two catalyst samples should be owing to the unselective NH₃ oxidation by O₂ [19]. Furthermore, the activities of the two samples after the activity test (CeO₂-used-1 and CeO₂-N-used-1) were also evaluated. Apparently, the NO_x conversion of CeO₂-used-1 decreases obviously compared to CeO₂. In contrast, CeO₂-N-used-1 exhibits a slight activity decrease in the whole reaction temperature range. Additionally, NH₃ treatment also helps to improve the N₂ selectivities of CeO₂ and CeO₂-used-1, as shown Fig. 1(B).

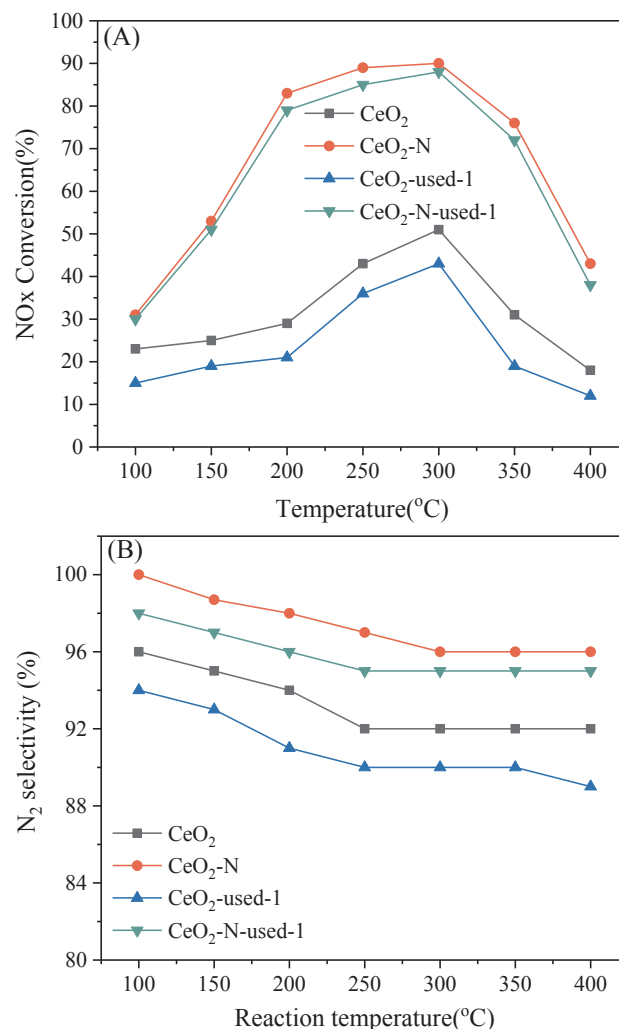


Fig. 1. (A) NO_x conversions (B) N₂ selectivities over CeO₂, CeO₂-N, CeO₂-used-1 and CeO₂-N-used-1 catalysts. Reaction conditions: [NO] = [NH₃] = 600 ppm, [O₂] = 5%, balance Ar, GHSV = 108,000 h⁻¹.

3.2. Stability analysis

The stability experiment is performed to evaluate the durability of NH₃-treated CeO₂. In particular, the stability experiment is conducted under the same experimental conditions as the SCR activity test at 250 °C for 48 h, as presented in Fig. 2. It is evident that the NO_x conversion over fresh CeO₂ drops from 43% to 23.8% in 48 h. In contrast, CeO₂-N shows a relatively less activity decrease, which is from 89% to 81.3% in 48 h. Thus, NH₃-treated CeO₂ obviously possesses a better stability.

3.3. BET and XRD analysis

As the BET results listed in Table 1, it is noteworthy that the treatment of CeO₂ with NH₃ results in a slight decrease of its BET surface area, which may be caused by the block of micropores on the catalyst surface during the treatment process. However, in comparison with pure CeO₂, CeO₂-N possesses better SCR performance, suggesting that specific surface area plays an unimportant role in this reaction. Noticeably, the specific surface areas of CeO₂-used-1 and CeO₂-N-used-1 decrease slightly, which may be caused by the sintering of catalysts in reaction process. Further decrease of specific surface area is also observed on CeO₂-used-2 and CeO₂-N-used-2 owing to the much longer reaction time.

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