



The role of ceria on the activity and SO₂ resistance of catalysts for the selective catalytic reduction of NO_x by NH₃



Dong Wook Kwon, Ki Bok Nam, Sung Chang Hong*

Department of Environmental Energy Engineering, Graduate School of Kyonggi University, 94-6 San, Iui-dong, Youngtong-ku, Suwon-si, Gyeonggi-do 443-760, Republic of Korea

ARTICLE INFO

Article history:

Received 29 July 2014

Received in revised form 31 October 2014

Accepted 3 November 2014

Available online 13 November 2014

Keywords:

Ceria effect
SO₂ resistance
NH₃-SCR
V/Sb/Ce/Ti
CeO₂

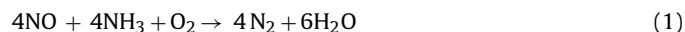
ABSTRACT

We investigated the influence of Ce on the catalytic activity of V/Sb/Ce/Ti and its deactivation due to SO₂. We studied the properties of the catalyst using physio-chemical techniques, including transmission infrared spectroscopy (IR), NH₃ and SO₂ temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), H₂ temperature programmed reduction (H₂-TPR), and thermal gravimetric analysis (TGA). The catalysts V/Sb/Ti and V/Sb/Ce/Ti showed an excellent NO_x conversion and N₂ selectivity in the temperature range of 200–400 °C. Increasing Brønsted acid sites and the NH₃ adsorption positively affected the efficiency of the catalyst. The Ce⁴⁺ ratio increased upon the addition of Sb and V to Ce/Ti. The catalyst V/Sb/Ce/Ti was prepared by controlling the Ce⁴⁺ ratio and exhibited an excellent activity upon increasing the Ce⁴⁺ ratio. The V/Sb/Ti (or V/W/Ti) showed one route in which NH₄HSO₄ formed by converting SO₂ into SO₃ upon the injection of SO₂ in the selective catalytic reduction (SCR) reaction. In addition to this route, the reaction in the presence of V/Sb/Ce/Ti can proceed via a second route, in which Ce₂(SO₄)₃ is formed in the reaction of Ce with SO₂ and O₂. Thus, V/Sb/Ce/Ti can inhibit the formation of NH₄HSO₄ due to the consumption of SO₂ in the formation of Ce₂(SO₄)₃. Therefore, V/Sb/Ce/Ti was found to have excellent SO₂ resistance compared to V/Sb/Ti (or V/W/Ti).

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Nitrogen oxides (NO_x) are a major air pollutant. They are primarily emitted during the combustion of fossil fuels from stationary and mobile sources [1–3]. It is well known that the selective catalytic reduction (SCR) of NO_x with NH₃ is a superior technology for the removal of NO_x in terms of removal efficiency, stability, and costs. In this process, NO_x contained in the fuel gases is reduced to N₂ and H₂O by NH₃ [4]:



Various studies on the development of SCR catalysts have been conducted in order to improve their activities, e.g. through the addition of metals. For example, the support [5], V₂O₅-MnO_x-TiO₂ [6], and different alkali and alkaline earth metals (Na, K, Ca, and Mg) have been used to supplement V₂O₅-WO₃/TiO₂ [7], F-doped V₂O₅-WO₃/TiO₂ [8], and Cr-V₂O₅/TiO₂ [9]. In particular, a recent study demonstrated high NO_x conversion rates at low temperatures using ceria (CeO₂) as co-catalyst [10–13]. Ceria has been extensively

studied regarding its redox properties and its exceptional ability to store and release oxygen via the redox shift between Ce⁴⁺ and Ce³⁺ under oxidizing or reducing conditions, respectively [14]. Ceria accelerates the oxidation of NO to NO₂ and the SCR of NO to N₂ by ammonia [15].

Most fossil fuels contain sulfur, and the exhaust gas contains a substantial amount of sulfur dioxide (SO₂). According to some reports, SO₂ forms sulfate species on the catalyst surface and enhances the SCR activity. Guo et al. claimed that an excellent NO reduction activity was observed since the density of Brønsted acid sites increases upon the sulfation of V₂O₅/TiO₂ [16]. According to Amiridis et al. [17], the turnover frequency was increased under conditions of a low vanadium surface coverage if the surface of the sulfate species was formed on the V₂O₅ catalyst. In addition, SO₂ poisons the NH₃-SCR catalyst at low temperatures since sulfur compounds can form at the catalyst in the presence of SO₂. Various studies have been performed to inhibit the degradation of vanadium-titanium-based catalysts by SO₂. Kobayashi et al. [18,19] confirmed that the oxidation rate of SO₂ decelerates as the SiO₂ concentration increases, provided the SiO₂ concentrations in V₂O₅/SiO₂-TiO₂ and V₂O₅/SiO₂-TiO₂-MoO₃ were below 20 wt%. Seo et al. [20] reported that the milling process enhanced non-stoichiometric oxide concentrations (V^{x+} (x ≤ 4) and Ti^{y+} (y ≤ 3))

