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Article

Ho-modified Mn–Ce/TiO_2 for low-temperature SCR of NO_x with NH_3: Evaluation and characterization

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ABSTRACT

Low-temperature selective catalytic reduction (SCR) of NO with NH_3 was tested over Ho-doped Mn–Ce/TiO_2 catalysts prepared by the impregnation method. The obtained catalysts with different Ho doping ratios were characterized by Brunauer-Emmett-Teller (BET), X-ray diffraction (XRD), temperature-programmed reduction (H_2-TPR), temperature-programmed desorption of NH_3 (NH_3-TPD), X-ray photoelectron spectroscopy (XPS), and scanning electron microscopy (SEM). The catalytic activities were tested on a fixed bed. Their results indicated that the proper doping amount of Ho could effectively improve the low-temperature denitrification performance and the SO_2 resistance of Mn–Ce/TiO_2 catalyst. The catalyst with Ho/Ti of 0.1 presented excellent catalytic activity, with a conversion of more than 90% in the temperature window of 140–220 °C. The characterization results showed that the improved SCR activity of the Mn–Ce/TiO_2 catalyst caused by Ho doping was due to the increase of the specific surface area, higher concentration of chemisorbed oxygen, higher surface Mn^{4+}/Mn^{3+} ratio, and higher acidity. The SO_2 resistance test showed that the deactivating influence of SO_2 on the catalyst was irreversible. The XRD and XPS results showed that the main reason for the catalyst deactivation was sulfates that had formed on the catalyst surface and that Ho doping could inhibit the sulfation to some extent.

1. Introduction

Nitrogen oxide (NO_x) emitted from mobile sources and stationary sources can lead to ozone depletion, acid rain, photochemical smog, and global warming [1,2]. Nearly 46% of NO_x emission comes from coal-fired power plants [3]. Low-temperature selective catalytic reduction (SCR) is believed to be a promising technique for treatment of NO_x from stationary sources because the device can be located downstream from the precipitator and desulfurizer. As the key component of the SCR process, the low-temperature catalyst should have better performance and durability at low temperature [4,5]. Recently, researchers have focused on the preparation of new catalysts and the modification of catalysts to obtain high-performance low-temperature SCR [1]. Among these strategies, improving the preparation method, selecting high-quality raw materials, and doping elements have often been used in the modification of low-temperature catalysts [6–11]. Elements such as Sn, Ni, Co, Zr, Cr, Ni, and others already have been used to dope Mn-based catalysts, and the low-temperature SCR activity was improved in all experimental studies [12–16]. Among the widely studied catalysts, Mn and Ce containing catalysts such as Mn–Ce [17,18], Mn–Ce–Ti [19], and Mn–Ti [20] catalysts have been investigated extensively. Man-

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ganese oxides contain various types of labile oxygen, which have been considered to play an important role in the SCR catalytic circle, and ceria can store and release oxygen, which can effectively improve NO_x removal efficiency [20–22].

Holmium has been used commonly in the field of photocatalysis, and it has been reported that Ho doping can effectively improve the photocatalytic activity of TiO_2. Wu et al. [23] prepared Ho-doped TiO_2 nanoparticles and found that the phase transformation from anatase to rutile could be inhibited and that the growth of TiO_2 grains could be suppressed by Ho doping. Shi et al. [24] found that Ho^{3+} doping restrained the increase of grain size leading to crystal expansion. Additionally, Ho_2O_3 oxide can provide Lewis acid sites, which promote the SCR reaction. It has also been proven that Ho-modified Fe–Mn/TiO_2 catalyst has a broad operating temperature window and superior resistance to sulfur poisoning [25].

It is very important to study the performance of catalysts containing Mn, Ce, and Ho further. However, there are few reports about the performance of Ho-doped Mn–Ce/TiO_2 catalysts in low-temperature SCR. Hence, research pertaining to the performance of Mn–Ce–Ho/TiO_2 catalysts is very valuable. In this study, Mn–Ce–Ho/TiO_2 catalysts with different amounts of Ho were prepared to identify the effect of the introduction of Ho on catalytic performance. The activity, structural, redox, and acidic properties of the Ho-doped catalysts were investigated and the optimal Ho doping amount was identified.

