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Precisely fabricating Ce-O-Ti structure to enhance performance of Ce-Ti based catalysts for selective catalytic reduction of NO with NH_3

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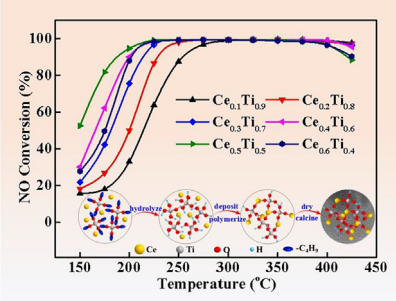
HIGHLIGHTS

- Ce_aTi_{1-a} catalysts were prepared by a spontaneous-deposition/freeze-drying method.
- Abundant Ce-O-Ti active species were effectively constructed in Ce_aTi_{1-a} catalysts.
- Ce_aTi_{1-a} catalysts exhibited excellent activity and stability in NH_3-SCR reaction.
- Langmuir-Hinshelwood mechanism predominated in NH_3-SCR over Ce_aTi_{1-a} catalysts.

GRAPHICAL ABSTRACT



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ABSTRACT

A series of Ce-Ti mixed oxides (Ce_aTi_{1-a}) were successfully synthesized by a spontaneous deposition method and evaluated in selective catalytic reduction of NO with NH_3 (NH_3-SCR). The structures and properties of the Ce_aTi_{1-a} catalysts were characterized by means of XRD, Raman, TEM, N_2-sorption, XPS, H_2-TPR and NH_3-TPD. The results demonstrated that lots of Ce-O-Ti species were formed because of the strong synergistic interaction of gelation of TiO_2 and deposition of Ce^{3+} during the preparation process of Ce_aTi_{1-a} catalysts. As results, the Ce_aTi_{1-a} catalysts exhibited excellent redox ability, enrichment of Ce^{3+} species, high surface adsorbed oxygen concentration, and abundant acid sites. The Ce_aTi_{1-a} catalysts showed remarkable catalytic activity with broad operation temperature window, and $Ce_{0.5}Ti_{0.5}$ catalyst exhibited the best catalytic activity and extraordinary H_2O/SO_2 durability. The *in-situ* FTIR results revealed that the mechanisms of L-H and E-R existed synchronously during the NH_3-SCR reaction, and the former one was predominant due to its rapid reaction rate.

1. Introduction

Nitrogen oxides (NO_x), as one of the main air pollutants, emitted from automobile exhausts and coal-fired flue gasses, triggered a lot of environmental problems, such as ozone depletion, acid rain, and photochemical smog [1,2]. Compared with other techniques, NH_3-SCR has been demonstrated as an efficient technique for the emission reduction of NO_x [3–7]. The commercial V_2O_5-WO_3(MoO_3)/TiO_2 catalysts have been extensively applied for NH_3-SCR reaction for several decades [8]. However, the practical applications of such catalysts have

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some unavoidable problems, such as the relatively narrow temperature window, the toxicity of vanadium species, and the susceptible poisoning caused by high concentration of dust and SO_2 in coal-fired flue gasses [9–11]. Therefore, it is especially significant to design a novel eco-friendly catalyst with great activity and selectivity for NO_x removal.

Recently, the CeO_2-based catalyst has attracted extensive attention in NH_3-SCR reaction due to its nontoxicity, significant oxygen storage ability and excellent reducibility [12–16]. Previous studies have revealed that CeO_2/TiO_2 displayed high NH_3-SCR reaction activity, and superior resistance to SO_x poisoning [17–22]. Then, many researchers have tried to exploit novel CeO_2/TiO_2 catalysts with better de-NO_x performance. For example, the CeO_2/TiO_2 catalyst with strong interaction between ceria and titania was produced by a sol–gel method in Gao's group, and the catalyst showed excellent NH_3-SCR performance due to the high concentration of amorphous or highly dispersed nanocrystalline ceria [23]. Moreover, a homogeneous precipitation method was applied by He et al. for the preparation of Ce-Ti based catalysts, and the highly dispersed active component CeO_2 remarkably improved its low-temperature NH_3-SCR activity [24]. Further, the Ce-O-Ti species were confirmed to be the active sites in Ce-Ti mixed oxides for NH_3-SCR reaction [25]. All in all, the excellent NH_3-SCR performance of Ce-Ti based catalysts was interpreted as the result of the formation of the Ce-O-Ti structure. Thus, it is of great significance in searching for a suitable method to synthesize Ce-Ti mixed oxides with plentiful Ce-O-Ti species. Unfortunately, there is hardly any report in the literatures about the strategy for construction of the Ce-O-Ti structure in Ce-Ti based catalysts.

In the current work, Ce-Ti based catalysts were prepared by a novel method developed in our group, which could be regarded as the strong interaction of gelation of TiO_2 and deposition of Ce^{3+} during the preparation process. As a result, a completely amorphous structure with abundant Ce-O-Ti species was formed in these catalysts. In addition, these Ce-Ti based catalysts exhibited outstanding NH_3-SCR performance and H_2O/SO_2 poison resistance. Further, the formation and transformation of various intermediates were studied by *in-situ* FTIR experiments, and a reasonable mechanism for the remarkable NH_3-SCR performance of the current catalyst was proposed.

