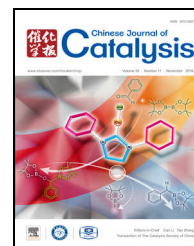


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Article

Low-temperature activity and mechanism of WO₃-modified CeO₂-TiO₂ catalyst under NH₃-NO/NO₂ SCR conditions

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ABSTRACT

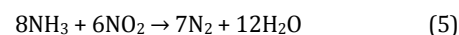
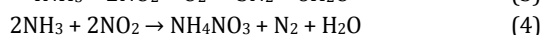
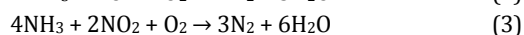
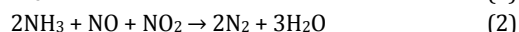
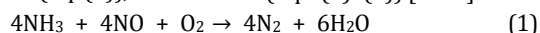
The CeO₂-TiO₂ (CeTi) and CeO₂/WO₃-TiO₂ (CeWTi) catalysts were prepared by a sol-gel precipitation method and their NH₃-NO/NO₂ selective catalytic reduction (SCR) performance was studied. N₂O formation and effect of oxygen concentration on SCR performance over CeWTi catalyst were also investigated while varying the NO₂/NO_x ratio. Results indicate that fast SCR behavior of CeWTi catalyst has the best NH₃-NO/NO₂ SCR performance due to the catalyst reoxidation rate by NO₂ higher than by O₂. Compared with CeTi catalyst, CeWTi catalyst exhibits higher de-NO_x performance under NH₃-NO/NO₂ SCR conditions. As the CeTi and CeWTi catalysts exhibit similar redox property, addition of WO₃ provides more acid sites which accelerate the reaction between NH₄NO₃ and NO to get a superior low-temperature activity. Amount of N₂O formation shows a peak at 250 °C mainly derived from NH₄NO₃ decomposition.

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1. Introduction

Nitrogen oxides NO_x (NO and NO₂) produced from mobile and stationary sources are major sources cause of photochemical and smog acid rain [1–3]. Selective catalytic reduction (SCR) by ammonia is one of the most efficient methods used for removal of NO_x [4,5]. It is widely used in power plants and other industrial settings [6–8]. The ratio of NO to NO₂ from exhaust gas entering the SCR catalytic converter affects the catalytic activity of the main reactions. NH₃-SCR generally occurs via three types of reaction paths, which are standard SCR (Eq. (1)), fast SCR (Eq. (2)), and NO₂ SCR (Eqs. (3)–(5)) [9–12].



Reaction (1) shows the standard SCR reaction. As the fraction of NO₂ increases, Reaction (2) occurs. When the mole ratio of NO₂ to NO is 1:1, the reaction rate is faster than standard SCR reaction [13]. Reaction (2) so called fast SCR does not involve oxygen [14]. If the NH₃:NO₂ mole ratio is increased up to 2.0, the reaction follows Reaction (3) and its reaction rate is very slow. When the reaction temperature is below 180 °C, as shown in Reaction (4), ammonium nitrate salt is formed, which may deactivate the catalyst. Reaction (5) occurs at temperatures above 300 °C [15]. It is known that NO₂ SCR Reactions (3)–(5) are much slower than the fast SCR Reaction (2). In addition, byproduct (nitrous oxide) is detected in a certain temperature range, which is a characteristic of NO₂ SCR. The proportion of NO₂ might facilitate or inhibit the SCR reaction. Therefore, NO₂ has an important effect on the reaction between NO, O₂, and

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NH₃.

The comparative researches of standard, fast and NO₂ SCR mechanisms have been studied. Several papers have addressed the effect of the NO₂/NO_x ratio on SCR activity, such as V₂O₅-WO₃/TiO₂ [16,17], Fe-ZSM-5 [18,19] and Cu-zeolite [11,20]. In addition, CeO₂ based catalysts have attracted much attention in the NH₃-SCR field, due to its superior ability to store/release oxygen and nontoxicity [21–23]. CeO₂/WO₃-TiO₂ (CeWTi) catalyst as a typical deNO_x catalyst has been widely reported. Chen et al. [24] found the standard SCR activity of the CeO₂/TiO₂ catalyst was enhanced by the addition of WO₃. Because CeWTi catalyst provided more adsorbed NO_x and NH₃ species, and simultaneously enhanced the activity of both species resulting in the improvement of SCR activity. Zhang et al. [25] reported that WO₃ could interact with CeO₂ to improve the electron gaining capability of CeO₂ species and acted as electron donating groups to transfer the electrons to CeO₂ species. But these works did not research the difference of reaction route and mechanism between CeO₂-TiO₂ (CeTi) and CeWTi catalyst, especially under NH₃-NO/NO₂ SCR conditions. In addition, a few researches have reported the effect of NO/NO₂ ratios on the NO_x conversion over the CeO₂ based catalyst. However, there is few quantitative data describing detailed relationships among the NH₃-NO/NO₂ SCR reactions over CeO₂ based catalyst despite the fact that this information helps us understand activity data associated with a catalytic converter. Furthermore, the oxygen supply capacity of cerium based catalysts needs to be investigated.

