Modification of Cu/ZSM-5 catalyst with CeO_2 for selective catalytic reduction of NO_x with ammonia

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Abstract: Cu/ZSM-5 and CeO_2-modified Cu/ZSM-5 catalysts were prepared by a wetness impregnation method. The addition of CeO_2 was found to enhance the NO_x selective catalytic reduction (SCR) activity of the catalyst at low temperatures, but the high-temperature activity was weakened. The catalysts were characterized by X-ray diffraction (XRD), nitrogen physisorption, inductively coupled plasma optical emission spectrometry (ICP-OES), X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), H_2 temperature-programmed reduction (TPR) and NH_3 temperature-programmed desorption (TPD). The results showed that more CuO clusters instead of isolated Cu^{2+} species were obtained on the modified catalyst. These active CuO clusters, as well as the Cu-Ce synergistic effect, improved the redox property of the catalyst and low-temperatures SCR activity via promoting the oxidation of NO to NO_2 and fast SCR reaction. The loss in high-temperatures activity was attributed to the enhanced competitive oxidation of NH_3 by O_2 and decreased surface acidity of the catalyst.

Keywords: Cu/ZSM-5; CeO_2 modification; NH_3-SCR; CuO clusters; surface acid sites; rare earths

Vehicle exhaust emission standards have recently become stricter, due to the hazardous nature of exhaust emissions and increasingly serious haze weather in China[1]. However, due to the intrinsic characteristics of diesel combustion, nitrogen oxides (NO_x) are generated in the localized high-temperature reaction zone and particular matters (PM) are formed in the diffusion combustion zones. Several technologies are being implemented to reduce these harmful pollutants. One of the promising technologies for reducing NO_x is known as urea-selective catalytic reduction (SCR)[2,3]. The SCR is a means of converting NO_x with the aid of a catalyst into N_2 and H_2O. The aqueous urea solution which is injected into the hot exhaust stream, generates ammonia (NH_3) during H_2O decomposition, thermal urea decomposition, and hydrolysis. Vanadia (V_2O_5) is generally used as an SCR catalyst[4–7], but zeolite catalysts such as Cu-zeolite and Fe-zeolite have been researched and commercialized because of the toxicity of vanadium. The Cu-based zeolite catalysts have higher SCR activity than Fe-based zeolite catalysts in low temperature range[8].

In recent years, the de-NO_x performance of Cu-zeolite catalysts with superior low-temperature activity has been improved in many studies[9–12]. Moreover, the effects of additive addition on catalytic activity have been studied[13–15]. Seo et al.[16] modified the Cu-ZSM-5 catalyst

with ZrO_2. They found that the addition of ZrO_2 improved the low-temperature activity of the SCR catalyst. Ceria has been applied as a promoter in a number of catalysts[17–20]. Nevertheless, the modification mechanisms of additives on Cu/ZSM-5 catalyst for NH_3-SCR reaction have been rarely reported. In this work, a CeO_2 doped Cu/ZSM-5 catalyst was prepared and the role of ceria was discussed.

1 Experimental

1.1 Catalyst preparation

Cu/ZSM-5 and CeO_2-modified Cu/ZSM-5 (SiO_2:Al_2O_3= 25:1) catalysts were synthesized by wetness impregnation[21] using $Cu(NO_3)_2 \cdot 3H_2O$ and $Ce(NO_3)_3 \cdot 6H_2O$ (Shanghai Ling Feng Chemical Reagent, China) and ZSM-5 (Nankai Catalyst Company, China) powders as the precursors, and the obtained catalysts were denoted as CuZ and CuCeZ, respectively. The nominal contents of Cu and CeO_2 in the catalysts was 2 wt.% and 5 wt.%, respectively.

1.2 Activity measurement

The NH_3-SCR activity was evaluated in a fixed bed quartz reactor, and the effluent gases were monitored by

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infrared spectroscopy (Thermo Nicolet 380). The reaction gas consisted of 500 ppm NO, 500 ppm NH$_3$, 5% O$_2$, 10% H$_2$O, and N$_2$ in balance. The flow rate of the reaction gas was 1000 mL/min, the amount of catalyst (sieved to 50–80 mesh) used was 300 mg, and the gas hourly space velocity (GHSV) was kept at 100000 h^{-1}. The concentration of NO$_x$ (NO, N$_2$O, and NO$_2$) was detected at the ppm level. The NO$_x$ conversion of the catalysts was calculated using Eq. (1):

$$\text{NO}_x \text{ conversion (\%)} =$$

$$\frac{\text{NO}_{in} - \text{NO}_{out} - \text{NO}_{2out} - 2\text{N}_2\text{O}_{out}}{\text{NO}_{in}} \times 100 \qquad (1)$$

