



Impacts of niobia loading on active sites and surface acidity in $\text{NbO}_x/\text{CeO}_2\text{-ZrO}_2$ $\text{NH}_3\text{-SCR}$ catalysts



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ABSTRACT

A series of $\text{NbO}_x/\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ catalysts for the selective catalytic reduction of NO with ammonia ($\text{NH}_3\text{-SCR}$) were synthesized using a wetness impregnation method. The effect of niobia loading was studied in relation to the active sites and surface acidity. NH_3/NO oxidation, X-ray diffraction, Infrared spectroscopy, ultraviolet-visible spectroscopy, X-ray photoelectron spectroscopy, H_2 temperature-programmed reduction, O_2/NH_3 temperature-programmed desorption, and diffuse reflectance infrared Fourier transformed spectroscopy experiments were performed to correlate the catalyst structure and surface properties to catalytic performance after Nb_2O_5 modification. The catalyst with 15 wt.% Nb_2O_5 loading showed high $\text{NH}_3\text{-SCR}$ activity and nearly 100% N_2 selectivity within a broad operation temperature window (190–460 °C) at a high space velocity (300,000 h^{-1}). On this catalyst, Nb^{n+} was mainly distributed in the form of typical monomeric and polymeric NbO_x species, and was partially incorporated into the $\text{Ce}_{0.75}\text{Zr}_{0.25}\text{O}_2$ lattice at the $\text{Nb}^{n+}\text{-O-Ce}^{n+}$ (Zr^{n+}) interface. The electron redistribution effect arising from the occupation of cerium sites by Nb^{n+} ions promoted the formation of Ce^{3+} ions, oxygen vacancies and active oxygen species. This interaction was closely associated with the distribution of NbO_x species which varied with niobia loading. NbO_x themselves were acid sites and by attracting electrons they enhanced Lewis acid sites on CZ surface, which promoted the adsorption of NH_3 and inhibited the unselective oxidation of NH_3 to NO_x . The increased amounts of active oxygen species over NbCZ catalysts promoted the adsorptive oxidation of NH_3 to NH_2 and NO to NO_3^- at low temperatures, and thus facilitated the reaction of ads- NH_3 and ads- $\text{NO}_3^-/\text{NO}_2^-$ species. This effect as well as the increased amount of acid sites led to good $\text{NH}_3\text{-SCR}$ performance of Nb15CZ in a wide temperature range.

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1. Introduction

Nitrogen oxides (NO_x) emitted from stationary boilers and mobile engines lead to various environmental problems, e.g. acid rain, photochemical smog, ozone depletion and greenhouse effect [1–3]. Due to the strong polluting effects of nitrogen oxides, regulations of emission levels are becoming ever more stringent, especially in Europe, Japan, the United States [1] and China [4]. Among the various treatment techniques that have been proposed

or developed for NO_x abatement, the selective catalytic reduction (SCR) using ammonia as a reductant in the oxygen-rich exhausts is the most efficient way to fulfill this task [1–3]. Nowadays, the well-studied types of catalysts in NO_x removal are $\text{V}_2\text{O}_5/\text{WO}_3$ (MoO_3)– TiO_2 and transition-metal exchanged zeolites [2,3,5–7]. However, some drawbacks remain for vanadium-based catalysts, including the narrow operation temperature window, the toxicity and volatility of V_2O_5 species and the easy transformation of the TiO_2 support from anatase to rutile at high temperature. On the other hand, although zeolites catalysts show as potential substitutes of vanadium-based catalysts, the durability to severe thermal deactivation induced by combustion of stored HCs is still unsatisfactory [5–7]. Generally, $\text{NH}_3\text{-SCR}$ catalysts in diesel engines should provide several specific catalytic properties, such as satisfactory $\text{NH}_3\text{-SCR}$ performance in a considerable wide temperature window, high durability to chemical impurities poisoning from the exhaust gases, and ultra-high hydrothermal stability to resist timed

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thermal shock induced by the regeneration of diesel particulate filters (DPF) installed upstream of the SCR convertor [1–3,7]. Therefore, it is imperative to develop novel vanadium-free catalysts with high deNO_x activity, high N₂ selectivity, excellent hydrothermal stability, and insensitivity to exhaust components poisoning such as HC, SO₂ and alkali metals.

Ceria, considered as a very active oxide in the SCR reaction, possesses considerable oxygen storage capacity owing to the redox cycling between Ce³⁺ and Ce⁴⁺, which has been already widely used as a crucial component in three-way catalysts (TWCs). Its acid-base properties, lack of toxicity and low cost also attract much attention. Recently, much research has been focused on the ceria-based NH₃-SCR catalysts, such as CeO₂-TiO₂ [8–10], CeO₂-WO₃ [11–18], CeO₂-SO₄²⁻ [19–21], CeO₂-Nb₂O₅ [22–26], CeO₂-PO₄³⁻ [27,28] and CeO₂-MoO₃ [29,30]. The SCR performance of ceria-based catalysts could be remarkably enhanced by introducing solid acid components such as tungsta, niobia, phosphate and sulfate, which mainly due to both excellent redox ability and strong acidity. Among them, CeO₂-Nb₂O₅ based catalysts appear to be a more promising candidate for diesel after-treatment systems due to its multifunctionality, such as (1) the SCR of NO with NH₃, (2) the hydrolysis of urea to NH₃ and (3) the oxidation of soot [23,24]. It has been reported that the addition of Nb₂O₅ could promote the acidity of the catalysts due to the acidic nature of NbO_x species [22–25]. Furthermore, the fact that amount of chemical defects (oxygen vacancies) in Nb-Ce mixed oxides is increased after Nb doping, which is confirmed by the concomitant increase in electron conductivity, has been revealed in some studies [31,32]. However, despite some studies on SCR performance in different reaction conditions, the comprehensive study in structure-activity relationship of CeO₂-Nb₂O₅ based catalysts is still lacking, e.g. the correlation of deNO_x activity to surface acidity and redox ability. In our previous study [26], a significantly enhanced activity for NO_x reduction was attained by addition of Nb₂O₅ into CeO₂-WO_x/TiO₂ catalyst, which is due to the synergistic effect between Ce and Nb.

