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Effect of fluorine additive on $CeO_2(ZrO_2)/TiO_2$ for selective catalytic reduction of NO by NH_3

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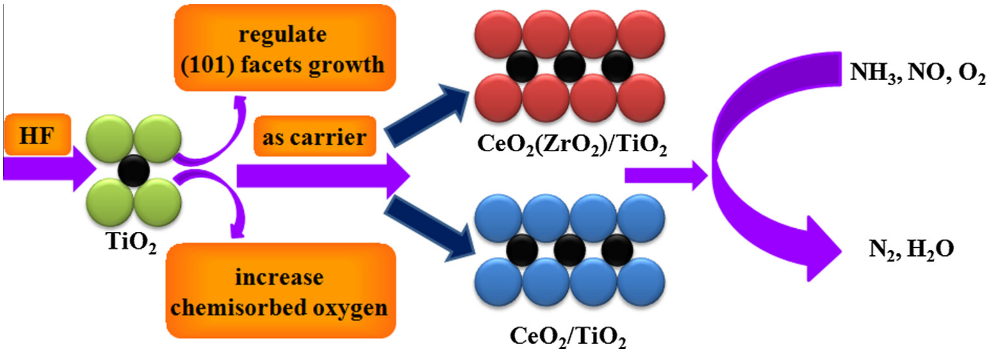
GRAPHICAL ABSTRACT



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ABSTRACT

A series of $CeO_2(ZrO_2)/TiO_2$ catalysts with fluorine additive were prepared by impregnation method and tested for selective catalytic reduction (SCR) of NO by NH_3. These samples were characterized by XRD, N_2-BET, Raman spectra, SEM, TEM, NH_3-TPD, H_2-TPR and XPS, respectively. Results showed that the optimal catalyst with the appropriate HF exhibited excellent performance for NH_3-SCR and more than 96% NO conversion at 360 °C under GHSV of 71,400 h^{-1}. It was found that the grain size of TiO_2 increased and the specific surface area reduced with the modulation of HF, which was not good for the adsorption of gas molecule. However, the modulation of HF exposed the high energy (0 0 1) facets of TiO_2 and increased the surface chemisorbed oxygen concentration, oxygen storage capacity and Ce^{3+} concentration of catalyst. In addition, the synergy of (1 0 1) and (0 0 1) facets was beneficial to the improvement of catalytic activity.

1. Introduction

Nitrogen oxides (NO_x) are one of the major factors responsible for the worsening environment problems such as acid rain, photochemical smog and the greenhouse effect [1,2]. Denitrification has become an active demand to protect the ecological environment. Selective catalytic reduction of NO with NH_3 (NH_3-SCR) is the most widely employed technology for the abatement of the emission of

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NO. Currently, the most commercially used catalysts are $V_2O_5(WO_3, MoO_3)/TiO_2$ catalysts [3]. However, the operation temperature window of V_2O_5/TiO_2 catalysts is relatively narrow. Moreover, the V_2O_5-based catalyst still suffers from a low N_2 selectivity and sublimation of V_2O_5 at high temperatures even after modification with molybdenum and tungsten species [4,5]. Consequently, more and more attention has been given to develop environment-friendly NH_3-SCR catalysts with highly NO conversion and broad active temperature window.

Owing to its chemical inertness, long-term stability and environmental friendliness, TiO_2 has been applied in many fields, such as gas sensor application [6], coating [7] and photocatalysis [8]. For the NH_3-SCR, TiO_2 is often used as a catalyst carrier. In addition, CeO_2 is a widely used catalytic material because of its unique redox properties and high oxygen storage capacities, such as photocatalysis [9], fuel cell [10] and oxygen permeation membrane [11]. Based on the above reasons, many ceria-based catalysts have been developed, such as CeO_2/TiO_2 [12,13], Ce-W-O_x/TiO_2 [14–16], CeO_2/TiO_2-SiO_2 [17,18], Ce-Zr-O_x/TiO_2 [19,20], Mn-Ce-O_x/TiO_2 [21–24] and so on. These catalysts could show effective denitration activity in a wide active temperature window.

Many previous researches have been proved that the fluorine additive can enhance the catalytic activity for NH_3-SCR [25–27]. In addition, Many theoretical and experimental studies have been developed to control the growth of different TiO_2 crystal faces, and the modulation of HF can expose the (0 0 1) facets. For anatase TiO_2, it has been found that the order of the average surface energies is $\gamma(1\,1\,0) > \gamma(0\,0\,1) > \gamma(1\,0\,0) > \gamma(1\,0\,1)$ [28]. In other words, the anatase TiO_2 with (0 0 1) facets are more reactive than the (1 0 1) facets, which is favorable to the increase of catalytic performance in many fields. Therefore, the exposure of TiO_2 crystal faces can be regulated with the modulation of HF, and the HF modified TiO_2 will be used as a catalyst carrier, which might enhance the catalytic activity of $CeO_2(ZrO_2)/TiO_2$ (CZT for short) catalysts theoretically. Based on the previous researches of our team, the aim of this work is to explore the rule for effect of fluorine additive on catalytic activity in the CZT catalysts.