* Corresponding author. Tel.: +82 31 249 9733; fax: +82 31 254 4941.
E-mail addresses: schong@kgu.ac.kr, schong@kyonggi.ac.kr (S.C. Hong).

as well as the redox capacity of the V_2O_5/TiO_2 catalyst. In addition, it was reported that the formation of ammonium sulfate salts was inhibited. Liu et al. [21] claimed that the SCR activity and the H_2O/SO_2 durability were excellent since the surface of $FeVO_4/TiO_2$ was enriched with VO_x species that acted as the true active sites. According to Ha et al. [22], Sb at 2 wt% showed a better SO_2 resistance than tungsten at 10 wt% because of its high electrical conductivity. Wu et al. [23] reported an increased efficiency and SO_2 resistance at $150^\circ C$ due to the addition of ceria to Mn/TiO₂. Lee et al. [24] claimed that the SO_2 adsorption decreased and SO_2 resistance increased by the addition of ceria to the SbV/TiO₂ catalyst. Thus far, many studies have been conducted to examine the efficiency of the NH_3 -SCR catalyst and the promotion of SO_2 resistance.

Among these studies, experiments showing an improved activity and SO_2 resistance due to the addition of Sb and Ce provide very interesting results. Therefore, on the basis of the above literature, we aim to investigate the role of Ce in the catalyst V/Sb/Ce/Ti. We studied the correlation between the catalysts Ce valence state and its activity. In addition, we clearly identified the cause of the increased SO_2 resistance by deactivating the catalyst with the addition of Ce. We studied the properties of the catalyst using physio-chemical analyses, which included transmission infrared (IR) spectroscopy, NH_3 and SO_2 temperature programmed desorption (TPD), X-ray photoelectron spectroscopy (XPS), H_2 temperature programmed reduction (H_2 -TPR), and thermal gravimetric analysis (TGA).

2. Experiments

2.1. Catalyst preparation

V/Ce/Ti and V/Sb/Ce/Ti were prepared by the wet impregnation of vanadium (2 wt% V) and antimony (2 wt% Sb) on a prepared Ce/Ti support. V/Sb/Ti was prepared by wet impregnation of vanadium and antimony on a prepared Ti support. V/W/Ti was prepared by wet impregnation of vanadium and tungsten (5 wt% W) on a prepared Ti support. The required quantity of ammonium metavanadate (NH_4VO_3 , Aldrich Chemical Co.) was added to an oxalic acid ($(COOH)_2$, Aldrich Chemical Co.) solution and heated to form an ammonium oxalate solution. An aqueous solution of antimony was prepared using antimony acetate ($Sb(CH_3COO)_3$, Alfa Aesar). Ammonium metatungstate hydrate ($(NH_4)_6H_2W_{12}O_{40}$, Aldrich Co.) was used as W precursor. Both of these solutions were added to the beaker containing the calculated amount of the Ce/Ti powder; TiO_2 was combined with this solution by gradual stirring. This mixed solution, which was in a slurry state, was then stirred for more than an hour. Subsequently, the water was evaporated at $70^\circ C$ using a rotary vacuum evaporator (Eyela Co. N-N series). Then, the samples were dried for an additional 24 h at $103^\circ C$ in a dry oven to remove residual water. The samples were then calcined in air for 4 h at $500^\circ C$. The Ce/Ti support was synthesized by a deposition precipitation method followed by the hydrolysis with ammonium hydroxide (Aldrich, 25%) [25]. Therefore, the required quantities of cerium(III) nitrate (10 wt% Ce; $Ce(NO_3)_3 \cdot 6H_2O$, Aldrich Chemical Co.) and commercial TiO_2 (DT-51, Cristal Global Co.) powders were mixed in water. To this solution, dilute aqueous ammonia was added as a precipitating agent, and the resultant precipitate was filtered. The sample was dried for an additional 24 h at $103^\circ C$ in a dry oven to remove residual water. Then, the sample was calcined in air for 4 h at $500^\circ C$ [24]. The x in V/Sb/Ce/Ti(x) is denoted as follows: x = the calcination temperature of the Ce/Ti support at 400, 450, 500, 550, and $600^\circ C$. V/Sb/Ce/Ti(x) were prepared using commercial TiO_2 (G-5, Cristal Global Co. G-5 was used as titanic acid, which was in this state prior to the final calcination step upon the manufacture of anatase TiO_2).