Considering the redox property and thermal stability [28,33,34], Ce_{0.75}Zr_{0.25}O₂ mixed oxides with a Ce/Zr mole ratio of 3:1 was chosen as a ceria based support in this work. Various characterizations related to the structure, adsorption and redox properties of NbO_x/Ce_{0.75}Zr_{0.25}O₂ catalysts were performed aiming to elucidate this relationship. We also present a primary scheme regarding to the correlation between deNO_x performance, surface acidity and redox property modulated by Nb₂O₅ content.

2. Experimental

2.1. Catalyst preparation

Ce_{0.75}Zr_{0.25}O₂ (CZ) powder was synthesized by a sol-gel method using Ce(NO₃)₄·6H₂O and Zr(NO₃)₄·5H₂O as the precursors. Citric acid was used as the complexing agent. Precursor salts, citric acid, and deionized water were mixed at a mole ratio of 1:2:100. The mixed solution was magnetically stirred in a water bath at 80 °C until a spongy yellow gel was formed. The gel was dried at 110 °C in an oven overnight. The resulting product was subsequently subjected to decomposition at 300 °C for 1 h and calcination at 550 °C for 3 h in a muffle and finally ground to a fine powder. The NbO_x/Ce_{0.75}Zr_{0.25}O₂ (NbCZ) catalysts were synthesized by impregnating the as-received Ce_{0.75}Zr_{0.25}O₂ powders with C₁₂H₇NbO₂₄ solution. The nominal loadings of niobia (calculated in Nb₂O₅) were 5 wt.%, 10 wt.%, 15 wt.% and 20 wt.%, respectively, which were denoted as Nb(x)CZ with *x* representing the mass percentage of Nb₂O₅. The impregnated powders were dried at 110 °C overnight and calcined at 550 °C for 3 h in static air. For comparison, the pure Ce_{0.75}Zr_{0.25}O₂ (CZ) powders also underwent the same thermal

treatment. In some characterizations, Nb₂O₅ was also used as reference; in this case it was prepared by calcination of a C₁₂H₇NbO₂₄ precursor at 600 °C for 4 h. The conventional V₂O₅/WO₃-TiO₂ catalyst was also prepared by impregnating 1 wt.% V₂O₅ on the 10 wt.% WO₃-TiO₂ mixed oxides.

The as-received Nb15CZ catalyst was treated in 10% H₂O/air at 760 °C for 24 h and denoted as the hydrothermally aged catalyst (A-Nb15CZ). Sulfur poisoning of Nb15CZ was performed in 100 ppm SO₂ + 10% H₂O/air at 400 °C for 24 h, and the obtained sample was denoted as the sulfur poisoned catalyst (S-Nb15CZ).

2.2. Activity measurement

The NH₃-SCR activity measurement was carried out in a fixed-bed quartz reactor with the effluent gases monitored by Thermo Nicolet 380 FTIR spectrometer. Samples of 200 mg (0.1 ml) sieved to 40–80 mesh were used for evaluation under the following conditions: 500 ppm NO, 500 ppm NH₃, 5% O₂, 12% CO₂, 5% H₂O (when used), N₂ as balance, 500 ml min⁻¹ total flow rate, and GHSV = 3 × 10⁵ h⁻¹. The inlet and outlet gas pipes were maintained above 150 °C to prevent formation and deposition of ammonium nitrates. The measurement was performed with 50 degrees stepwise ranging from 100 to 500 °C. The NH₃-SCR activity, N₂ selectivity and the pseudo-first order rate constant (*k*) of catalysts were calculated as follows (Eqs. (1–3)). In Eq. (3), *F* was the total flow rate, *W* the weight of catalyst and *X* the NO_x conversion of the catalyst [13,25].

$$\text{NO}_x \text{ conversion (\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}}}\right) \times 100 \quad (1)$$

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

$$k = -\frac{F}{W} \ln(1 - X) \quad (3)$$

NH₃/NO oxidation experiments were performed under similar conditions as the SCR reaction, except that either NO or NH₃, respectively, was excluded from the gas mixture. The NH₃ conversion was calculated based on Eq. (4). The selectivity to N₂ in the NH₃ oxidation was estimated based on the nitrogen balance (Eq. (5)) [13].

$$\text{NH}_3 \text{ conversion (\%)} = \left(1 - \frac{[\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}}\right) \times 100 \quad (4)$$

$$\text{N}_2 \text{ selectivity (\%)} = \left(1 - \frac{2[\text{N}_2\text{O}]_{\text{out}} + [\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}\right) \times 100 \quad (5)$$

2.3. Catalyst characterization

X-ray diffraction (XRD) experiments were performed on a Shimadzu s-7000 diffractometer (Japan) employing Cu Kα radiation (λ = 0.15418 nm) operated at 40 kV and 120 mA. The X-ray diffractogram was recorded at 0.02° intervals in range of 20° ≤ 2θ ≤ 80° with a scanning velocity of 4° min⁻¹. The crystalline phases were identified using JCPDS (Joint Committee on Powder Diffraction Standards) cards.

Nitrogen adsorption isotherms were measured on a JW-BK122F (JWGB, China) instrument. All the samples were degassed at 220 °C for 1 h prior to the nitrogen adsorption measurements. The BET surface area was determined by a multipoint BET method,

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