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Regular Article

Improvement of catalytic activity over Mn-modified $CeZrO_x$ catalysts for the selective catalytic reduction of NO with NH_3

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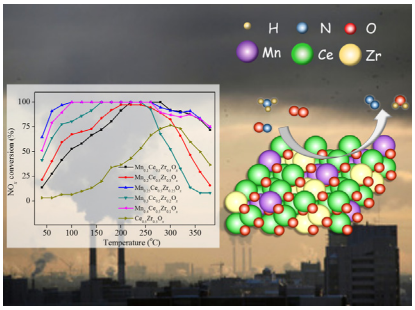
GRAPHICAL ABSTRACT



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ABSTRACT

A series of $MnCeZrO_x$ mixed oxide catalysts were facilely synthesized using the impregnation-$NH_3{\cdot}H_2O$ coprecipitation method and tested for selective catalytic reduction (SCR) of NO with NH_3. Doping manganese significantly improved the catalytic activity and the best performing SCR catalyst, $Mn_{0.25}Ce_{0.5}Zr_{0.25}O_x$, was shown to achieve NO conversion > 80% in the temperature range (60–350 °C), with the denitration effect up to 50% at room temperature (conditions: $[NO] = [NH_3] = 500$ ppm, $[O_2] =$ 5 vol%, He as balance, flow rate = 100 mL/min, GHSV = 40, 000 h^{-1}). Characterization of the catalyst using BET, XRD, XPS, H_2-TPR, and *in-situ* FTIR proved that the improved SCR activity may be attributed to the large surface area, great reduction ability and increased amount of surface adsorbed oxygen afforded by the introduction of manganese. The SCR reaction mechanisms were also investigated by analyzing *in-situ* FTIR spectra and the SCR reaction pathway over the $Mn_{0.25}Ce_{0.5}Zr_{0.25}O_x$ catalyst was shown to mostly follow the E-R mechanism.

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1. Introduction

NO_x emissions from the combustion of fossil fuels have long been recognized as one of the most threatening atmospheric pollutants globally [1–3]. A variety of technologies have been developed to reduce NO_x emissions from both stationary and mobile combustion facilities and devices, among which selective

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catalytic reduction (SCR) with NH_3 as a reducing agent has attracted great attention for its high NO_x conversion, low cost, and being environmentally friendly [4–6]. The main reactions in a typical SCR process include:

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \quad (1)$$

$$4NO+2NH_3+2O_2 \rightarrow 3N_2+6H_2O \quad (2)$$

$$2NO_2+4NH_3+O_2 \rightarrow 3N_2+6H_2O \quad (3)$$

$$NO+NO_2+2NH_3+2O_2 \rightarrow 2N_2+3H_2O \quad (4)$$

The commonly adopted commercial denitration catalyst is the vanadium based catalyst (V_2O_5-MoO_3 (WO_3)/TiO_2), which has many shortcomings, such as high reaction temperature (300–400 °C), narrow operating temperature window and biological toxicity [7–9]. In recent years, V-free composite metal oxide catalysts have attracted increased interests by both academia and industry researchers for their high rates of NO_x conversion, and broadened operating temperature ranges [10,11]. In particular, Ce-Zr mixed metal oxide catalysts have been extensively studied for their excellent SCR performance and low cost. Li et al. [12] synthesized a WO_3-CeO_2-ZrO_2 catalyst for selective catalytic reduction (SCR) of NO with NH_3, reaching complete conversion at 250–500 °C and the superb catalytic performance was attributed to the superior redox properties of CeO_2-ZrO_2, and the presence of highly dispersed or amorphous WO_x species. Masaaki et al. [13] loaded rhodium into a ceria-zirconia solid solution by incipient wetness impregnation for SCR by unburned hydrocarbons in the presence of O_2. However, there are still some deficiencies in the Ce-Zr catalysts, such as poor SCR performance at low temperatures and still narrow operating temperature window. Manganese oxides (MnO_x) involve several kinds of labile oxygen which is favorable to the redox cycle. Therefore, Mn-based catalysts are well-known for its distinguished SCR effect at low temperatures and may be an effective and economical choice as SCR catalysts [14].

Based on the hypothesis of the combined advantages of Mn-based and Ce-Zr mixed metal oxides catalysts, we synthesized a series of $MnCeZrO_x$ catalysts and tested for NH_3-SCR in the present work. Specific attention was paid to the effect of Mn/Ce molar ratio on the SCR performance. The physical and chemical properties of the Mn-doping catalysts were systematically characterized using Brunauer-Emmertt-Teller (BET), X-ray Diffraction (XRD), X-ray Photoelectron Spectroscopy (XPS), H_2-Temperature Program (H_2-TPR) and *in situ* Fourier transform infrared spectroscopy (FTIR). The reaction pathway over the $Mn_{0.25}Ce_{0.5}Zr_{0.25}O_x$ catalyst was also proposed based on the intermediate species observed in the SCR process.

