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Influence of calcining conditions on DeNO*x* efficiency of V_2O_5/TiO_2 catalysts

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Abstract : In this research, the DeNO*x* efficiency of V_2O_5/TiO_2 catalysts was measured in a self-designed lab-scale experimental system. The V_2O_5/TiO_2 catalysts were prepared under different calcining conditions, including calcining temperature and calcining time. Moreover, the Brunauer-Emmett-Teller method, the X-ray diffraction technology, and the scanning electron microscope technology were applied to analyze the microstructure properties of catalysts. The experimental results show that the efficiency of catalysts all increased as the reaction temperature rose from 200 °C to 400 °C, but it decreased when the temperature exceeded 400 °C. The catalyst calcined under 500 °C performed greater DeNO*x* efficiency than others. The influence of calcining time on the DeNO*x* efficiency was less than that of calcining temperature.

Keywords : V_2O_5/TiO_2; Calcining temperature; Calcining time; DeNO*x* efficiency; Microstructure property.

INTRODUCTION

The pollution resulting from the burning of fossil fuels seriously hurts the global environment, especially the recent decades[1]. The NO*x* (NO and NO_2) emissions generated during the combustion processes in industries and transportation engines (car, train, aircraft, *etc.*) not only do harm to human's health, but lead to urban smog, acid precipitation and other environmental problems[2,3]. Therefore, selective catalytic reduction (SCR) is worldwidely adopted to control the NO*x* emissions, and the catalysts used in the SCR process draw more and more attention of experts and researchers all over the world[4-6].

In coal boilers and automobile engines, V/Ti catalysts are the most widely used catalysts. Generally speaking, V_2O_5 is loaded on TiO_2 and different amounts of WO_3 or MoO_3 are often added to improve the efficiency of catalysts[7-10]. Moreover, different carriers such as Al_2O_3, SiO_2, ZrO_2 and so on have also been tested to explore new types of catalysts[11-13]. Feng Gao *et al.* studied the reaction kinetics of Cu-SSZ-13 catalysts with various Cu loadings[14]. The adhesion and surface characteristics of monolithic Cr-V/TiO_2/cordierite catalysts were investigated for low-temperature NH_3-SCR reactions by Hai-feng Huang *et al.*[15].

Although many studies have been conducted on V/Ti catalysts in recent years, little work has been published on the effect of calcining conditions on the DeNO*x* efficiency of V/Ti catalysts. In the research described here, the influence the calcining temperature and the calcining time on the DeNO*x* efficiency of V/Ti catalysts was explored by experiments, and the characterization methods of Brunauer-Emmett-Teller (BET) method, the X-ray diffraction (XRD) technology, and the scanning electron microscope (SEM) technology were applied to research the microscopic properties and analyze the causes for the different performance.

EXPERIMENTAL

Experimental setup

The experimental installation is as shown in Figure 1 and it is made up of a gas feeding system, a gas reaction system and a gas analysis system. Pure gases from gas cylinders are dosed with mass flow controllers and are fed into the reactor. In the experiments, the total gas flow rate was kept 1 L/min (STP, the same below), which contains 4% O_2, 500 ppm NH_3 and 500 ppm NO with the balance N_2. The gas reaction system is composed of a one-dimensional quartz tube furnace and a temperature controller. The exhausted gas after DeNO*x* reaction flew into a gas analyzer through a PTFE pipe, which was heated to 105 °C. The flue gas analyzer (GASMET FTIR Dx4000) measures the concentration of gases (NO, NO_2, N_2O, *etc.*) to be as low as 0.2 ppm, with the measurement accuracy of ±2%.

Catalyst preparation

The preparation procedure of granular V_2O_5/TiO_2 catalyst is as shown in Figure 2. Appropriate amount of NH_4VO_3 and COOH-COOH was accurately weighed and mixed with proper deionized water, which was then heated in 40 °C water bath until the color of the solution turned from yellow to dark blue.

