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The NO oxidation performance over $Cu/Ce_{0.8}Zr_{0.2}O_2$ catalyst

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ABSTRACT

The Cu-doped $Ce_{0.8}Zr_{0.2}O_2$ (CZ) catalyst was investigated in terms of its NO oxidation activity, structure and surface characteristics. The Cu/CZ catalyst with 6 wt% Cu loading and 550 °C calcination temperature of CZ support showed the best catalytic performance, and over 50% NO conversion was obtained in a wide temperature range (250–370 °C). Moreover, this catalyst showed good resistance to H_2O and SO_2. The dispersion of CuO species on the smaller crystallite size CZ support was favorable for NO adsorption. The Cu–Ce–Zr solid solution provided the sites of oxygen vacancies, prompted the formation of active oxygen, which in sum improved the oxidation activity of NO.

1. Introduction

Nitrogen oxides (NO_x), which include NO (nitrogen monoxide), NO_2 (nitrogen dioxide), and N_2O (nitrous oxide), are currently considered to be among the most dangerous air pollutants, as they cause acid rain, photochemical smog, ozone depletion and have direct harmful effects on human health. For all these reasons, in the last decades NO_x emissions have been regulated in industrialized countries by more and more restrictive legislation [1]. Popular techniques tackling the NO_x removal include selective catalytic reduction (SCR) and NO_x storage and reduction (NSR), both of which convert NO_x into nitrogen [2]. It was reported that NO oxidation into NO_2 played a key role to NO_x conversion in both technologies, since NO_2 was more effective to be either reduced into N_2 or adsorbed on catalysts as nitrates [3]. For example, Kang et al. proposed a two-stage catalyst system for SCR with the pre-oxidation of NO during the first stage [4]. Cuenya et al. also developed high-performance Pt catalysts under mild operation conditions for a critical step in the NSR [5]. Particularly, the ability to efficiently catalyze NO oxidation into NO_2 is one of the major technological challenges at temperatures as low as 200–300 °C [6]. Generally, the NO oxidation efficiency in normal conditions was relatively slow, which was also complicated because of the complex chemical nature of fuel gas and the different particulate size distributions. Therefore, many efforts have been focused on the development of SCO catalyst with high oxidation activity.

The platinum catalyst was usually involved in NO oxidation and exhibited superior activity and life span, but were limited by their high cost. So it was of high necessity to develop active, stable and non-precious catalysts for substitution of the current Pt materials. Among them, Ce-based catalysts have been reported to be effective for the oxidation reaction because of their excellent ability of releasing or storing oxygen [7]. It had been also found that the doping effect of Zr^{4+} improved the thermal stability, oxygen storage capacity and redox property of CeO_2, thus the catalytic activity in oxidation reaction could be significantly enhanced in Ce–Zr mixed oxides [8,9]. In addition, as a relatively more cost-effective material, Cu catalysts with have been also studied for soot oxidation due to the superior redox property of CuO. Therefore, Cu-based Ce–Zr mixed oxides were the most promising candidates as NO oxidation catalysts for its superior performance and the application of Cu doped Ce–Zr mixed oxides for emission control has not been studied.

In this work, $Cu/Ce_{0.8}Zr_{0.2}O_2$ catalyst was synthesized by the surfactant-templated method. The structural and textural properties were determined by several characterization techniques as BET, XRD, H_2-TPR, UV–vis and Raman spectroscopy. Moreover, the roles of Cu and Ce–Zr species in the oxidation process were studied.

2. Experimental

2.1. Catalyst preparation

The $Ce_{0.8}Zr_{0.2}O_2$ mixed oxides support was prepared via a surfactant-templated method using cerium (III) nitrate

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($Ce(NO_3)_3{\cdot}6H_2O$) and zirconium nitrate ($Zr(NO_3)_4{\cdot}5H_2O$) as precursors. For a typical synthesis, an aqueous solution containing cetyltrimethyl ammonium bromide (CTAB) was added to an mixed aqueous solution of $Ce(NO_3)_3{\cdot}6H_2O$ and $Zr(NO_3)_4{\cdot}5H_2O$. The molar ratio of CTAB/([Ce] + [Zr]) was 0.4. The mixture was stirred for 0.5 h and then aqueous ammonia (25%) was slowly added with stirring till the pH equaled 10. The above mixture was stirred for another 12 h and then the homogeneous slurry mixture was hydrothermally treated at 90 °C for 24 h in a Teflon-lined autoclave vessel. After hydrothermal treatment, the precipitates were filtered and washed with deionized water and absolute ethanol until Br species were undetectable by an $AgNO_3$ solution. Finally, the obtained solids were dried at 100 °C overnight and then calcined at different temperatures: 450 °C, 550 °C, 650 °C and 750 °C for 3 h in air. These $Ce_{0.8}Zr_{0.2}O_2$ supports were referred to as CZ–Y, where Y denoted the calcination temperature.

Copper was then dispersed onto each CZ supports by deposition-precipitation to obtain a series of Cu/CZ catalysts [10]. Firstly, the CZ support was immersed in the aqueous solution of copper nitrate, which was stirred vigorously. The ratio of CZ support to solution was 0.5 g/60 cm^3. Then the aqueous ammonia (25%) was slowly added with stirring till the pH equaled 10. Subsequently, the precipitates were filtered, washed with deionized water until Br species were undetectable by an $AgNO_3$ solution. Finally, the obtained solids were dried at 100 °C overnight and then calcined at 450 °C for 3 h in air. These catalysts are denoted as X–Cu/CZ, where X represented the weigh percent of Cu.

