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The superior performance of Nb-modified Cu-Ce-Ti mixed oxides for the selective catalytic reduction of NO with NH₃ at low temperature

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ABSTRACT

In this paper, a series of Nb modified Cu-Ce-Ti mixed oxides (Nb_yCCT) were synthesized using wetness impregnation method for the selective catalytic reduction of NO with ammonia (NH₃-SCR). The activity tests indicated that Nb_yCCT catalysts had shown superior SCR performances. Among which, Nb_{0.05}CCT catalyst exhibited a NO conversion of more than 90% within a broad operation temperature window (180–360 °C) under the GHSV of 40,000 h⁻¹. After that, corresponding characterizations were performed to correlate the physical structures and surface properties to catalytic performances. These results revealed that the strong interactions among the active phases induced by Nb addition could not only enhance the redox property of the catalysts but also inhibit the over-oxidation of NH₃, which would be beneficial to SCR performance within a wide temperature range and good reaction selectivity. Furthermore, DRIFTS results suggested that the doping of Nb could promote the formation of NO₂, thereby enhancing the “fast” SCR reaction process (Langmuir-Hinshelwood reaction pathway). Moreover, the Nb_{0.05}CCT catalyst showed a better sulfur tolerance compared to Nb free catalyst that over 85% NO conversion could be retained after 12 h SCR reaction in the presence of SO₂ and H₂O.

1. Introduction

As a major source of air pollutants, nitrogen oxides (NO_x) have caused a series of environmental problems including photochemical smog, acid rain and haze [1–3]. And industrial combustion of fossil fuels is one of the main sources of NO_x emission [4]. The selective catalytic reduction with ammonia (NH₃-SCR) is a well-established and high-efficient technology for NO_x emissions control from industrial sources, especially power plant [3,5]. However, the working temperature of the commercial catalyst [V₂O₅-WO₃(MoO₃)/TiO₂] is too high (300–400 °C) to fit the flue gas condition of lots of industrial boilers/furnaces. Moreover, some nonnegligible shortages like the toxicity of vanadium [3,5,6] and oxidation of SO₂ to SO₃ [5,7–9] also limit its application. Consequently, it is necessary to develop novel vanadium free NH₃-SCR catalysts with high activities in medium-low temperature region (below 300 °C), which would be a solution to the above mentioned shortcomings.

Cerium-based oxides were considered as a promising candidate to V₂O₅-WO₃(MoO₃)/TiO₂ catalysts for the NH₃-SCR process at low temperature due to the high oxygen storage capacity and excellent redox property of CeO₂ [10–12]. Up to date, TiO₂-based SCR catalysts modified by ceria have been investigated extensively [11,13–15]. To

broaden the operation temperature window at medium-low temperature of the catalysts, some advanced preparing methods were employed on CeO₂/TiO₂ catalysts by improving the dispersion of ceria on the support and inducing strong metal support interactions (SMSI) [11,15]. On the other hand, transition metal doping into the Ce-Ti catalysts system to enhance the low-temperature SCR performance has received considerable attentions in the past decades [16–24]. And these works could be divided into two major categories. Firstly, the doping of transition metal (such as Cu, Fe, Co, Mn) oxides, which possessed excellent reducibility, could greatly promote the activation of ammonia, thereby enhancing the SCR activity at low temperature. However, these modifications would also result in the over-oxidation of NH₃ at an elevated temperature, thereby decreasing the activity at high temperature. The other one was adding the transition metals (such as W and Nb) with unique property by forming strong interactions between the transition metal and cerium, which would lead to the enhancement of ceria dispersion, surface active oxygen and acidity, facilitating the SCR performances [17,20]. However, the low-temperature activity (especially under 200 °C) of these modified catalysts still need further improved.

Copper oxide, due to its quite high reducibility at low temperature, was widely used in the development of catalysts for low-temperature

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SCR deNO_x process [21,25–28] and VOCs catalytic combustion [29–31]. Doping Cu into the Ce-Ti SCR catalysts has also been reported by several previous studies [19,32–35]. According to the causes mentioned above, Cu-Ce-Ti catalysts still suffered the drawbacks, such as the narrow operation temperature window and the producing of ozone-depleting N₂O at high temperatures [19,32,33,36]. Recently, Nb was widely used as promoter in ceria based SCR catalysts to improve the physicochemical properties via its strong interactions with ceria [17,37–43]. And such effect could inhibit the over oxidation of NH₃ according to the previous literatures [37,39,41,43]. Therefore, it was motivated that the co-doping of Nb and Cu into CeO₂/TiO₂ catalyst system could achieve synergistic effect on both low-temperature SCR activity and broad temperature window.

In the present study, a series of bimetallic Cu and Nb doped CeO₂/TiO₂ catalysts were synthesized by a wetness impregnation method. And their NH₃-SCR performances including NO conversion and N₂ selectivity, stability were then investigated. Characterization experiments of different catalysts were also carried out to reveal the changes in the physicochemical properties induced by modifications and their relationships with the SCR performances.

2. Experimental section

2.1. Materials

The Ce(NO₃)₃·6H₂O, Cu(NO₃)₂·3H₂O and citrate were all purchased from Aladdin Reagent Co., Ltd. (Shanghai, P. R. China). C₁₀H₅NbO₂₀ was supplied by Macklin Inc. TiO₂ support and oxalic acid were purchased from sinopharm reagent. Deionized water was used in the experiments.

