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A study on chemisorbed oxygen and reaction process of Fe–CuO$_x$/ZSM-5 via ultrasonic impregnation method for low-temperature NH$_3$-SCR

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ABSTRACT

Fe–CuO$_x$/ZSM-5 catalyst was prepared for low-temperature selective catalytic reduction (SCR) of NO$_x$ with ammonia by ultrasonic impregnation method. The catalyst were characterized by HRTEM, XRD, H$_2$-TPR, XPS, in situ DRIFTS and tested for their activities in a fixed-bed reactor. The NO$_x$ conversion over Fe(0.67)–Cu/ZSM-5 sample reached 98% within the temperature range from 180 to 360 °C. Ultrasonic impregnation can promote active component to highly disperse into the channel of ZSM-5, greatly improving low-temperature SCR performance compared to conventional impregnation according to characterization of XRD, HRTEM. XPS results showed that chemisorbed oxygen had catalytic oxidation activity against NO and NH$_3$, the proportion of chemisorbed oxygen was affected by molar ration of iron and copper. When the molar ratio of iron and copper was 2:1, the maximum chemisorbed oxygen by XPS and the minimum reduction temperature of 263 °C by H$_2$-TPR were obtained. In situ DRIFTS results revealed that catalyst had oxidation activity against NO and NH$_3$ under oxygen-free condition due to action of chemisorbed oxygen, reaction rate of SCR is much faster than the reaction between adsorbed ammonia and oxygen, nitrate as a kind of intermediate was produced by reaction of NH$_3$ and NO in the SCR process.

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1. Introduction

Nitrogen oxides (NO, NO$_2$ and N$_2$O) in the exhaust gases from combustion of fossil fuels remain a major source for air pollution. They contribute to photochemical smog, acid rain, ozone depletion and greenhouse effects. Selective catalytic reduction (SCR) of NO$_x$ (x = 1, 2) with ammonia in rich oxygen is current efficient technology for reducing nitrogen oxides emissions from power plants [1]. Low-temperature NH$_3$-SCR reactor can be located downstream in the tail-end configuration where most of the SO$_2$ and ash have been removed after passing through the desulphurizer and particulate removal device, reducing the catalyst poisoning and extending the catalyst lifetime; lower reaction temperature also can reduce the side reaction of NH$_3$ oxidation, thus low-temperature SCR catalyst shows a good application prospect [2,3]. Proper oxidbillity of active center is necessary to low-temperature NH$_3$-SCR reaction, which can not only promote NH$_3$ adsorbed on active center to transform into intermediate product through oxidation-dehydrogenation process, but also contribute to NO oxi-

dation to NO$_2$, promoting the fast SCR reaction [4]. However, excessive oxidbillity for active center will lead to the formation of N$_2$O due to further oxidation of NH$_3$, thus how to choose active center is significant. Metal oxides with different valence states show unique catalytic properties for the low-temperature SCR reaction due to the unsaturation of outer electrons [5–7]. A series of MoO$_3$ doped CeAlO$_x$ mixed oxide catalysts with different Mo/Al molar ratios were prepared by Li and Li [8] and used for NH$_3$-SCR, result shown that Ce–Mo–AlO$_x$ catalyst with the Mo/Al molar ratio of 0.5 exhibited excellent activity at 250 °C due to the enhance of redox capacity and total acidity of catalyst by the introduction of MoO$_3$. Catalysts of Mn–Ce–M/TiO$_2$ (M = Fe, Ni) prepared via co-precipitation method for low temperature NH$_3$-SCR under the influence of alkali metals were investigated by Zhang et al. [9], which showed higher SCR activity and better resistance to alkali poisoning because of the characteristics of large surface area, pore volume, the increased chemisorbed oxygen and the enhanced oxidative ability of manganese species. Masaaki Yoshikawa investigated the low-temperature SCR activity of Fe$_2$O$_3$, Co$_2$O$_3$ and Mn$_2$O$_3$ loaded on the ACF, the experimental results showed that activated carbon fiber highly dispersed the metal oxide particles and provided larger gas phase contact area, improving SCR performance [10]. Cao investigated Cu-SAPO-34 and CuCe-SAPO-34

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catalysts, the experimental results suggested that interaction of Ce with copper could improve the dispersion of copper species and increase the amount of isolated Cu^{2+} ions, so that CuCe-SAPO-34 performed better NH_3-SCR activity than Cu-SAPO-34 [11]. Iron and copper oxides have gained significant attention because of their adsorptive properties of NO and environmental friendliness. For the Fe_2CuO_4/ZSM-5, showing good catalytic activity in the low-temperature SCR reaction [12], more than one valence states of the iron or copper (Fe^{3+} and Fe^{2+}, Cu^{2+} and Cu^+) could promoted the mutual transformation between the electrons and formation of oxygen vacancy caused by charge mismatching, which result in formation of chemisorbed oxygen.

ZSM-5 molecular sieve has sub-nanometer porous structure with rich acidic centers, which can interact with NH_3 to generate intermediate NH_4^+ through fast adsorption and activation process, the interior space can be regarded as a kind of miniature "nano reactor", providing an advantageous reaction space and electronic environment for the generation of highly dispersed transition metal oxides clusters, showing unique catalytic activity in SCR reaction [13–15]. Ultrasonic cavitation effect can promote the active component to disperse within micro-pores of ZSM-5 and reduce the relative supersaturation of solution, thus inhibiting secondary nucleation of precursors and further growing up of crystal nucleus, which is conducive to the formation of oxide clusters and nanoparticles. Oxide clusters and nanoparticles can provide more active centers, showing excellent catalytic activity at low temperature.

