



Enhanced NO_x removal performance of amorphous Ce-Ti catalyst by hydrogen pretreatment



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ABSTRACT

Hydrogen pretreatment was processed on the amorphous Ce-Ti catalyst which notably enhanced its NH₃-SCR performance. We concluded that 3-h and 400 °C were the most suitable and efficient pretreatment conditions, whereas the NO_x conversion rate was above 95% from 210 °C to 360 °C for such pretreated catalyst. XRD, PL, H₂-TPR, XPS and Raman analyses found that the enhancement was attributed to the effects generated by the pretreatment: Ce⁴⁺ reduced to active Ce³⁺, the increase of the oxygen vacancies, the chemisorbed oxygen, and the formation of superoxide ions. The NO adsorption oxidation capability, and the acid sites were also promoted by the pretreatment, which were favorable for the SCR reaction. The reaction among NO, O₂ and NH₃ on catalysts were studied by in-situ DRIFT. The adsorption of NH₃ was dominant under the SCR reaction conditions. The enhancement demonstrated good durability. The stability of catalyst under water vapor and sulfur dioxide were also tested.

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1. Introduction

Nitrogen Oxides (NO_x) generated from stationary and mobile sources is one of the major atmospheric pollutants nowadays and has contributed to many environmental problems such as acid rain, photochemical smog and ozone hole [1]. This leads to stringent environmental regulations for nitrogen oxides. Selective catalytic reduction (SCR) of NO_x with NH₃ is the mainstream technology of the treatment for NO_x emissions at present. The added NH₃ is able to reduce NO_x to N₂ and H₂O in the presence of excess oxygen [2,3]. V₂O₅-WO₃(MO₃)/TiO₂ is currently the most common commercial catalyst due to its good catalytic activity and high resistance to sulfur dioxide [4]. But the narrow operation temperature (300–400 °C) and the potential hazards caused by the loss of V₂O₅ are main disadvantages for it.

As an abundant, inexpensive and nontoxic material, cerium oxides have shown applications in solid oxide fuel cells, oxygen storage capacitors, and the three way catalyst (TWC) of which are used for gasoline engine emission control [5,6]. Because of the redox shift between Ce⁴⁺ and Ce³⁺ under oxidizing and reducing conditions [7], it has unique performance to store&release oxygen. This is favorable to the oxidation of NO to NO₂, which makes it

widely used in SCR reaction either as a promoter or as an active center. As a promoter, studies reported that the addition of Ce significantly improved the low temperature SCR performance of Mn/TiO₂ [8,9], V-W/TiO₂ [10], Cu/TiO₂ [11], Cu-SAPO-34 monolith catalyst [12], etc. These studies all mentioned that the improvement was based on the increase of chemisorbed oxygen and acidity after Ce doping, and well dispersion of active species as well. Some works also pointed out the Ce loaded TiO₂ catalyst or amorphous Ce-Ti itself could obtain excellent NH₃-SCR activity, which is attributed to the advantages in reduction state Ce³⁺, abundant acid sites and the chemisorption oxygen in the lattice [13–15]. We focused on the amorphous Ce-Ti catalyst in our previously work [16], and found a remarkably increase in SCR efficiency at low temperature by doping non-metal (fluorine) into amorphous ceria-titania catalyst. It was confirmed that the improvement was related to the increase in oxygen vacancy, chemisorbed oxygen, acid sites and NO adsorption species [17].

Other than this, reducing atmosphere pretreatment was commonly used to strengthen the activities for metal oxide catalysts by reducing the valence state of the active species and producing more surface defects, especially oxygen vacancies [18–20]. These positive influences by pretreatment could also be favorable to the performance of Ce-Ti catalyst in SCR reaction, which has not been researched so far. In previous research, we found that H₂ pretreatment on Ce-Ti could indeed display a promoting effect for NH₃-SCR, which attracted our interest. In this study, we prepared a ceria-titania (designated as Ce-Ti) catalyst by co-precipitation method

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and pretreated it by H₂-N₂ mixed flow. Several characterization such as XRD, PL, H₂-TPR, XPS, Raman, TPD and in-situ DRIFT were carried out to help us find out the properties difference caused by the pretreatment. This paper would offer a possibility of further modification and application for amorphous Ce-Ti catalyst.

2. Experimental

2.1. Catalysts preparation

The Ce-Ti catalyst was prepared by a co-precipitation method, which had been reported in our previous manuscript [16], the molar ratio of Ce/Ti for catalyst is 0.3. To obtain the H₂-pretreat catalyst, pretreatment was performed in a U-tube quartz reactor. The Ce-Ti was first purged with N₂ stream at 120 °C for 0.5 h, then pretreated with 50 mL/min H₂ + N₂ mixed gas at different temperature for hours, in which the H₂ was 1 v%. The resultant was designated as xCe-Ti/H-y, of which x means the pretreat period (x h) whereas y stands for the pretreat temperature (y °C) for catalysts.

2.2. Characterization

X-ray diffraction (XRD) was recorded on a XD-3 diffractometer (Bruker D8 ADVANCE, Germany) using Cu K α radiation ($\lambda = 0.15406$ nm) at room temperature in the 2θ ranging from 5° to 50°.

The surface atomic composition and chemical environment were characterized by the X-ray photoelectron spectroscopy (XPS) using a PHI Quantera II (ULVAC-PHI, Japan) XPS System equipped monochromatic Al-K α excitation. All the binding energy values were calibrated by using C1s peak at 284.8 eV as a reference.