2.2. Catalysts preparation

In this work, all the catalysts were prepared by the wet impregnation method. For the preparation of Ce-Ti catalyst, 0.1 mol of TiO₂, 0.02 mol of Ce(NO₃)₃·6H₂O, 0.1 mol of Citrate and 0.05 mol of oxalic acid were added in deionized water of 100 mL. The mixed solution was under vigorous stirring at room temperature for 3 h, and then dried at 120 °C for 12 h. The as-obtained solid was calcined at 500 °C in air for 6 h, and crushed and sieved to 40–60 mesh. The synthesis processes of Cu-Ce-Ti, Nb-Ce-Ti and Nb modified Cu-Ce-Ti samples were similar to that of Ce-Ti, in which 0.001 mol of Cu(NO₃)₂·3H₂O and 0.001–0.01 mol of C₁₀H₅NbO₂₀ (if use) were added during this process for different catalysts according to the calculated atomic proportion. The catalyst CT represented the Ce_{0.2}TiO_x, the catalyst CCT represented the Cu_{0.01}Ce_{0.2}TiO_x, the catalyst Nb_yCT represented the Nb_yCe_{0.2}TiO_x and the catalyst Nb_yCCT represented the Nb_yCu_{0.01}Ce_{0.2}TiO_x, where y represented the atomic ratio of Nb to Ti.

2.3. Catalysts characterization

The specific surface area, pore volume and pore size were determined by the BET-BJH method on a nitrogen adsorption apparatus (JW-BK132F, China). Samples were pretreated at 200 °C for 2 h under vacuum.

TEM test was conducted by a model Tecnai G2 F20 S-TWIN (FEI Company, USA) with high-resolution transmission electron microscope (HR-TEM, 400 kV accelerating voltage) instrument.

The crystal phases of the samples were analyzed by using X-ray diffraction with CuKα radiation (XRD: model D/max RA, Rigaku Co., Japan). The data was collected for scattering angles (2θ) ranging between 10° and 80°.

X-ray photoelectron spectroscopy with Al Kα X-ray (hν = 1486.6 eV) radiation operated at 150 W (XPS: Thermo ESCALAB 250, USA) was used to investigate the surface properties of the samples. C 1s level at 284.8 eV was used to correct the shift of binding energy.

Temperature-programmed desorption (TPD) and temperature-programmed reduction (TPR) both were recorded on a mass detector (HIDEN QGA, UK) and a traditional thermal conductivity detector (TCD) (TP-5089, TianJin Xianquan Co. Ltd., P. R. China). 50 mg and 100 mg samples were used for H₂-TPR and for NH₃-TPD (or O₂-TPD), respectively. The samples were pretreated at 400 °C for 1 h in the flow of pure He gas and then cooled to 30 °C. The process of TPR was performed from 100 to 800 °C at a heating rate of 10 °C/min with H₂ (6% H₂/N₂, 30 ml/min). For TPD experiments, the catalysts were first saturated with anhydrous NH₃ (4% NH₃/He, 50 ml/min) for half an hour at 30 °C or O₂ (5% O₂/He, 30 ml/min) for two hours at 400 °C. And the desorption process was performed at a heating rate of 10 °C/min from 100 to 500 °C for NH₃-TPD and 100 to 800 °C for O₂-TPD under a flow rate of 20 ml/min pure He, respectively.

In situ DRIFT tests were performed on a Bruker Tensor 27 FTIR spectrometer. The catalysts were pretreated under 400 °C with He (30 mL/min) for 1 h to remove surface impurities and physical adsorbed species, and then cooled to 150 °C to collect the background spectrum under a flow of pure He. The DRIFT spectra of each sample were recorded at 150 °C by accumulating 64 scans with a resolution of 4 cm⁻¹.

2.4. SCR activity tests and measurements

Selective catalytic reduction of NO with NH₃ was carried out in a fixed-bed reactor. The experiments were performed under atmospheric pressure at 100–360 °C. The catalyst was sieved to 40–60 mesh before use. The typical reaction gas compositions were: 600 ppm NO, 600 ppm NH₃, 3% O₂, 5% water vapor and balanced N₂. The gas hourly space velocity (GHSV) was about 40 000 h⁻¹ for this system.

NO, NO₂ and O₂ concentrations were monitored by a flue gas analyzer (Testo 350, Testo Inc., USA) and N₂O was detected by an infrared gas analyzer (Photon II, Madur Electronics, Austria). NO_x conversion was calculated as follows:

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

where the subscripts in and out indicate the inlet and outlet concentration of NO_x at steady state, respectively.

3. Results and discussion

3.1. NH₃-SCR activity of the catalysts

The experiment results regarding the NO conversion and N₂O formation of all catalysts as a function of temperature were listed in Fig. 1. As indicated in Fig. 1a, the CT catalyst did not show sufficient activity below 250 °C, similar results could be found in others work [44,45]. Unsurprisingly, the addition of Cu into CT catalyst enhanced the low temperature activity, while the temperature window of the catalyst was very narrow owing to the over oxidation of NH₃ at higher temperature. This finding also fitted well with the previous studies [20]. After the doping of Nb into CCT, both the NO conversion and working temperature window were dramatically enhanced. For instance, the Nb_{0.05}CCT catalyst exhibited a NO conversion of over 90% at the temperature range of 180–360 °C. It could be also found that SCR activity increased rapidly with the Nb loading amount increased from 1 to 5 at.%. Further increase of Nb doping content did not show obvious improvement in NO conversion, and the SCR activity decreased when the loading amount reached 20 at.% (see Fig. S1). Moreover, Fig. 1b has indicated that Nb doping also led to an increase in the N₂ selectivity since the N₂O production was suppressed over Nb containing samples, which might be attributed to the strong interactions between Nb and the active phases and the enhancement in surface acidity [17,37–39,46]. The Nb_{0.05}CCT herein also showed a better SCR performance (including low temperature activity and selectivity) than the

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