2.2. Catalytic activity tests

SCR activity tests were carried out in a fixed-bed quartz-reactor with an inner diameter of 8 mm. The reactant gases were fed to the reactor using a mass flow controller (MKS Co.). The reaction conditions were as follows: 750 ppm NO, 48 ppm NO_2 , 800 ppm NH_3 , 3 vol% O_2 , 6 vol% H_2O , and 500 ppm SO_2 in Ar. Approximately, 0.3 g of the catalyst (40–50 mesh, 0.6 cm^3) was used for each test. Under ambient conditions, the total flow rate was $600\text{ cm}^3/\text{min}$ and the gas hourly space velocity was $60,000\text{ h}^{-1}$. The composition of the feed gases and the effluent streams were continuously monitored on-line using non-dispersive infrared gas analyzers: ZKJ-2 (Fuji Electric Co.) for NO/ NO_2 , and Ultramat 6 (Siemens Co.) for N_2O , and the pulsed fluorescence gas analyzer 43 C-High level (Thermo Co.) for SO_2 . Before the gas flowed into the analyzers, the moisture was removed with a moisture trap inside the chiller. The NO_x conversion and rate constant were calculated from the concentrations of the gases at steady state according to the following equations:

$$NO_x \text{ conversion (\%)} = \frac{([NO + NO_2]_{in} - [NO + NO_2]_{out})}{[NO + NO_2]_{in}} \times 100 \quad (2)$$

$$N_2 \text{ selectivity (\%)} = \frac{(([NO]_{in} + [NH_3]_{in}) - [NO_2]_{out} - 2[N_2O]_{out})}{([NO]_{in} + [NH_3]_{in})} \times 100 \quad (3)$$

$$NH_3 \text{ conversion (\%)} = \frac{[NH_3]_{in} - [NH_3]_{out}}{[NH_3]_{in}} \times 100 \quad (4)$$

2.3. Catalyst characterizations

In situ DRIFTS analysis was used in this study and performed with an FT-IR 660 Plus (JASCO Co.). A DR (Diffuse Reflectance) 400 accessory was used for solid reflectance analysis. The CaF_2 window was used as a plate for DR measurement; spectra were collected using a mercury cadmium telluride (MCT) detector. All of the catalysts used in the analysis were ground using a rod in the sample pan of an in situ chamber with an installed temperature controller. To exclude the influence of moisture and impurities, the sample was preprocessed with Ar at a rate of $100\text{ cm}^3/\text{min}$ at $300^\circ C$ for 1 h; then, the vacuum state was maintained using a vacuum pump. To collect the spectra of the catalyst, a single-beam spectrum of the preprocessed sample was measured as background, and all analyses were performed through auto scanning at a resolution of 4 cm^{-1} .

NH_3 temperature programmed desorption measurements were carried out with 0.3 g samples of the catalysts under a total flow rate of $50\text{ cm}^3/\text{min}$. Before the TPD measurements, the catalysts were pretreated in a flow of 5% O_2/Ar at $300^\circ C$ for 0.5 h and subsequently cooled to $50^\circ C$. The samples were then treated with 1% NH_3/Ar for 1 h. The NH_3 was purged with Ar for 2 h before starting the TPD experiments. During the TPD experiments, the quantity of NH_3 (m/e 15) was continuously monitored using a quadrupole mass spectrometer (QMS 422) while the temperature was increased to $600^\circ C$ at a rate of $10^\circ C/\text{min}$.

An ESCALAB 210 (VG Scientific) was used for X-ray photoelectron spectroscopy (XPS) analysis with monochromatic Al $K\alpha$ (1486.6 eV) as the excitation source. After the complete removal of moisture from the catalysts by drying at $100^\circ C$ for 24 h, the analysis was performed without surface sputtering and etching, so that the degree of vacuum in the XPS equipment was maintained at 10^{-6} Pa. Spectra were analyzed using the XPS PEAK software (version 4.1). The intensities were estimated from the integration of each peak, subtraction of the Shirley background, and fitting of the experimental curve to a combination of Lorentzian and Gaussian curves of various proportions. All binding energies were referenced to the C 1s line at 284.6 eV. Binding energy values were measured with a precision of $\pm 0.3\text{ eV}$.

The temperature programmed reduction (TPR) of H_2 was measured using 10% H_2/Ar and 0.3 g of the catalyst at a total flow rate

Download English Version:

<https://daneshyari.com/en/article/45695>

Download Persian Version:

<https://daneshyari.com/article/45695>

[Daneshyari.com](https://daneshyari.com)