Oxygen vacancies were analyzed by photoluminescence (PL) spectra at room temperature using a Labram-HR800-type spectrophotometer (Jobin Yvon CO., France) with a He-Cd laser ($\lambda = 325$ nm) as the light source.

Raman spectra were recorded on a Renishaw Invia Raman Microscope with Ar⁺ radiation (514 nm). The laser light was focused on the samples by using a microscope equipped with an $\times 50$ objective lens.

Temperature Programmed Desorption of Nitric Oxide (NO-TPD) or Ammonia (NH₃-TPD) and Hydrogen temperature programmed reduction (H₂-TPR) were carried out in a quartz U-tube reactor on an automated chemisorption analyzer (Quantachrome Instruments) by the GC method. Before the measurements, each 100 mg catalyst was pretreated in the He stream at 50 mL/min from room temperature to 300 °C to purge the surface and the furnace temperature was lowered to 50 °C. For TPD, the catalyst was then saturated with NO or NH₃ (1% in N₂) at a flow rate of 50 mL/min for 1 h, the measurement was taken from 50 up to 700 °C at 10 °C/min under 50 mL/min He. H₂-TPR was performed by heating the catalyst from 50 °C to 700 °C at 10 °C/min under 50 mL/min H₂-N₂ mixture gas (10% H₂, v/v). All signal was recorded by a thermal conductivity detector (TCD).

In-situ Diffused reflectance infrared Fourier transform (DRIFT) spectroscopy experiments were carried out by a Nicolet IZ10 FTIR spectrometer, equipped with a liquid-nitrogen-cooled MCT detector. 32 scans were averaged for each spectrum, which were recorded at a resolution of 4 cm⁻¹. Prior to each experiment, background was taken by recording the IR spectrum of KBr in a N₂ stream at 240 °C, and had been deducted for each spectrum. The samples were then pretreated in the in-situ cell at 400 °C in a flow of N₂ for 30 min to remove any adsorbed species. During the experiment, NO, O₂ and NH₃ were fed into N₂ flow when required, the spectrum and response time was recorded when surface species changed or eventually stabilized.

2.3. Catalytic test

The activities test of NH₃-SCR were carried out at 120–390 °C in a fixed-bed flow reactor (inner diameter 7 mm) using 300 mg catalyst with a gas hourly space velocity (GHSV) of 48,000 h⁻¹. The feed gas mixture contained 500 ppm NO, 500 ppm NH₃, 5% O₂, and N₂ as a balance with a total flow rate of 150 mL/min. Concentration of N₂O, NO and NO₂ were analyzed in a Servopro 4900 analyzer, and NO_x was calculated by adding N₂O, NO and NO₂. The NO_x conversion is defined as:

$$X = \frac{NO_{x_{in}} - NO_{x_{out}}}{NO_{x_{in}}} \times 100\%$$

3. Results and discussions

3.1. Catalytic performance

Fig. 1 shows the NO_x conversion of catalysts from 120 to 390 °C. From Fig. 1(a), the SCR catalytic performance substantially increased in the following order: Ce-Ti < 3Ce-Ti/H-500 < 3Ce-Ti/H-300 < 3Ce-Ti/H-400. For all catalysts, the NO_x conversion increased with temperature at low temperature range (120–240 °C). The untreated Ce-Ti show the lowest NO_x conversion among catalysts, which reached 58.8%, 77.2% and 81.4% at 180, 210 and 240 °C, then rapidly dropped. The catalytic performance improved within the temperature range after Ce-Ti was pretreated in the mixed gas at 300 °C for 3 h. The NO_x conversion could reach 90.5% and 92.3% at 240 and 270 °C, which verified a benefit effect by pretreatment. 3Ce-Ti/H-400 sample demonstrated the best activity and widest temperature window in all catalysts we tested, the NO_x conversion was above 95% from 210 °C to 360 °C, which still remained 88.9% at 390 °C. In comparison with 3Ce-Ti/H-400, the activity obviously declined when the pretreatment temperature rose to 500 °C. The NO_x conversion at high temperature range (above 300 °C) was even lower than 3Ce-Ti/H-300. This would be caused by the destruction of amorphous form and formation of crystalline by higher pretreatment temperature, which would decrease the catalytic activity. The results indicated that H₂-pretreatment could promote favorable effects on SCR activity and broad its operating temperature window, and 400 °C was the optimum pretreatment temperature for Ce-Ti catalyst.

Fig. 1(b) displays the NO_x conversion of samples with different pretreatment period at the most efficient temperature of 400 °C. The NO_x conversion for Ce-Ti was already improved after 2 h pretreatment. Compared to the 2Ce-Ti/H-400, a notable raise was observed on the catalysts with at least one more hour pretreatment, which means that 2 h pretreatment was insufficient to fully activating the catalyst. Fig. 1(b) also presented that when the pretreatment time reached 3 h, it was difficult to impact the activity of catalyst by lengthening the pretreatment period. Based on the active results above, we concluded that 3 h and 400 °C were the most suitable and efficient pretreatment conditions. The such obtained 3Ce-Ti/H-400 was further characterized and analyzed to identify the reasons for the enhancement. For brevity, the 3Ce-Ti/H-400 will be marked as Ce-Ti/H in the ensuing discussion.

3.2. Catalysts characterization

3.2.1. XRD results

XRD measurement was performed to explore the polymorphs and possible structural changes for catalysts, the results are shown in Fig. 2. Only the presence of a weak broad peak at $2\theta = 19\text{--}36^\circ$ was detected, which proved the ceria and titania were displayed in amorphous state for all catalysts [21]. No distinct peak belonging to the phase of Anatase TiO₂ (PDF#21-1272) or Cerianite

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