2.2. Catalyst characterization

N_2 adsorption/desorption isotherms at about -196 °C were obtained using a Quantachrom AutoSorb-6B analyzer. The specific surface area was calculated using the Brunauer–Emmett–Teller (BET) method. The pore size distributions were determined from desorption branches by the Barrett–Joyner–Halenda (BJH) method.

The X-ray diffraction (XRD) experiment was recorded on a Bruker AXS-D8 Advance powder diffractometer with monochromatic detector equipped with CuKα radiation. The samples were scanned from 2θ of 20–85° with a step size of 0.02°.

Raman spectra were recorded on a Thermo Scientific DXR type Laser Raman microscope spectrometer with an excitation wavelength of 532 nm (Visible Raman) and the laser power of 3 mW.

H_2 temperature programmed reduction (H_2-TPR) was performed on a Micromeritics AutoChem II 2920 instrument. Typically, 100 mg of sample were exposed to a flow of H_2/Ar mixture. The temperature was ramped from room temperature to 1000 °C at a heating rate of 10 °C/min.

The diffuse reflectance UV–vis spectra were obtained on a spectrometer (JASCO, 60 UV-550) and the samples were scanned in a wavelength range of 190–800 nm.

The temperature programmed desorption (TPD) was performed in a fixed-bed reactor using quadrupole mass spectrometer (GSD 320). The mass signals of NO (m/e = 30) and O_2 (m/e = 32) were recorded. Typically, 150 mg of sample were pretreated in a flowing stream of He at 200 °C for 1 h After that, the catalyst was saturated by a flow of NO or O_2. The reactor was then purged with He for a further 1 h Then He was passed through the reactor and the temperature was ramped from room temperature to 600 °C at a rate of 10 °C/min.

2.3. Catalytic activity tests

The catalytic performance of Cu/CZ catalysts in the NO oxidation was studied in a fixed-bed flow reactor (8 mm in interior diameter). The composition and amount of the inlet gas mixture were set by mass flow controllers. The typical reactant gas composition was as follows: 500 ppm NO, 5 vol% O_2, and balance He. Each test was carried out with loading 200 mg of catalyst. The total flow rate of the reaction mixture was 200 ml/min, and the gas hourly space velocity (GHSV) was about 80,000/h. The inlet and outlet gas were analyzed by the MRU air emission monitoring system equipped with electrochemical sensors. The signal of all reactants and possible products were measured step by step after stabilization of the signals at a given temperature. The NO conversion to NO_2 was defined as:

$$\text{NO conversion to } NO_2 = \frac{(NO_{2\ out} - NO_{2\ in})}{NO_{in}} \times 100\%$$

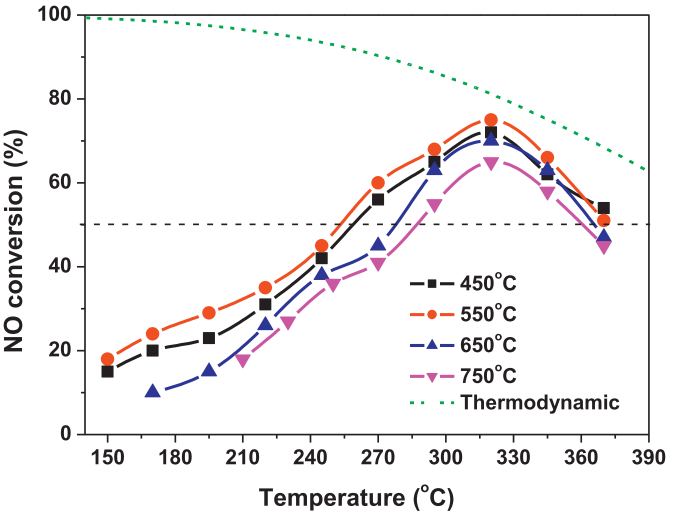

Fig. 1. NO conversion on over 6-Cu/CZ catalysts for the support at various calcination temperatures.

3. Results and discussion

3.1. NO oxidation activity of Cu/CZ catalysts

Fig. 1 reveals the effect of calcination temperature of CZ support on NO conversion over Cu/CZ catalysts. The result indicated that the calcination temperature significantly influenced the oxidation activity of NO to NO_2. As shown in Fig. 1, the 6-Cu/CZ-550 catalyst exhibited best catalytic activity at the widest temperature range, above 50% NO conversion was obtained in a wide temperature range (250–370 °C). However, when the calcination temperature of CZ support was increased from 550 °C to 750 °C, the NO oxidation activity of 6-Cu/CZ catalysts decreased gradually. The 6-Cu/CZ-750 sample showed poor activity with 50% NO conversion from 285 to 360 °C, and the temperature window was narrowed. This suggested that the calcination temperature of CZ support was an important factor for NO oxidation activity. In brief, 550 °C was a comparatively appropriate calcination temperature of CZ support to obtain better NO oxidation activity over 6-Cu/CZ catalysts.

Fig. 2 shows the NO conversion of Cu/CZ-550 catalysts with various Cu loadings. It was obvious that the loading of Cu element could indeed influence the NO oxidation activity of Cu/CZ catalysts. Over the entire temperature range tested, it should be noted that the NO conversion of Cu/CZ catalyst enhanced significantly compared with that pure CZ. Meanwhile, the NO oxidation activity increased with the increase of Cu loading from 4 to 6 wt%, and then it decreased when the Cu loading exceeded 6 wt%. This indicated that the increasing of Cu loadings could not always promote NO oxidation activity. Sample 6-Cu/CZ catalyst exhibited the highest efficiency and broadest temperature window.