2. Experimental

2.1. Catalyst preparation

$Mn_xCe_{0.5}Zr_{0.5-x}O_y$ (x = 0, 0.1, 0.2, 0.25, 0.3, 0.4, 0.5) catalysts with different Mn/Ce molar ratios were synthesized via the impregnation-$NH_3 \cdot H_2O$ coprecipitation method. The precursors manganese acetate (($(CH_3COO)_2Mn \cdot 4H_2O$), cerium nitrate (Ce $(NO_3)_3 \cdot 6H_2O$), zirconium nitrate ($Zr(NO_3)_4 \cdot 5H_2O$) were dissolved in 200 mL deionized water with different Mn/Zr molar ratios. Then ammonia (25 wt%) was added into the solution slowly until the pH reached 9.5. The mixture was then stirred for 3 h at room temperature and aged for 2 h. The precipitate obtained was washed with distilled water and ethanol several times, then dried and calcined at 400, 550 and 650°C for 6 h, respectively. After grinding, the $MnCeZrO_x$ mixed metal oxide catalysts were obtained.

2.2. Catalytic activity test

SCR activity measurement with excess oxygen over the catalysts was carried out in a temperature programmed fixed bed reactor made of a quartz tube with an internal diameter of 6 mm. In a typical SCR test, a catalyst (200 mg, 40–60 mesh) was placed in the quartz reactor and heated from 50 to 350 °C at a heating rate of 5 °C/min and pretreated in a He stream at 350 °C for 50 min. The reaction gas mixture containing NO, NO_x, NH_3 and O_2 and their contents at the inlet and exit of the reactor were continuously monitored using a Testo 350 gas analyzer.

The typical composition of the reaction gas mixture was: [NO] = [NH_3] = 500 ppm, [O_2] = 5 vol%, He as balance, flow rate = 100 mL/min, GHSV = 40, 000 h^{-1}.

2.3. Catalyst characterization

XRD (X-ray Diffraction) measurements to characterize the crystalline phase, phase composition and crystallite size of the materials were performed using a RigakuD/Max 2550VB/PC X-ray powder diffractometer with a Cu Kα radiation (λ = 0.15406 nm) within a 2θ range of 20–80° at the step of 0.0167° at room temperature.

XPS (X-ray photoelectron spectroscopy) spectra of the catalysts were recorded by using a Kratos AXIS Ultra DLD spectrometer using Al Kα radiation (1486.7 eV). Binding energies of Ce 3p and O 1 s were calibrated using C 1 s (BE = 285.6 eV) as a standard.

The Brunauer-Emmett-Teller (BET) specific surface areas of the samples were measured using physical adsorption of N_2 at −196 °C using NOVA 1200 (Quanta Chrome) and calculated according to the BET formula. In a typical rule, a sample was degassed at 300 °C for 4 h under vacuum before the BET determination.

H_2-TPR (temperature-programmed reduction of H_2) analysis was performed using a Chembet PULSAR TPR/TPD (p/n02139-1). Prior to the measurement, 50 mg of a sample was pretreated at 200 °C for 30 min in an Ar stream followed by cooling to room temperature. The TPR measurement was taken from 100 °C to 700 °C at a heating rate of 10 °C/min in a stream of 10 vol% H_2/Ar at 50 mL/min. The consumption of H_2 was detected using a TCD detector.

2.4. In situ FTIR studies

In situ FTIR analysis was undertaken with VERTEX 70-FTIR (Bruker) to investigate the NH_3/NO adsorption and activity ability of the catalysts and the SCR reaction pathway. Before each experiment, a sample (20 mg) was pressed into a disk with a diameter of 10 mm and pretreated in a stream of He at 300 °C for 40 min to remove water on the surface and then cooled to the desired temperature. The reaction conditions were 500 ppm NO, 500 ppm NH_3, and 10 vol% O_2 with He as balance and the total gas flow rate was 100 mL/min.

3. Results and discussion

3.1. NH_3-SCR activity

It can be seen from Fig. 1a, NO conversions for the $Ce_{0.5}Zr_{0.5}O_x$, $Mn_{0.1}Ce_{0.5}Zr_{0.4}O_x$, $Mn_{0.2}Ce_{0.5}Zr_{0.3}O_x$, $Mn_{0.25}Ce_{0.5}Zr_{0.25}O_x$, $Mn_{0.3}Ce_{0.5}Zr_{0.2}O_x$ and $Mn_{0.4}Ce_{0.5}Zr_{0.1}O_x$ catalysts calcined at 550 °C first increased as temperature increased, remained stable and then decreased as the temperature increased further in the range of 50–350 °C. The NO_x removal efficiency at low temperatures followed the order: $Mn_{0.25}Ce_{0.5}Zr_{0.25}O_x > Mn_{0.4}Ce_{0.5}Zr_{0.1}O_x > Mn_{0.3}Ce_{0.5}Zr_{0.2}O_x > Mn_{0.2}Ce_{0.5}Zr_{0.3}O_x > Mn_{0.1}Ce_{0.5}Zr_{0.4}O_x > Ce_{0.5}Zr_{0.5}O_x$. Without Mn doping, the $CeZrO_x$ catalyst showed rather poor SCR activity in the whole temperature region with the maximum NO_x

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