2. Experimental

2.1. Catalyst preparation

A series of Ce-Ti mixed oxides were prepared via a spontaneous deposition (SD) method [26,27]. In a typical synthesis, stoichiometric ratio requirement of tetrabutyl titanate ($Ti(OC_4H_9)_4$), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$) (The total mole of these two substances is 0.1 mol.) were mixed with 125 mL ethanol (CH_3CH_2OH) and 40 mL deionized water under vigorous stirring for 0.5 h at 25 °C to yield a transparent solution. Subsequently, 50 mmol glacial acetic acid, 100 mmol formamide and 100 mL 1,2-epoxypropane were added into the solution successively. The gelation was obtained from above-mentioned sol at 60 °C and aged under the condition of reflux for 6 h. The obtained sample was washed two times with ethanol to remove the residual impurities. To maintain the original structure and avoid the condensation phenomenon of the catalyst precursor, the sample was dried in a freeze dryer which was based on the sublimation of organic solvents [28]. The dried catalyst precursor was calcined at 500 °C for 3 h in air and the catalysts were denoted as Ce_aTi_{1-a}, where a represented the mole ratio of Ce/(Ce + Ti).

2.2. Catalyst characterization

X-ray diffraction (XRD) analysis was performed on a SmartLab X-ray Diffractometer (Rigaku Corporation, Japan) using Cu Kα radiation (λ = 0.1541 nm) in 2θ range of 10–80° with a step of 0.02° at 40 kV and 100 mA.

The Raman spectra were taken on Horiba Jobin Yvon LabRam HR800 Micro Raman spectrometer. The internal 514.5 nm line from He-Cd excitation was used as the source. The spectral resolution is 2 cm^{-1} in a scanning range of 100–1000 cm^{-1}.

Scanning electron microscopy (SEM) images were taken on a Hitachi S-3000 N scanning electron microscope. JEOL JEM-2100 electron microscope was used to get the high-resolution TEM images (HRTEM).

N_2 physisorption was carried out on a BEL sorp II apparatus. All catalysts were degassed in vacuo for 2 h at 200 °C before adsorption. The BET theory was applied to calculate the surface area. The BJH method was used to determine the pore size.

The H_2 temperature-programmed reduction (H_2-TPR) experiment was conducted on AutoChemII 2920 apparatus. Briefly, quantitative catalyst (50 mg, 40–60 mesh) was placed in a U-type quartz reactor and pretreated at 200 °C for 1 h in Ar flow. After being cooled to 50 °C, the catalyst was heated to 900 °C at a heating rate of 10 °C·min^{-1} under 50 mL·min^{-1} 10 vol.% H_2/Ar flow. The H_2 consumption was monitored by TCD detector and was calibrated by the quantitative reduction of Ag_2O to Ag.

The X-ray photoelectron spectroscopy (XPS) spectra were recorded using a PHI 5000 Versa Probe high performance electron spectrometer. All binding energies (B.E.) were calibrated using C 1s (B.E. = 284.8 eV) as a standard.

NH_3 temperature-programmed desorption (NH_3-TPD) experiment was carried out using AutoChemII 2920 apparatus. Briefly, quantitative catalyst (50 mg, 40–60 meshes) was placed in a U-type quartz reactor and pretreated at 200 °C for 1 h in He flow. After being cooled to 100 °C, the catalyst was exposed to 30 mL·min^{-1} 10 vol.% NH_3/He flow for 1 h. Subsequently, the catalyst was flushed with high purified He (30 mL·min^{-1}) to remove gaseous NH_3. Finally, NH_3-TPD profiles were recorded under He flow of 30 mL·min^{-1} from 50 °C to 500 °C at a heating rate of 10 °C·min^{-1}.

In-situ FTIR spectra were recorded using IS50 infrared spectrometer equipped with a *in-situ* diffuse reflectance pool containing CaF_2 window and MCT detector. The reaction temperature was controlled by the programmable temperature controller precisely. The total gas flow was kept at 100 mL·min^{-1}, and concentrations of the feed components were controlled as follows: 1000 ppm NO, 1000 ppm NH_3, 3 vol.% O_2 and N_2 as balance gas. Prior to gases adsorption, the catalyst was pretreated under N_2 stream at 500 °C for 1 h. All spectra were recorded by accumulating 32 scans at a resolution of 4 cm^{-1}.

2.3. Catalytic evaluation

The NH_3-SCR reaction was conducted on a fixed bed quartz reactor (i.d. = 6 mm) with 0.2 g catalysts of 16–40 mesh. The catalyst was diluted with 1.0 g of quartz sands, and the catalyst bed was 3.0 cm. The total gas flow was kept at 500 mL·min^{-1} (GHSV = 120,000 h^{-1}), and concentrations of the feed components were controlled as follows: 1000 ppm NO, 1000 ppm NH_3, 3 vol.% O_2, 100 ppm SO_2 (when used), 10 vol.% H_2O (when used), and N_2 as balance gas. The composition and concentration of the product gas were continually monitored by VARIO industrial flue gas analyzer (MRU Corporation, German). The data were collected when the NH_3-SCR reaction reached steady-state condition at each temperature in the range from 150 to 425 °C. The NO conversion was defined as follows:

$$x_{NO} = (c_{in} - c_{out})/c_m \times 100\%$$

where x_{NO} represents NO conversion rate, c_{in} and c_{out} represent the NO concentration of inlet and outlet, respectively.

3. Results and discussion

The formation of Ce-O-Ti species in Ce-Ti based catalysts with a strong interaction of Ce and Ti could significantly improve NH_3-SCR