Appropriate amount of dry TiO_2 powder was gradually impregnated with NH_4VO_3/COOH-COOH water solution (TiO_2:solution=1 g:1.1 ml) and stirred constantly, and then the catalyst after impregnation was oscillated in a ultrasonic oscillator for 30 minutes. Let stand for 24 hours at 25 °C, the catalyst was then dried for 12 hours at 110 °C in a drying oven and calcined in a muffle furnace at specific temperature (x °C) for specific time (y hours). Finally, the prepared catalyst was ground to 40-65 mesh particles and weighed 1.0 g every time for the efficiency test.

The V_2O_5 content of the catalysts prepared in this research was stable 1%. Catalysts prepared under different calcining conditions were marked as V1/Ti-x-y, where x and y respectively represented the calcining temperature (°C) and the calcining time (h).

RESULTS AND DISCUSSION

Influence of calcining temperature and calcining time on the DeNO*x* efficiency

Figure 3 shows the DeNO*x* efficiency changing trend of catalysts calcined at different temperature (300 °C, 400 °C, 500 °C, 600 °C, and 700 °C) with the reac-

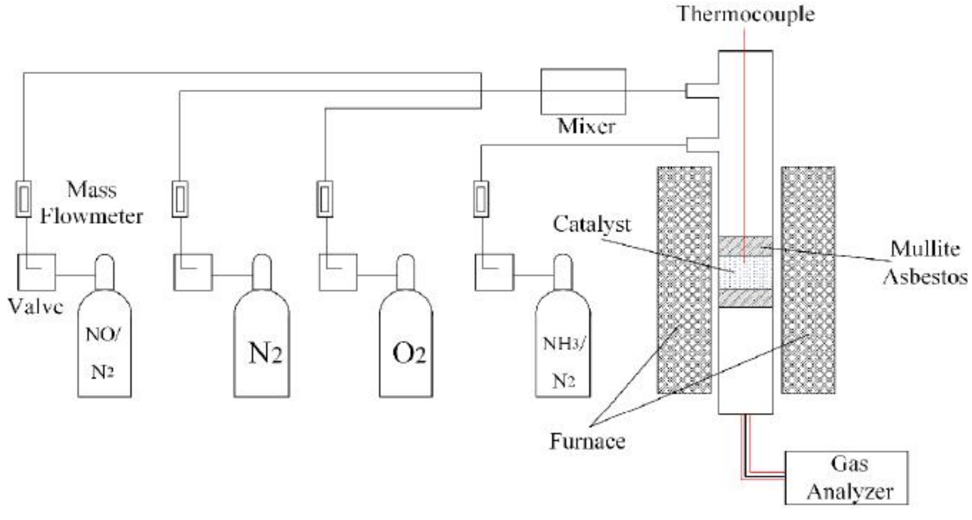


Figure 1 : Experimental setup

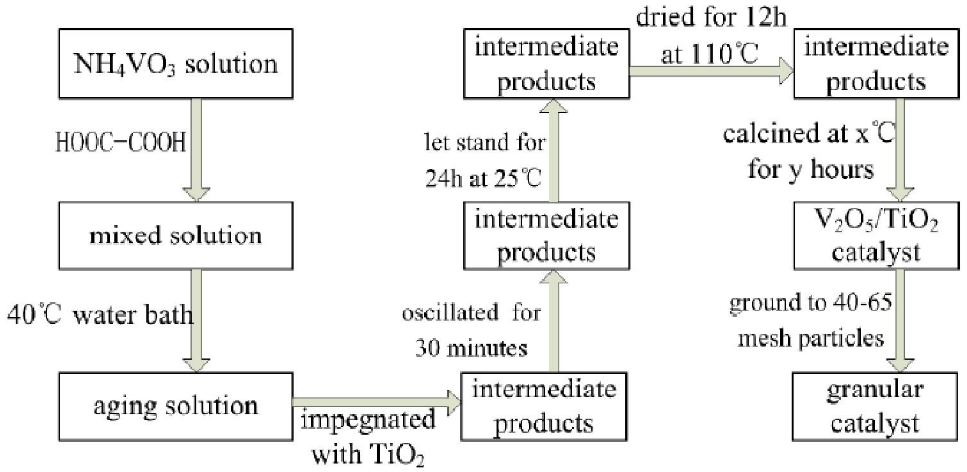


Figure 2 : Preparation process of granular V_2O_5/TiO_2 catalysts