The NH$_3$/NO oxidation tests were performed for the catalysts using a feed gas composition of 500 ppm NH$_3$/NO, 5% O$_2$, 10% H$_2$O and N$_2$ in balance. The NH$_3$ and NO conversion were calculated by Eqs. (2) and (3), respectively:

$$\text{NH}_3 \text{ conversion (\%)} = \frac{\text{NH}_{3in} - \text{NH}_{3out}}{\text{NH}_{3in}} \times 100 \qquad (2)$$

$$\text{NO conversion (\%)} = \frac{\text{NO}_{2out}}{\text{NO}_{in}} \times 100 \qquad (3)$$

1.3 Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a diffractometer (D8 ADVANCE, Bruker, Germany) employing Cu Kα radiation (λ=0.15418 nm). Data were collected in the range of 5°≤2θ≤50° with a scanning velocity of 6 (°)/min.

Textural properties were determined by nitrogen physisorption at −196 °C using a JW-BK122F (Beijing JWGB, China) instrument. Prior to the measurements, the samples were degassed at 0.01 Pa at 220 °C. The specific surface area and desorption pore volume were assessed using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda methods, respectively.

The actual contents of Cu, Ce, Al and Si were determined on an Agilent 5100 inductively coupled plasma optical emission spectrometry (ICP-OES) instrument.

Electron paramagnetic resonance (EPR) spectra in the X-band were recorded on a CW spectrometer JES-FA200 (JEOL) at microwave power of 1 mW, modulation frequency of 100 kHz, and central field of 300 mT. Before the measurements, the samples were heated in vacuum from room temperature to 100 ºC for 30 min. The samples were then cooled to −150 ºC. Mn^{2+} was used as an external reference sample, and the g value and EPR spectral intensity of Cu^{2+} were determined.

Hydrogen temperature-programmed reduction (H$_2$-TPR) was performed on a Micromeritics Auto Chem II. Prior to the H$_2$-TPR experiment, the test sample (50 mg) was treated with He at a total flow rate of 50 mL/min at 300 ºC for 30 min and subsequently cooled to room temperature and flushed with He for 10 min. The atmosphere was then changed to 10% H$_2$/Ar (50 mL/min), and the reactor temperature was raised to 600 ºC at a heating rate of 10 ºC/min. H$_2$ consumption during the experiment was monitored with a thermal conductivity detector.

Ammonia temperature-programmed desorption (NH$_3$-TPD) analysis was performed using a TP 5000-II multiple adsorption apparatus (Xianquan, China). The samples (~50 mg) were pretreated in He at 500 ºC for 30 min. When the temperature decreased to 50 ºC, NH$_3$ was introduced until adsorption on the samples was saturated. The samples were then purged with He to remove residual NH$_3$ from the surface of the samples. The samples were then heated in He from 100 to 500 ºC at a rate of 10 ºC/min for subsequent NH$_3$ desorption.

2   Results and discussion

2.1   Structural properties

The modification of CeO$_2$ on the structure of the catalysts was investigated by XRD, and the results are shown in Fig. 1. For comparison, the diffraction pattern of ZSM-5 zeolite was included. All the catalysts exhibit the typical peaks corresponding to ZSM-5 zeolite, which implied that the original zeolite structure remains intact[22]. After copper impregnation, the diffraction peaks of CuO are identified, indicating that the copper species aggregate on the surface of the ZSM-5 support due to the impregnation method adopted. For the CeO$_2$ modified catalyst, the diffraction peaks of CuO almost disappear, while ceria can be detected by XRD[23], indicating the improved dispersion of CuO by the CeO$_2$ addition.

The specific surface areas and micropore volumes of the catalysts are summarized in Table 1. The S_{BET} and pore volume of the catalysts are lower than those of the ZSM-5 support, owing to coverage of CuO and CeO$_2$ on the external surface and pore structure of the zeolite. Interestingly, the textural data of the CeO$_2$ modified Cu/ZSM-5 catalyst are higher than those of Cu/ZSM-5
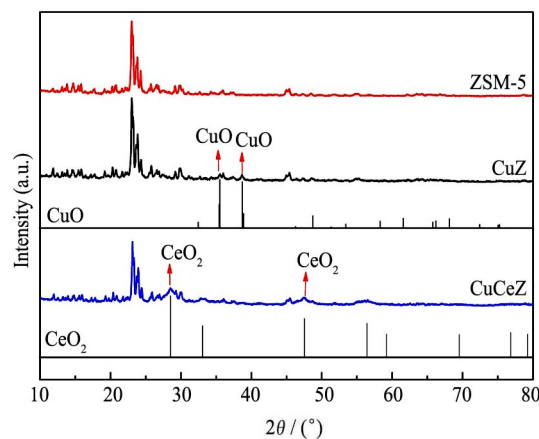

Fig. 1 XRD patterns of the support and catalysts as well as the standard data of CuO and CeO$_2$