Full Length Article

Promotional effect of Al_2O_3 on WO_3/CeO_2-ZrO_2 monolithic catalyst for selective catalytic reduction of nitrogen oxides with ammonia after hydrothermal aging treatment

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A B S T R A C T

Hydrothermal stability of catalysts for selective catalytic reduction of NO_x with NH_3 (NH_3-SCR) has always been recognized as a challenge in development of candidate catalysts for applications in diesel engine emissions. In this study, Al_2O_3 was introduced into CeO_2-ZrO_2 to improve the NH_3-SCR activity of WO_3/CeO_2-ZrO_2 after hydrothermal aging (HA) treatment at 800 °C for 12 h. The activity results indicated that the NH_3-SCR activity of WO_3/CeO_2-ZrO_2-HA was obviously improved in the whole reaction temperature range after doping Al_2O_3 into CeO_2-ZrO_2, for example, the average and maximum NO_x conversion were separately increased by ca. 20% and 25% after HA treatment. XRD, Raman, TEM and EDX results revealed that the introduction of Al_2O_3 inhibited the sintering and agglomeration of CeO_2-ZrO_2 and WO_3 and the formation of $Ce_2(WO_4)_3$ after HA treatment. Accordingly, WO_3/CeO_2-ZrO_2-Al_2O_3-HA showed remarkably improved structural stability and reducibility, increased surface acidity, and facilitated the reactivity between adsorbed NH_3 and nitrate species, which together contributed to its better catalytic performance after hydrothermal aging treatment.

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1. Introduction

Nitrogen oxides (NO_x) emitted from the coal fired power plants as stationary resources and the diesel engines as mobile resources, are the major air pollutants, which can cause seriously adverse environment issues, such as acid rain, greenhouse effect, photochemical smog and ozone depletion [1,2]. Currently, the selective catalytic reduction of NO_x with NH_3 as reducing agent is the most effective technology to remove NO_x and has been widely used [3]. Many metal oxide catalysts have been reported as the active species for NH_3-SCR reactions, among them, V_2O_5-WO_3/TiO_2 catalyst is the most typical commercial catalyst today due to its high activity [4,5]. However, it still possesses some disadvantages, such as a narrow reaction temperature range, low N_2 selectivity, low hydrothermal stability and harmfulness to human body originated from the tox-

icity and volatility of vanadium oxides [6,7]. Consequently, it is imperative to develop novel mixed oxides NH_3-SCR catalysts with high NO_x conversion (especially at the low-temperature range) and N_2 selectivity, excellent hydrothermal stability and a considerable wide operation temperature window, which will be a promising candidate to replace the conventional vanadium-based SCR catalysts.

Ceria, with the advantages of considerable oxygen storage capacity and excellent redox property, has been proved to be an environmental friendly active species or a part of the support in the NH_3-SCR reactions. Recently, increasing attentions have been paid to the Ce-based NH_3-SCR catalysts [3]. Considering the redox property, acid-base property and thermal stability, ceria-zirconia mixed oxides were considered to be one of the most promising support materials for the purification of NO_x [8,9]. Thus, much research has been focused on the ceria-zirconia based NH_3-SCR catalysts in recent years, such as WO_3/CeO_2-ZrO_2 [10–12], MnO_x/CeO_2-ZrO_2 [13,14], $CeMZrO_x$ (M = Nb, Mo) [15,16], $Ce_{0.75}Zr_{0.2}Mo_{0.05}O_x$ [17], NiO-CeO_2-ZrO_2 [18], $Ce_{0.75}Zr_{0.25}O_2$-PO_4^{3-} [19], CuO-CeO_2-ZrO_2 [20], Fe_2O_3-$WO_3/Ce_{0.68}Zr_{0.32}O_2$ [21,22]. These catalysts showed

