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Article

Low-temperature activity and mechanism of WO_3-modified CeO_2-TiO_2 catalyst under NH_3-NO/NO_2 SCR conditions

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ABSTRACT

The CeO_2-TiO_2 (CeTi) and CeO_2/WO_3-TiO_2 (CeWTi) catalysts were prepared by a sol-gel precipitation method and their NH_3-NO/NO_2 selective catalytic reduction (SCR) performance was studied. N_2O formation and effect of oxygen concentration on SCR performance over CeWTi catalyst were also investigated while varying the NO_2/NO_x ratio. Results indicate that fast SCR behavior of CeWTi catalyst has the best NH_3-NO/NO_2 SCR performance due to the catalyst reoxidation rate by NO_2 higher than by O_2. Compared with CeTi catalyst, CeWTi catalyst exhibits higher de-NO_x performance under NH_3-NO/NO_2 SCR conditions. As the CeTi and CeWTi catalysts exhibit similar redox property, addition of WO_3 provides more acid sites which accelerate the reaction between NH_4NO_3 and NO to get a superior low-temperature activity. Amount of N_2O formation shows a peak at 250 °C mainly derived from NH_4NO_3 decomposition.

1. Introduction

Nitrogen oxides NO_x (NO and NO_2) 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 NO_2 from exhaust gas entering the SCR catalytic converter affects the catalytic activity of the main reactions. NH_3-SCR generally occurs via three types of reaction paths, which are standard SCR (Eq. (1)), fast SCR (Eq. (2)), and NO_2 SCR (Eqs. (3)–(5)) [9–12].

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O \quad (2)$$

$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \quad (3)$$

$$2NH_3 + 2NO_2 \rightarrow NH_4NO_3 + N_2 + H_2O \quad (4)$$

$$8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O \quad (5)$$

Reaction (1) shows the standard SCR reaction. As the fraction of NO_2 increases, Reaction (2) occurs. When the mole ratio of NO_2 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 NH_3:NO_2 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 NO_2 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 NO_2 SCR. The proportion of NO_2 might facilitate or inhibit the SCR reaction. Therefore, NO_2 has an important effect on the reaction between NO, O_2, and

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NH_3.

The comparative researches of standard, fast and NO_2 SCR mechanisms have been studied. Several papers have addressed the effect of the NO_2/NO_x ratio on SCR activity, such as V_2O_5-WO_3/TiO_2 [16,17], Fe-ZSM-5 [18,19] and Cu-zeolite [11,20]. In addition, CeO_2 based catalysts have attracted much attention in the NH_3-SCR field, due to its superior ability to store/release oxygen and nontoxicity [21–23]. CeO_2/WO_3-TiO_2 (CeWTi) catalyst as a typical deNO_x catalyst has been widely reported. Chen et al. [24] found the standard SCR activity of the CeO_2/TiO_2 catalyst was enhanced by the addition of WO_3. Because CeWTi catalyst provided more adsorbed NO_x and NH_3 species, and simultaneously enhanced the activity of both species resulting in the improvement of SCR activity. Zhang et al. [25] reported that WO_3 could interact with CeO_2 to improve the electron gaining capability of CeO_2 species and acted as electron donating groups to transfer the electrons to CeO_2 species. But these works did not research the difference of reaction route and mechanism between CeO_2-TiO_2 (CeTi) and CeWTi catalyst, especially under NH_3-NO/NO_2 SCR conditions. In addition, a few researches have reported the effect of NO/NO_2 ratios on the NO_x conversion over the CeO_2 based catalyst. However, there is few quantitative data describing detailed relationships among the NH_3-NO/NO_2 SCR reactions over CeO_2 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 NO_2 [26]. In this work, we investigated the effect of WO_3 modified CeTi catalysts on NH_3-NO/NO_2 SCR reactions. The NO_x reduction activity over CeWTi catalyst occurs by changing the NO_2/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 NH_3-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 TiO_2 powders (DT-51, Millennium Chemicals, France) were mixed in deionized water according to a mass ratio of CeO_2: WO_3: TiO_2 = 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 catalyst CeTi was prepared by the same method.

In order to investigate the reaction behavior of NH_4NO_3 over different catalysts, a series of reference samples were prepared as follows. CeTi and CeWTi powder were mixed with 10 wt% NH_4NO_3 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 NH_3-SCR activity was carried out in a fixed-bed quartz tube from 100 to 500 °C with an interval of 50 ºC. 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 NH_3, 1000 ppm NO_x (NO and NO_2), O_2 (0–10%), 2% H_2O and N_2 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.

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

2.3. Catalyst characterization

The NH_3 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 NH_3 or NO, 5% O_2, 2% H_2O and N_2 in balance, and the GHSV was 150000 h^{-1}. The NH_3 or NO conversion was calculated as follows:

$$\mathrm{NH_3\ conversion}\ (\%) = \frac{[\mathrm{NH_3}]_{\mathrm{in}} - [\mathrm{NH_3}]_{\mathrm{out}}}{[\mathrm{NH_3}]_{\mathrm{in}}} \times 100 \quad (7)$$

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

H_2 temperature-programmed reduction (H_2-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% H_2/Ar gases. The H_2 consumption was recorded continuously.

Temperature-programmed desorption of ammonia (NH_3-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% O_2/N_2 for 30 min. Then the samples were cooled down to 100 °C and purged with NH_3 until saturation, followed by flushing with N_2 to avoid the physisorption of NH_3. Afterwards, the NH_3-saturated samples were ramped to 500 °C at a rate of 10 °C min^{-1} in N_2.

DRIFT spectra of adsorbed species arising from NH_3 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 N_2