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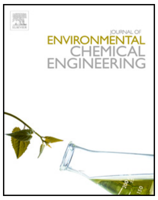

CeO_2 added V_2O_5/TiO_2 catalyst prepared by chemical vapor condensation (CVC) and impregnation method for enhanced NH_3-SCR of NO_x at low temperature

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ABSTRACT

In this study, we confirm the role of CeO_2 in promoting the catalytic activity of a selective catalytic reduction (SCR) catalyst, prepared using chemical vapor condensation (CVC)-TiO_2 nanoparticles, and the effect of the V_2O_5-CeO_2/CVC-TiO_2 catalyst on the NH_3-SCR of DeNO_x with/without SO_2 and water vapor process. The catalyst showed good SCR activity for NO_x removal, and also exhibited enhanced SCR activity in the presence of SO_2 and water vapor at low temperatures, significantly. In addition, the catalyst was characterized by various physicochemical analysis techniques. In summary, CeO_2 existed in the amorphous (poor crystallinity) phase. The catalyst with added CeO_2 contained more Ce^{3+} ions that provided more redox-active sites. CeO_2 provided more surface chemisorbed oxygen, thus dramatically increasing reducibility, and more acid sites.

1. Introduction

Nitrogen oxides (NO_x) are major air pollutants that cause severe problems in the environment, such as acid rain, photochemical smog, ozone (O_3) depletion (this is related to the generation of volatile organic compounds (VOCs)) on the ground, and greenhouse effect. Moreover, NO_x cause diseases such as pneumonia, hay fever, bronchitis, and cancer [1]. Recently, the Tier 4 Environmental Protection Agency (EPA) regulation began to take effect in the United States. In other countries, the regulation for controlling NO_x emission has been reinforced. Thus, many efforts are underway to reduce NO_x emission and conform to the guidelines mentioned in the regulation.

Existing methods for reducing/removing NO_x emissions from several pollution sources include selective non-catalytic reduction using a reducing agent and controlled combustion. However, these methods suffer from poor efficiency. Currently, selective catalytic reduction (SCR) using ammonia (NH_3) as the reductant is one of the most efficient methods for removing NO_x from stationary sources such as waste incinerators [2]. A vanadia (V_2O_5)-loaded titania (TiO_2) SCR catalyst has been widely used for the NH_3-SCR of NO_x because of its relatively higher SCR activity under actual flue gas conditions than other catalysts prepared from different materials [3,4]. However, most of the commercial and differently prepared V_2O_5/TiO_2 catalysts operate at temperatures above ~350 °C. However, stationary sources, such as waste incinerators, require the removal of NO_x at low temperatures with/without SO_2 and water vapor.

Until now, several studies have been conducted to develop SCR catalysts for solving these problems. One of these efforts was to develop suitable TiO_2 supports for NH_3-SCR catalysts. TiO_2 support materials have been manufactured using diverse methods such as hydrothermal, combustion, chemical vapor deposition (CVD), chemical vapor synthesis (CVS), and chemical vapor condensation (CVC). Among these methods, the SCR catalyst prepared using TiO_2, synthesized by CVC method in our laboratory, exhibited better NH_3-SCR activity for De-NO_x and different physicochemical characterization of the material surface than the other catalysts [5–7]. In particular, the surface of the SCR catalyst, in the case of vanadia–titania, prepared using CVC-TiO_2 method, showed important differences such as increased concentration of V^{4+} ions and more Brønsted acids because of the inherent property of CVC-TiO_2.

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Other studies [9–13] have focused on developing SCR catalysts for removing NO_x at low temperatures with/without SO_2 and water vapor. In particular, Lee et al. [14] and Q. Li et al. [8] reported that a CeO_2-added V_2O_5/TiO_2 catalyst exhibited good SCR activity for the NH_3-SCR of NO_x in the presence of SO_2 and water vapor at diverse temperatures. As known from previous studies, CeO_2 has good reducibility because it plays the role of oxygen storage, and the different oxidation states of Ce ions were attributed to different reactions during catalysis.

In this study, we sought answers to the following questions: (1) "What are the physicochemical and structural characterizations for the CVC catalyst, CeO_2?" (2) "What is the relationship between the different states of CeO_2 and their effect on the CVC catalyst with NH_3-SCR activity for NO_x?" (3) "How much NO_x can be removed under SCR reaction conditions and with/without SO_2 and water vapor at low temperatures (in the operation temperature range 250–300 °C) using the SCR catalyst in which CeO_2 was added to vanadia–titania?" We assumed that the CeO_2-added SCR catalyst, prepared using CVC-TiO_2, exhibits different catalytic activity under NH_3-SCR conditions and with/without SO_2 and water vapor, and the prepared SCR catalyst has important surface and structural properties, such as the state and ratio of Ce ions, reducibility, and acid site content, contributing to the catalytic activity of CeO_2-added SCR catalyst prepared using CVC-TiO_2.

To answer these questions, we prepared CeO_2-added V_2O_5/CVC-TiO_2 as the SCR catalyst. Next, we studied the chemical and physical structure of the CeO_2-added V_2O_5/CVC-TiO_2 catalyst using various analysis techniques. The physicochemical properties of all the catalysts were determined by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) surface area analysis, high-resolution transmission electron microscopy (HR-TEM), X-ray photoelectron spectroscopy (XPS), Fourier transform-infrared (FT-IR) spectroscopy, H_2-temperature-programmed reduction (TPR), and NH_3-temperature-programmed desorption (TPD) analyses. In addition, catalytic activity was investigated in the NH_3-SCR of NO_x with/without SO_2 and water vapor at low temperatures; the results were compared with those obtained for commercial P25-TiO_2.