2. Experiment

2.1. Catalyst preparation

TiO_2 with the modulation of HF was prepared by a hydrothermal method. In a typical preparation, the appropriate HF solution (concentration: 40 wt.%), 10 mL distilled water and 50 mL $Ti(OC_4H_9)_4$ were mixed together in a 100 mL Teflon-lined autoclave, and then kept at 180 °C for 24 h. The resulting white precipitate was washed three times with ethanol and distilled water. The residual solid was dried at 80 °C for 6 h and then calcined at 500 °C for 2 h. The added contents of HF were 0 mL, 5 mL, 10 mL and 15 mL, respectively.

The molar ratio of Ti:Ce:Zr (when used) in the catalyst was designed as 4:1:1. The TiO_2 supports were dipped in the mixed aqueous solution of $ZrOCl_2\cdot 8H_2O$ and $Ce(NO_3)_3\cdot 6H_2O$, and the mixed solution was stirred for 2 h at room temperature. Then the product was followed by drying in air at 80 °C for 24 h and the solid was calcined at 500 °C for 2 h. The catalysts were designated as CT-XF and CZT-XF (X = 0, 5, 10 and 15), respectively.

2.2. Catalytic activity and selectivity measurement

The catalytic activity measurements of the prepared catalysts for NH_3-SCR of NO were carried out in a fixed-bed quartz reactor (6 mm inner diameter), with 0.7 mL catalysts (particle sizes of 0.3–0.45 mm) and 833 mL min^{-1} gas flow rate corresponding to a GHSV of 71,400 h^{-1}. The reactant gas typically consisted of 600 ppm NO, 600 ppm NH_3, 6% O_2 and balance N_2. The NO concentrations at the inlet and outlet of the reactor were monitored on-line by a flue gas analyzer (MRU VarioPlus, Germany). The catalytic activity (X_{NO}) for NH_3-SCR of NO was expressed by Eq. (1). The analysis at each selected temperature was performed after 30 min since the reactor temperature was stabilized.

$$X_{NO} = ([NO]_{inlet} - [NO]_{outlet})/[NO]_{inlet} \times 100\% \tag{1}$$

The temperature range in which the catalytic activities were equal to or more than 90% of the maximum catalytic activity was defined as the catalytically active temperature window, expressed as T_r. The lowest temperature of T_r was named T_r-L, and the highest is named T_r-H.

The N_2 concentration at the outlet of the reactor was monitored on-line by a gas chromatography (GC2014, Japan), using a 5 Å molecular sieve column (2 m in length, sorbent particle sizes disperse from 60 mesh to 80 mesh), and a single-point corrected external standard method was adopted. The concrete GC detecting conditions were described as follows: injection volume was 1 mL, injector temperature was 90 °C, chromatographic column temperature was 80 °C, TCD detector was used at 120 °C, carrier gas was argon, hydrogen was 30 mL min^{-1}. Firstly we obtained the peak area of the known standard N_2/Ar (600 ppm, and balance Ar) and defined the area as S_0, and then we obtained the peak area of the detected N_2 at the outlet and defined the area as S. According to the following reaction:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \tag{2}$$

Thus, the NO_x concentration merely consumed by N_2: $[NO_x]_{N2consu} = [N_2] = 600\ S/S_0$ ppmv, while the total concentration of NO_x conversion: $[NO_x]_{conv}=[NO_x]_{inlet}-[NO_x]_{outlet}$. In order to facilitate the quantitative analysis and discussed the N_2 selectivity of the catalysts for NH_3-SCR of NO_x, the N_2 selectivity for NH_3-SCR of NO_x was expressed by Eq. (3):

$$\begin{aligned}\eta &= [NO]_{N2consu}/[NO]_{conv} \times 100\% \\ &= 600S/(S_0[NO]_{inlet} - S_0[NO]_{outlet}) \times 100\%\end{aligned} \tag{3}$$

2.3. Characterization

Powder X-ray diffraction (XRD) patterns were obtained on the X-ray diffractometer (Smartlab TM 9Kw, Rigaku, Japan) using Cu Kα radiation. The 2θ scans covered the range 10–80°, and the accelerating voltage and applying current were 45 kV and 200 mA, respectively. The microstructural natures of the catalysts have been investigated using a scanning electron microscope (JEOL, JSM-5900) and transmission electron microscopy (JEOL, JEM-2010UHR). The AXIS ULTRA DLD instrument was used for X-ray photoelectron spectroscopy (XPS) analysis, and monochromatic Al-Kα radiation was used as the excitation source. After complete removal of moisture from the catalysts by drying at 100 °C for 24 h, the catalysts were analyzed without surface sputtering or etching so that the degree of vacuum in the XPS equipment was maintained at 10^{-7} Pa. Visible Raman spectra of the catalysts were collected at room temperature on the LabRAMHR800 (Horiba Jobin Yvon). A 514 nm diode-pumped solid-state semiconductor laser was used as the excitation source with a power output of 30 mW.

The number of acidic sites and acid strength of the catalysts were evaluated by a temperature programmed desorption (TPD) of ammonia using CHEMBET-3000 (Quantachrome). The samples were preheated to 450 °C under a helium stream for 1 h, and then cooled to 100 °C for ammonia adsorption. Then ammonia was desorbed using helium at a flow rate of 30 mL min^{-1} from 100 °C to 800 °C at a heating rate of 10 °C min^{-1}. The ammonia desorption