Our previous work compared the standard and fast SCR by (TRA) and diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) method and analyzed adsorption and desorption steps of NO₂ [26]. In this work, we investigated the effect of WO₃ modified CeTi catalysts on NH₃-NO/NO₂ SCR reactions. The NO_x reduction activity over CeWTi catalyst occurs by changing the NO₂/NO_x ratio (0–100%) and oxygen concentration (0–10%) in small increments. We discussed the contributions from three SCR reactions based on the results and established the general chemistry of NH₃-SCR useful for the practical development of catalysts.

2. Experimental

2.1. Catalyst preparation

The CeWTi mixed oxide catalyst was prepared by a sol-gel method. Cerium nitrate hexahydrate (AR, Aladdin), ammonium paratungstate (AR, Beijing Chem. Plant) and commercial TiO₂ powders (DT-51, Millennium Chemicals, France) were mixed in deionized water according to a mass ratio of CeO₂: WO₃: TiO₂ = 5:5:90. And then citric acid (AR, Aladdin) and nitric acid (AR, Beijing Chem. Plant) were added. The solution was sufficiently stirred in a water bath and heated at 80 °C until a porous 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 600 °C for 3 h in a muffle. Finally, the samples were crushed and sieved to 40–60 mesh for catalytic activity measurements. The reference cata-

lyst CeTi was prepared by the same method.

In order to investigate the reaction behavior of NH₄NO₃ over different catalysts, a series of reference samples were prepared as follows. CeTi and CeWTi powder were mixed with 10 wt% NH₄NO₃ powder in a ball mill (QM-3SP04, China) for 3 h and the obtained samples were sieved to 40–60 mesh size for temperature-programmed surface reaction (TPSR) experiment.

2.2. Activity measurement

The measurement of NH₃-SCR activity was carried out in a fixed-bed quartz tube from 100 to 500 °C with an interval of 50 °C. 200 mg catalyst was sieved to a 40–60 mesh size and loaded into the reactor with a gas hourly space velocity (GHSV) of 150000 h⁻¹. The SCR feed stream consisted of 1000 ppm NH₃, 1000 ppm NO_x (NO and NO₂), O₂ (0–10%), 2% H₂O and N₂ in balance. The outlet gas was monitored by a Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific, USA) at 150 °C. The NO_x conversion was calculated as follows.

$$\text{NO}_x \text{ conversion (\%)} = \left(1 - \frac{[\text{NO}]_{\text{out}} + [\text{NO}_2]_{\text{out}}}{[\text{NO}]_{\text{in}} + [\text{NO}_2]_{\text{in}}}\right) \times 100\% \quad (6)$$

2.3. Catalyst characterization

The NH₃ or NO oxidation activity at 200–500 °C was measured in a fixed bed reactor with 200 mg powder catalyst (40–60 mesh) and detected by a Nicolet 380 FTIR spectrometer (Thermo Fisher Scientific, USA). The gas mixture included 500 ppm NH₃ or NO, 5% O₂, 2% H₂O and N₂ in balance, and the GHSV was 150000 h⁻¹. The NH₃ or NO conversion was calculated as follows:

$$\text{NH}_3 \text{ conversion (\%)} = \frac{[\text{NH}_3]_{\text{in}} - [\text{NH}_3]_{\text{out}}}{[\text{NH}_3]_{\text{in}}} \times 100 \quad (7)$$

$$\text{NO conversion (\%)} = \frac{[\text{NO}]_{\text{in}} - [\text{NO}]_{\text{out}}}{[\text{NO}]_{\text{in}}} \times 100\% \quad (8)$$

H₂ temperature-programmed reduction (H₂-TPR) experiments were conducted on a Micromeritics Autochem II 2920 chemisorption analyzer using 50 mg of the CeTi or CeWTi samples. The samples were preheated at 500 °C for 30 min in He flow. The temperature was increased from 50 to 1000 °C at a heating rate of 10 °C min⁻¹ with 10% H₂/Ar gases. The H₂ consumption was recorded continuously.

Temperature-programmed desorption of ammonia (NH₃-TPD) experiments were performed on a Nicolet 380 infrared (IR) spectrometer (Thermo Fisher, USA). Prior to the experiment, 200 mg sample was pretreated at 200 °C in a gas flow of 5% O₂/N₂ for 30 min. Then the samples were cooled down to 100 °C and purged with NH₃ until saturation, followed by flushing with N₂ to avoid the physisorption of NH₃. Afterwards, the NH₃-saturated samples were ramped to 500 °C at a rate of 10 °C min⁻¹ in N₂.

DRIFT spectra of adsorbed species arising from NH₃ adsorption at various temperatures, were recorded in the range of 4000–650 cm⁻¹ using a Thermo Nicolet 6700 FTIR spectrometer. The sample in a diffuse reflectance IR cell was purged by N₂

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