2. Experimental

2.1. Materials preparation

First, TiO_2 nanoparticles were synthesized by CVC method. The CVC method and the reaction conditions have been reported by Chin et al. [16] According to the TiO_2 reaction conditions developed by us, the reaction temperature of gaseous TiO_2 precursor (titanium tetraisopropoxide, TTIP) was fixed at 900 °C. The obtained TiO_2 was named "CVC-TiO_2". The commercial TiO_2 (Degussa, P25) was named "P25-TiO_2".

The SCR catalysts were prepared by the impregnation method. The precursors were ammonium metavanadate (99.0%, NH_4VO_3, Samchun Chem., Korea) and cerium nitrate (99.0%, $Ce(NO_3)\cdot 6H_2O$, Aldrich), with TiO_2 nanoparticles as the support material. The SCR catalysts were impregnated with stoichiometric amounts of the abovementioned precursors in oxalic acid (97.0%, $(COOH)_2$, Kanto Chem., Korea) solution. The loaded weight percent of V_2O_5 and CeO_2 were 7 wt% and 20 wt%, respectively. Appropriate quantities of V_2O_5 and CeO_2 precursors were dissolved separately in distilled water and mixed together. After the impregnation, the SCR catalysts were dried overnight at 110 °C and calcined at 500 °C for 2 h. Next, each of the prepared SCR catalysts was crushed and ground to powder with a size of 250–850 μm. The obtained SCR catalysts were named as "V_2O_5-CeO_2/[preparation method]-TiO_2", such as V_2O_5-CeO_2/CVC-TiO_2.

2.2. Characterization of materials

The XRD experiments of the catalysts were conducted with a focal size of 5 mm^2 and Cu rotating anode, and the catalysts were scanned from 20 to 60° (2θ) at a rate of 2° min^{-1}. The specific surface areas, SSAs ($m^2\,g^{-1}$), of the catalysts were determined using nitrogen (N_2) adsorption (>99.999%) at 77 K using a Micromeritics Tristar 3000 apparatus by the BET method. Moreover, the particle sizes of the catalysts were calculated from the SSAs, which were determined using the above mentioned BET method. The HR-TEM analyses were performed using a JEM 2100 field-emission (FE)-TEM at the nanoscale imaging spectroscopy and properties (NISP) laboratory in the University of Maryland at College Park, USA. The FT-IR spectra were recorded using a Dilor (Omars 89 model) spectrophotometer equipped with an intensified photodiode array detector and a Bruker (model is IFS110) spectrometer. The surface chemical constituents of the catalysts were observed using XPS. The XPS spectra were recorded using an AXIS-NOVA analyzer, Kratos Inc., Japan. The H_2-TPR and NH_3-TPD experiments were carried out by linear heating at a rate of 10 °C/min (up to 600 °C) in 5% H_2 in Ar and 5% NH_3 in He at a flow rate of 30 mL/min using a temperature program equipment, BELCAT-M, BEL Inc., Japan.

2.3. Activity tests for NH_3-SCR of $DeNO_x$

The activity tests for the NH_3-SCR of $DeNO_x$ were performed with experimental feed gas without and with SO_2 and water vapor, using a metallic fixed-bed reactor (inner diameter, 5 mm) at 1 atm. The prepared SCR catalysts were placed at the center of the reactor, where the electric furnace was heated using a programmable temperature controller.

First, to simulate flue gas, the feed gas, without SO_2 and water vapor, consisted of 500 ppm NO and NH_3 and 5 vol% O_2, N_2 balanced using a mass flow controller (MFC), was injected into the reactor with a total flow rate (TFR) of 500 mL/min and a gas hourly space velocity (GHSV) of 100,000 h^{-1}. The other feed gas with SO_2 and water vapor consisted of 500 ppm NO and NH_3, 5 vol% O_2, 200 ppm SO_2, and 10 vol% water vapor. The TFR and GHSV conditions were the same as for the first feed gas.

The NO_x conversion was measured using a gas analyzer (model: MK9000, Ecom rbr). This "MK9000" gas analyzer was able to measure NO, NO_2, and NO_x ($NO+NO_2$) separately. NO_x conversion is expressed by the following equation, where C_1 is the concentration of NO and C_2 is the concentration of NO_2.

$$NO_x\,\text{conversion} = \frac{[C_1]_{\text{inlet}} - [C_1 + C_2]_{\text{outlet}}}{[C_1]_{\text{inlet}}} \times 100\%$$

3. Results and discussion

3.1. "What are the physicochemical and structural characterizations for the CVC catalyst, CeO_2?" and "What is the relationship between different characterizations of CeO_2 and their effect on CVC catalyst with the NH_3-SCR activity for NO_x?"

3.1.1. Surface chemical component analysis via XPS spectra

The XPS spectra show the chemical components on the surface of the catalysts (Fig. 1). Gaussian fittings of Ce_{4d} (Fig. 1(a)) and O_{1s} (Fig. 1(b)) are performed to confirm the type of cerium ions, which affect the acidity and redox properties, present on the surface of CVC-TiO_2 and P25-TiO_2 and the difference in the oxygen species (related to reducibility) and hydroxyl (OH) group (related to acidity).

As shown in Fig. 1(a), the Ce^{3+} ion binding energy of the catalysts prepared using CVC-TiO_2 and P25-TiO_2 mainly appeared at ~885 eV and ~900–903 eV, and the Ce^{4+} ion binding energy of