In this work, Fe–CuO$_x$/ZSM-5 catalyst has been prepared by ultrasonic impregnation method. XRD, HRTEM, H_2-TPR were used to characterize the morphology and reduction performance of catalyst. Effect of ultrasonic impregnation on dispersion of active component, property and function of chemisorbed oxygen, adsorption and reaction process of NO and NH_3 on catalyst surface were investigated deeply.

2. Experimental

2.1. Preparation of catalysts

According to the literature [16], Fe–CuO$_x$/ZSM-5 catalysts were prepared by ultrasonic impregnation method. A total of 0.6 mol $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ was dissolved in 40 mL deionized water. The solution of $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ was homogeneously mixed with 15 g ZSM-5 zeolite (Si:Al = 35:1), followed by placed into a microwave-ultrasound reactor to react for 2 h under the condition of 40 °C and 400 W. Solid samples were obtained after the solution was dried at 100 °C overnight. Finally, the samples were calcined at 350 °C for 4 h. The catalysts prepared in this way were denoted as Fe(y)–Cu/ZSM-5, where, y represented the molar ratio of Fe and Fe + Cu.

Catalysts was prepared by conventional impregnation method as follows: total of 0.6 mol $Fe(NO_3)_3 \cdot 9H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ was dissolved in 40 mL deionized water, then 15 g ZSM-5 zeolite was added and stirred for 2 h at room temperature. The samples were obtained after the solution was dried at 100 °C overnight and calcined at 350 °C for 4 h.

2.2. Characterization of catalysts

Crystal structure was determined using an X-ray diffractometer between 5 and 80° with a step of 10° min^{-1} operating at 40 kV and 30 mA using Cu Kα radiation. The XRD phases were identified by comparison with reference data from International Center for Diffraction Data (ICDD) files. The TEM images were taken on a Philips Tecnai 12 transmission electron microscope. In each H_2-TPR

(temperature-programmed reduction) experiment, 300 mg sample was loaded into a quartz reactor and then pretreated in N_2 at 200 °C for 1 h. The sample was then cooled down to room temperature. The reduction of the sample was carried out from room temperature to 800 °C in a flow of 10% H_2 at 10 °C min^{-1}. The consumption of H_2 was monitored continuously with a thermal conductivity detector. The water produced during reduction was trapped in a 5 A molecular sieve column. Electron spectroscopy for chemical analysis (XPS) was recorded using an X-ray photoelectron spectroscope (PerkinElmer, PHI Quantera II) with an Al Kα ($h\nu$ = 1486.6 eV) X-ray source; samples were dried under vacuum at 80 °C before detection. The DRIFTS spectra were obtained using a diffuse reflectance accessory connected to a DRIFTS spectrometer (Thermo Nicolet iZ10) that was equipped with an MCT detector cooled by liquid N_2. The samples were placed on a high-temperature cell with two KBr windows, allowing thermal treatments under flowing gas. The total gas flow was maintained by mass flow controllers. The background spectrum of the catalyst was recorded in N_2 gas flow of 8 mL/min and was subtracted from the sample spectrum that was taken at the same temperature.

2.3. Activity test

The SCR reaction was evaluated in a fixed-bed reactor. A sample of 1 g Fe–CuO$_x$/ZSM-5 (20–40 mesh) was put in a reaction tube and placed for 2 h in simulated flue gas. The gas mixture contained 1000 ppm NO, 1000 ppm NH_3, and 5% O_2, with N_2 used as balance gas. The total flow rate of the feeding gas was 150 mL/min. Concentrations of NO$_x$ (NO + NO_2) were measured by Germany ECOM-JZKNoal gas analyzer. The conversion was calculated according to the following equation:

$$NO_{x\,conversion} = \left[\frac{([NO_x]_{in} - [NO_x]_{out})}{[NO_x]_{in}} \right] \times 100\%$$

The oxidation rate of NO was also evaluated in above fixed-bed reactor. The gas mixture contained 1000 ppm NO and 5% O_2, with N_2 used as balance gas. The oxidation rate of NO to NO_2 was calculated according to the following equation:

$$NO_{oxidation} = \left[\frac{([NO_2]_{out} - [NO_x]_{in})}{[NO_x]_{in}} \right] \times 100\%$$

3. Results and discussion

3.1. SCR performance

The SCR performance of Fe–CuO$_x$/ZSM-5 is shown in Fig. 1 as a function of temperature. It can be observed from Fig. 1 that the molar ration of iron and copper had evident influence both on the high-temperature region and low-temperature region: NO$_x$ conversion increases in high-temperature region but drops rapidly at low temperature with the increase of iron proportion. NO$_x$ conversion nearly reaches 98% at 180 °C for all samples, but drops evidently over 240 °C for Fe(0.50)–Cu/ZSM-5 and 270 °C for Fe(0.62)–Cu/ZSM-5 with a narrow temperature window. NO$_x$ conversion of Fe(1.00)–Cu/ZSM-5 and Fe(0.85)–Cu/ZSM-5 is not ideal in low-temperature region, with only 42% and 65% NO$_x$ conversion at 120 °C. It can be concluded from curves in Fig. 1 that when the molar ration of iron and copper was 2:1 (Fe(0.67)–Cu/ZSM-5), the catalyst had relatively higher and most stable catalytic performance, which NO$_x$ conversion would achieve 90% at 150 °C and can keep more than 98% in range of 180–360 °C.