Preparation and Evaluation of Co-Cu-V / ZSM-5 Catalysts for Simultaneous Desulfurization and Denitrification of Flue Gas

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Abstract. A Co (1%)-Cu (1%)-V (1%) / ZSM-5 catalyst was prepared by impregnation. It was evaluated that the effects of different preparation and impregnation methods, catalytic elements, Co modifying and loading times, and reaction temperature, on the catalytic simultaneous desulfurization and denitrification. The results showed that V and Cu are the best elements for conversions of SO₂ and NO, which acted each other well, and that Co Pre-impregnation before simultaneous impregnation of V and Cu and the second impregnation of this procedure can improve the conversions. Under the optimum reaction temperature of 350 ℃ and 60mL/min gas flow conditions the average conversions of SO₂ and NO were 100% and 61%, respectively.

Introduction

At present, coal is 80% of total energy in China and mainly burned directly. The flue gas emitted from coal-fired boilers contains a large amount of SO₂ and NOx, which causes great harm to human health and environment.

The techniques of desulfurization and denitrification in domestic and foreign is still based on the traditional step-by-step removal of FWDG and SCR or SNCR. In the study on simultaneous dry removal include: calcium absorption, activated carbon adsorption, electron beam and catalytic oxidation. Li prepared by impregnation 10% Cu /ZSM-5 catalysts with CH₄ as a reducing gas [¹]. Ren prepared 12% Fe₂O₃-15% TiO₂/γ-Al₂O₃ catalysts by immersion method with 15% TiO₂/γ-Al₂O₃ prepared by sol-gel method [²]. Liu prepared Ni / Fe hydrotalcite catalysts the simultaneously desulfurization and denitrification conversions were 95% and 50% [³]. Li prepared 10% Fe₃O₄ / TiO₂ catalyst by hydrothermal synthesis at 100 ℃the simultaneous conversions of SO₂ and NO were 100% and 50%, respectively [⁴]. Yang prepared V₂O₅-Fe₂O₃ catalysts over the columnar activated carbon modified with H₂O₂ and HNO₃ and the maximum single denitrification conversion was 67.85% [⁵]. In order to find a catalyst with high efficiency and better thermal stability without reducing agents, the impregnation method of metal oxide catalysts for ZSM-5 was studied in this paper, which a fixed bed reactor was used for catalytic simultaneous desulfurization and denitrification of the coal-fired flue gas.

Experimental

The carries ZSM-5 (25)were pretreated by using hydrothermal treatment method that was soaked at 50°C for 4 hours, dried at 120°C for 6h and calcinated at 500 ℃ for 2h. Three different impregnation methods were optimized so that the best method without evaporating to dry was selected for reaction evaluation. The procedure was that: weighted 5g ZSM-5(25ml) and some catalyst element compounds by ratios of the element s to ZSM-5 and dissolved in 25ml of distilled water. The carrier was placed in a solution containing some concentration of the compounds and immersed at 60°C for 6 hours and the catalysts were dried at 120°C for 12h and calcinated at 500°C for 6h.
The catalysts were evaluated in a miniature fixed bed reactor (diameter 2 cm / height 10 cm) and the reaction gas was on-line analyzed by M-9000 combustion analyzer. Conversions were calculated by the initial and remaining concentrations of SO₂ and NO.

Results and Discussion

Selection of Loading Methods

The Cu (3%)-V (3%) / ZSM-5 catalysts were prepared by ion exchange, impregnation and impregnation-dry, respectively. The three catalysts obtained were evaluated under the same conditions of gas flow rate of 60 mL / min, 350 °C, and concentrations of 1200 ppm SO₂ 1000 ppm NO and 3%. O₂. The results shown in Figure 1.

From Fig.1 the influence order of denitrification are impregnation > ion exchange > impregnation-dry. The conversions of SO₂ all reached 100% after using 80 min, but the conversions of NO is the highest for impregnation.

Influence of Catalytic Elements on Simultaneous Removal of SO₂ and NO

Seven one-component catalysts were prepared by impregnation, which were evaluated under the same above conditions. The results are shown in Fig. 2.
Since the three elements (Fe, Mn, W) have not removal effects for SO2 and NO, it can be known that from Fig. 2, the best elements are V for desulfurization and Cu for denitrification. Cu in activity and stability and the conversions of SO2 and NO are 100% and 38.8%, respectively.

**Effect of Impregnation Sequence of Cu and V on Catalyst Activity**

Three kinds of V (1%)-Cu (1%) / ZSM-5 were obtained from different sequence of impregnation. The catalysts were evaluated under the above conditions. The results are shown in Fig. 3.

From Fig. 3, the Cu(1%)-V(1%) / ZSM-5 catalyst with co-impregnated are the best and the conversions of SO2 and NO are 100% and 49%(> 38.8%), respectively, which is better than that of the two one-component catalysts.

**Effect of Reaction Temperature on Catalyst Performance**

For the Cu (1%)-V (1%) / ZSM-5 catalyst, four temperatures of 350 °C, 400 °C, 450 °C and 500 °C were chosen for the experiment under the same above other conditions. The results are shown in Fig. 4.
Since the conversions of SO₂ are all 100% at the four temperatures, the conversions of NO increase with temperature decreasing and the highest one of NO is at 350°C. There is a strong physical adsorption when it C and the reaction rate becomes slow below 300°, therefore the optimum catalyst reaction temperature is at 350°C.

**Effect of Impregnation Times and Co Modification on Catalytic Activity**

The catalysts were prepared by co-impregnation of Cu-V after Co impregnation. The procedure was repeated and three kinds of catalysts (I, II and III) were obtained one time, two times and three times, respectively. Under the same above conditions, the catalysts were evaluated in Fig. 5.

Since all three catalysts can remove all SO₂, the NO conversion is only discussed. From Fig. 5 the NO conversions of II and III are basically the same that is about 61%, which is 4% higher than that of I (about 57%). Therefore, the Co (1%)-Cu (1%)-V(1%) /ZSM-5 catalyst impregnated two times was the optimal preparation methods.
Summary

1. The impregnation is the best preparing method for the Cu (1%)-V(1%)/ZSM-5 catalyst.
2. Cu is the best element for denitration and V is the best element for desulfurization.
3. The Co-impregnation of Cu and V on ZSM-5 is better than that of two others.
4. The pre-impregnation modification of Co and twice impregnation of the procedure can improve NO conversion by 7-10%.
5. The optimum reaction temperature is 350℃, the maximum conversions of SO₂ and NO are 100% and 61%, respectively.

References