Improvement in potassium and SO_2 resistance of commercial V_2O_5-WO_3/TiO_2 SCR DeNOx catalyst modified with Ce-Cu

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Abstract: To improve potassium and SO_2 resistance of commercial V_2O_5-WO_3/TiO_2 SCR DeNOx catalyst, Ce and Cu are added to modify it. The modified catalysts are prepared by impregnation method. Ce-Cu modified V_2O_5-WO_3/TiO_2 catalyst shows higher activity at low temperature (lower than 300℃) and improved resistance to both potassium and SO_2.
Keywords: SCR, potassium and SO_2 resistance, modification.

1. Introduction

Selective catalytic reduction (SCR) with NH_3 is one of the most effective methods for the removal of NO_x emissions from stationary sources. V_2O_5-WO_3/TiO_2 (VWT) is a widely used commercial SCR catalyst due to its high activity and high SO_2 resistance. However, this catalyst exhibits high conversions only within a narrow temperature range of 573–673 K, and can be easily deactivated by poisonous elements in the flue gas. Though V_2O_5-WO_3/TiO_2 shows high SO_2 resistance, some SO_2 will be oxidized to SO_3. SO_3 react with NH_3 and H_2O, producing NH_4HSO_4. NH_4HSO_4 is loaded on the surface of catalyst, which causes the deactivation of the catalyst[1]. It is also concluded that the poisoning effect of alkali metals considerably increases with their basicity[2]. That is why potassium was chosen as the representative of alkali metals in this work. Much research has been done to enhance potassium and SO_2 resistance of commercial V_2O_5-WO_3/TiO_2 catalyst. However, research on simultaneous potassium and SO_2 resistance is rare and the effect of modification is not very satisfactory. In this paper, Ce and Cu are added to commercial V_2O_5-WO_3/TiO_2 catalyst to improve its potassium and SO_2 resistance simultaneously.

2. Experimental

2.1. Catalysts preparation

The catalysts in this work were all prepared by the impregnation method. The synthesized catalysts were donated as VWCCT、VWCeT and VWCuT. The same impregnation method was applied to dope 0.5wt% of K (using kHCO3 as the precursor) on the commercial and VWCCT catalysts, donated as VWT-K and VWCCT-K, respectively. All the catalysts were crushed and sieved within 40–60 meshes for activity measurement.

2.2. SCR activity test

A fixed-bed quartz reactor (Φ10 mm × 600 mm) was used to measure the catalytic activity of the sample. 0.6 mL sample was placed in middle of the reactor. The gas mixture contained 500 ppm NO, 500 ppm NH_3, 500 ppm SO_2 (when used), 5.0vol% H_2O (when used) and 5.0% O_2/N_2. Total gas flow rate was maintained at 1000 mL/min^{-1}, which corresponded to a gas hourly space velocity (GHSV) of 100,000 h^{-1}. Concentrations of O_2, SO_2, NO and NO_2 in the gas were detected by a T-350 flue gas analyzer (Testo Company, Germany). NOx conversion was calculated as follows:

$$\text{NOx conversion}=\frac{[NOx]_{in}-[NOx]_{out}}{[NOx]_{out}}\times 100\%$$

where $[NOx]_{in}$ and $[NOx]_{out}$ represent the inlet and outlet concentrations of gaseous NOx;

3. Results and discussion

3.1.SCR activity and resistance to K-poisoning

The SCR activities of prepared samples are presented in Fig. 1. VWCCT shows the best activity when temperature is lower than 300℃. The NOx conversion can even be close to 100% at 300℃. But when temperature is higher than 300℃, its activity decreases sharply. The activity of VWCeT shows better than the commercial catalyst in the whole temperature range. It is indicated that the addition of Cu may decrease the activity in high temperature range.

The activities of fresh and K-poisoned samples are presented in Fig. 2. VWCCT-K exhibits an obviously higher NOx conversion than the fresh commercial VWT-K catalyst at temperature lower than 350℃. For example, at 300℃, the NOx conversion of VWCCT-K can reach 89% whereas that of the VWT-K is only 36%. It indicates that the addition of Ce and Cu is beneficial to potassium resistance.

3.2. Resistance to SO_2 and H_2O

Effect of SO_2 and H_2O on the SCR activity of VWCCT and VWT at 300℃ is presented in Fig. 3. It shows that the activities of both catalysts decrease continuously in the first 210 minutes after adding SO_2 and H_2O, which could be due to the competitive adsorption of H_2O and NH_3[3]. Then they are stable in around 93% and 85%, respectively. After stopping SO_2 and H_2O, both activities recover and even exceed the initial values, which possibly should be attributed to the enhanced surface acidities from the SO_2 sulfuration[4], providing more NH_3 adsorbing sites. The results indicate that VWCCT performs higher SO_2 resistance than VWT.

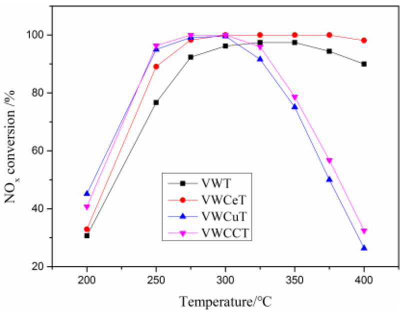

Figure 1. Activity comparison of samples.

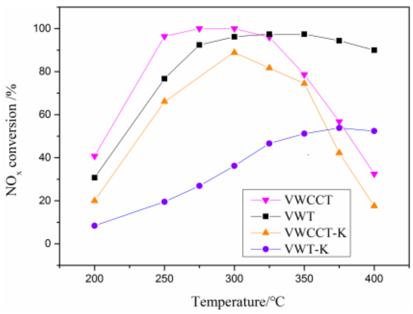

Figure2. Activity comparison of fresh and K-poisoned samples.

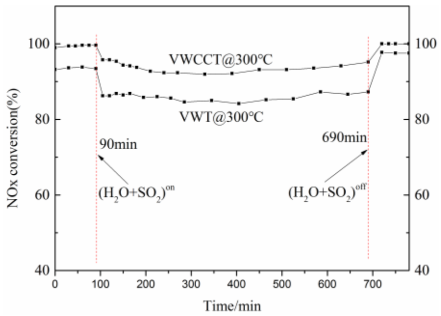

Figure3. Effect of SO_2 and H_2O on the SCR activity of VWCCT and VWT at 300C°

4. Conclusions

Ce-Cu modified V_2O_5-WO_3/TiO_2 catalyst (VWCCT) performed higher activity and improved potassium and SO_2 resistance at low temperature, which indicates that VWCCT seems to have a potential application as an effective SCR DeNOx catalyst under high-K and SO_2 conditions. But when the temperature is higher than 300℃, its activity decreases sharply, which may be due to the addition of Cu. The amount of Cu added will be adjusted to improve the activity and resistance to potassium and SO_2 in high temperature range of 300-400℃.

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