excellent deNO$_x$ activity, N$_2$ selectivity and H$_2$O/SO$_2$ tolerance under their measurement conditions. However, taking account into the requirements on the lifetime of NH$_3$-SCR catalysts for NO$_x$ regulation like EURO VI and higher temperature induced by the regeneration of the diesel partial filter (DPF), the NH$_3$-SCR catalyst must possess ultra-high hydrothermal stability at 800 °C for long time. Among the above modified ceria-zirconia based catalysts, CeNb$_3$Zr$_2$O$_x$ [16] and Ce$_{0.75}$Zr$_{0.25}$O$_2$-PO$_4{}^{3-}$ [19] displayed a relatively higher hydrothermal stability. Whereas, the conditions about the particle shape of the above two catalysts and high cost of niobium are far from the industrial application [23], thus, it is significant to develop monolithic ceria-zirconia based deNO$_x$ catalyst with a low cost. Our previous works reported that WO$_3$/CeZrO$_2$ monolithic catalyst could achieve higher than 90% NO$_x$ conversion in a considerably wide operation window of 224–445 °C under 30,000 h^{-1} with 1.25 L min^{-1}, and excellent H$_2$O/SO$_2$ tolerance [24,25]. It presented potential application of a NH$_3$-SCR catalyst applied in the diesel engine, if its hydrothermal stability could be solved with low-cost methods.

Al$_2$O$_3$ is one of the most common carrier materials due to its large surface area, high mechanical strength, excellent thermal stability and low cost [26]. The combination between Al$_2$O$_3$ and CeO$_2$-ZrO$_2$ has been systematically investigated in the three-way catalysts (TWCs). The results demonstrated that the catalytic performances of TWCs were remarkably increased due to enhancements in textural properties, redox properties and thermal stability, compared with single CeO$_2$-ZrO$_2$ or Al$_2$O$_3$ as the carrier of TWCs [27–30]. As far as we know, there are few reports about the utilization of Al$_2$O$_3$ modified cerium zirconium mixed oxides in the NH$_3$-SCR reactions. Therefore, in this work, we attempted to introduce Al$_2$O$_3$ into CeO$_2$-ZrO$_2$ by a conventional co-precipitation method to promote the hydrothermal stability of WO$_3$/CeO$_2$-ZrO$_2$ catalyst. The hydrothermal stability of catalysts was evaluated by treating the catalysts at 800 °C for 12 h, 10 vol.% H$_2$O in air, a GHSV of 30,000 h^{-1} and a gaseous rate of 1.25 L min^{-1}. It was interesting that the addition of Al$_2$O$_3$ remarkably improved the hydrothermal stability of WO$_3$/CeO$_2$-ZrO$_2$ catalyst, although the deNO$_x$ activity of WO$_3$/CeO$_2$-ZrO$_2$Al$_2$O$_3$ was depressed before hydrothermal aging treatment. Various characterizations related to the structure, redox property, and reactivity of adsorbed NH$_3$ and NO$_x$ species on the catalysts before and after HA treatment were systematically performed via N$_2$ physisorption, XRD, Raman, TEM, EDX, XPS, H$_2$-TPR, NH$_3$-TPD and in situ DRIFTS.

2. Experimental

2.1. Catalysts preparation

The support materials CeO$_2$-ZrO$_2$ (denoted as CZ) and CeO$_2$-ZrO$_2$Al$_2$O$_3$ (denoted as CZA) mixed oxides were prepared by the conventional co-precipitation method. In a typical preparation process, desired amounts of Ce(NO$_3$)$_3$·6H$_2$O, Zr(NO$_3$)$_4$·5H$_2$O and Al(NO$_3$)$_3$·9H$_2$O were dissolved in deionized water, respectively. Superfluous NH$_3$·H$_2$O-(NH$_4$)$_2$CO$_3$ buffer solution as precipitant was added drop-wise to the solution until the pH value rose to approximately 9, with continuous stirring at the boiling point (above 95 °C) for 6 h. Subsequently, the collected precipitate was filtered and washed by deionized water, followed by drying at 80 °C overnight and calcining at 600 °C for 3 h. The nominal loading of Al$_2$O$_3$ was 10 wt.% in CZA and the molar ratio of Ce/Zr was fixed at 68:32 in both materials.