2. Experimental

2.1. Catalyst preparation

The Mn–Ce–Ho/TiO_2 catalysts were prepared by the impregnation method. TiO_2 powder and specific amounts of manganese nitrate, ceria nitrate, and holmium nitrate were mixed together. Purified water was utilized as a solvent to be added to the aqueous solution. Then, the solution was stirred steadily in a magnetic stirring machine at room temperature for 6 h. The mixture was dried overnight at 105 °C, followed by a calcination at 450 °C for 4 h in a muffle furnace. The solid samples were crushed and sieved to 60–100 mesh sizes and were denoted as $Mn_{0.4}Ce_{0.07}Ho_x/TiO_2$, where x represents the molar ratio of Ho/Ti. The molar ratio of other components used for preparing the catalyst was Mn:Ce:Ti = 0.4:0.07:1.

2.2. Catalytic activity determination

Catalytic activities were measured over a fixed bed, as shown in Fig. 1, with a gas hourly space velocity (GHSV) of 10,000 h^{-1} at 80–220 °C. The reaction gases typically consisted of 0.08% NO, 0.08% NH_3, 5% O_2, and the balance N_2 to simulate the flue gas. In all tests, the total mass flow rate was maintained at 1000 mL/min. The concentrations of NO, NO_x, and N_2O were measured by OPTIMA7 flue gas analyzer (MRU GmbH, Germany). To assure the accuracy of the measurement, the reaction gas was accessed to the reactor until the inlet NO_x concentration was the same as that at the outlet to avoid absorption of the catalyst in the tube. The N_2 selectivity was calculated from [18]:

$$S_{N_2} = 1 - \frac{2C_{(N_2O)_{out}}}{C_{(NO_x)_{in}} - C_{(NO_x)_{out}}} \times 100\%$$

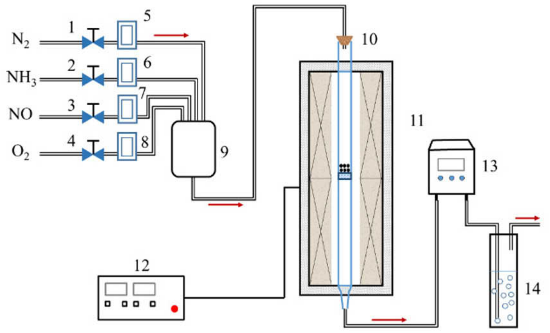

Fig. 1. Flow process diagram of the device used in the experiment. (1–4) N_2, NH_3, NO, and O_2 reaction gas, (5–8) flowmeters, (9) flue gas mixer, (10) temperature control device, (11) reaction tube, (12) heating furnace, (13) flue gas analyzer, (14) exhaust absorption.

2.3. Catalyst characterization

The specific surface area and pore volume of the catalysts were determined by N_2 absorption at −196 °C using a Micromeritics ASAP 2020 system and were calculated by the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halend (BJH) methods. Powder X-ray diffraction (XRD) measurement was used to analyze the crystal structure of the catalysts and the metal oxide crystalline phases on the supporters, and they were performed on an X'pert3 Powder X-ray diffractometer (PANalytical, Inc., Netherlands) with an angle of 10° to 90°.

Scanning electron microscopy (SEM) to examine the surface of the catalyst and obtain additional information was performed with a TESCAN MIRA3 system (TESCAN, Ltd.).

The characterizations of the valences of the surface elements and the atomic surface concentrations of the catalysts were examined using X-ray photoelectron spectroscopy (XPS) (AXIS-ULTRA DLD-600W; Shimadzu Kratos Corporation, Japan). The C 1*s* peak (284.6 eV) was used for calibration to obtain the precise binding energies of O 1*s*, Mn 2*p*, Ce 3*d*, and Ho 4*d*. During the measurement, the normal operating pressure used in the analysis was 10^{-9} Pa.

Temperature-programmed reduction (H_2-TPR) was carried out to study the redox behavior of the catalysts using a ChemBET pulsar TPR/TPD (Quantachrome, Inc., USA). Before the characterization, the samples were pretreated at 300 °C for 1 h in He gas and then cooled to room temperature. The temperature was raised to 600 °C at a heating rate of 10 °C/min.

Temperature-programmed desorption of NH_3 (NH_3-TPD) experiments were carried out to study the acidity properties on a Chem BET pulsar TPR/TPD (Quantachrome, Inc., America) using 0.1 g catalysts. The sample was pretreated in pure N_2 at 300 °C for 1 h, cooled to room temperature, and then saturated for 30 min with NH_3. Next, the catalyst was flushed in a pure N_2 flow for 30 min at 120 °C. Finally, the TPD of NH_3 was carried