The WO$_3$/CeO$_2$-ZrO$_2$ (W/CZ) and WO$_3$/CeO$_2$-ZrO$_2$Al$_2$O$_3$ (W/CZA) catalysts were synthesized by impregnating the as-received CZ and CZA powders with (NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$ (AR grade, 99%, Anda, China) solution, the loading of WO$_3$ was 10 wt.%. The impregnated powders were drying at 80 °C overnight, and then calcining at 600 °C for 3 h in air. The resulting two catalyst powders were subsequently coated on honeycomb cordierites (cylinder, diameter: 11 mm, length: 26 mm, bulk: 2.5 cm^3, 62 cell cm^{-2}, Corning, USA), and then dried at 120 °C overnight and calcining at 600 °C for 3 h. Finally, W/CZ and W/CZA monolithic catalysts with the coating content of about 160 g L^{-1} were obtained. The HA carriers and catalysts were obtained by treating the fresh catalysts in air containing 10 vol.% H$_2$O at 800 °C for 12 h with a GHSV of 30,000 h^{-1} and a gaseous rate of 1.25 L min-1 [31]. The hydrothermal aging samples were denoted as CZ-HA, CZA-HA, W/CZ-HA and W/CZA-HA, respectively.

2.2. Catalytic activity measurements

The NH$_3$-SCR activity measurements of the prepared monolithic catalysts were carried out in a fixed-bed quartz tube flow reactor at atmospheric pressure. The flue gas composition was as follows: 500 ppm NO, 500 ppm NH$_3$ (when used), 5% O$_2$, N$_2$ as balance. The premixed gases (2.0% NO in N$_2$, 2.0% NH$_3$ in N$_2$ and 99.99% O$_2$) were supplied by Testing Technology Research Institute, China. Reactant gases were regulated by mass-flow controllers before entering the reactor. In typical condition, 2.5 cm^3 monolithic catalyst sample was used in each run and the total flow rate was about 1.25 L min-1, yielding the GHSV of 30,000 h^{-1} by volume. The separate NO oxidation activity was tested in the absence of NH$_3$. The concentrations of NH$_3$, NO$_x$ and N$_2$O in the inlet and outlet gases were continually analyzed by an FT-IR (Antaris IGS, Nicolet). The data were recorded after 30 min when the reaction reached a steady state for each test.

The NO$_x$ conversions (X_{NOx}) and N$_2$ selectivity (S_{N2}) were calculated as follows:

$$X_{NO_x} (\%) = \frac{C_{in} - C_{out}}{C_{in}} \times 100 \tag{1}$$

$$S_{N_2} (\%) = (1 - \frac{2[N_2O]_{out}}{([NO_x]_{in} - [NO_x]_{out}) + ([NH_3]_{in} - [NH_3]_{out})}) \times 100 \tag{2}$$

where, [NO$_x$] = [NO] + [NO$_2$], C$_{in}$ and C$_{out}$ denoted the inlet and outlet gas concentration of NO$_x$, respectively.

2.3. Characterizations

The textural properties of all catalysts were measured by N$_2$ adsorption-desorption at −196 °C on Quantachrome automated surface area & pore size analyzer (Autosorb SI). The samples were pretreated at 300 °C for 3 h prior to the measurement. The surface areas were determined by Brunauer-Emmett-Teller (BET) model.

Powder X-ray diffraction (XRD) patterns of samples were collected in the 2θ range of 10−80° using Rigaku D/max-RA Diffractometer equipped with a Cu K_α (λ = 0.15406 nm) radiation resource operated at 40 kV and 100 mA, respectively.

Visible Raman spectra of all catalysts were collected on a Lab-RAM HR laser Raman spectrograph with a spectral resolution of 2 cm^{-1} at the room temperature. A Nd: Yag laser of 532 nm was used as the excitation source with a power output of 30 mW. All specimens were illuminated through a 50 × objective and in powder form to prevent diffusion problems. Raman spectra were collected and recorded over the spectral range of 200−1000 cm^{-1}. The specification of the grating was 600 g/mm.

Transmission electron microscopy (TEM) observations were obtained using a Tecnai G^2 F20 S-TWIN TEM (FEI Company, USA, 200 kV accelerating voltage) equipped with STEM, EDX and HAADF systems. Before the experiment, the powder specimens were suspended in ethanol and dispersed by ultra-sonic irradiation; after