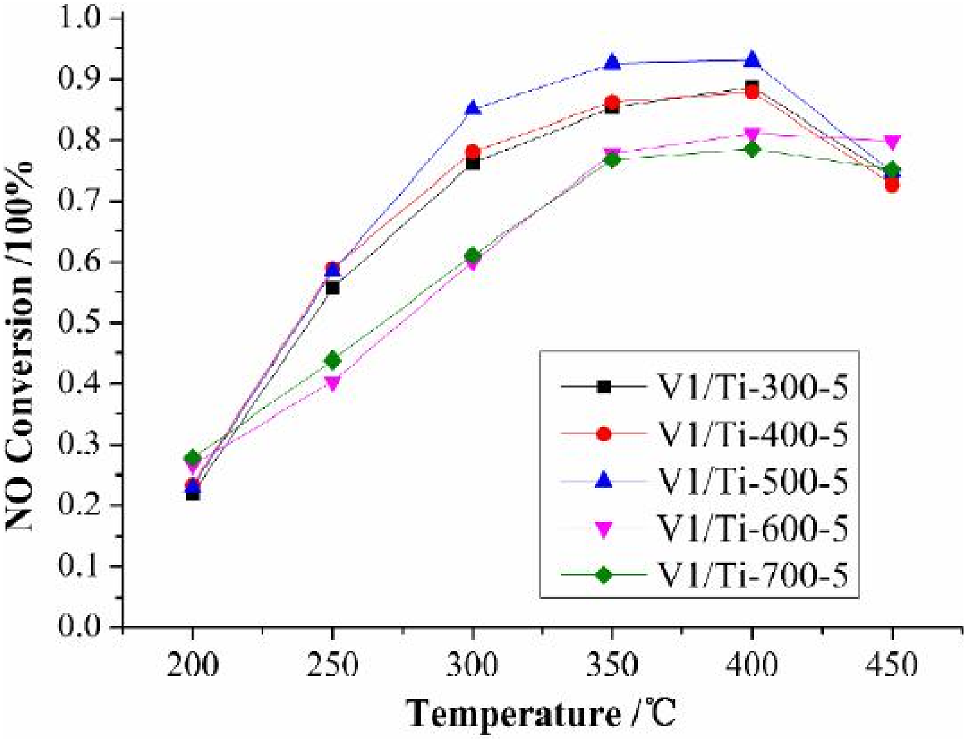


Figure 3 : DeNO*x* efficiency of catalysts calcined at different temperature

tion temperature varying from 200 °C to 450 °C. As shown in Figure 3, the DeNO*x* efficiency of catalysts prepared at different calcining temperature showed the same variation tendency, and they all firstly increased as the reaction temperature rose but fell off when the reaction temperature was above 400 °C. At 200 °C, all the catalysts performed similar DeNO*x* efficiency. However, as the reaction temperature increased, the catalyst V1/Ti-500-5 performed the highest efficiency. When the reaction temperature was higher than 400 °C, the efficiency of V1/Ti-600-5 and V1/Ti-700-5 declined slightly, while the efficiency of V1/Ti-300-5 and V1/Ti-400-5 decreased more obviously.

Figure 4 shows the influence of calcining time (3 hours, 5 hours, and 7 hours) on the DeNO*x* efficiency of catalysts calcined at 500 °C. From it we could see, the changing trend of the efficiency did not differ too much from Figure 3, and there still existed an optimum temperature window for the DeNO*x* reaction. Of all the catalysts, the efficiency of V1/Ti-500-3 and V1/Ti-500-7 was basically the same, and it was similar to the efficiency of V1/Ti-500-5 when the reaction tempera-

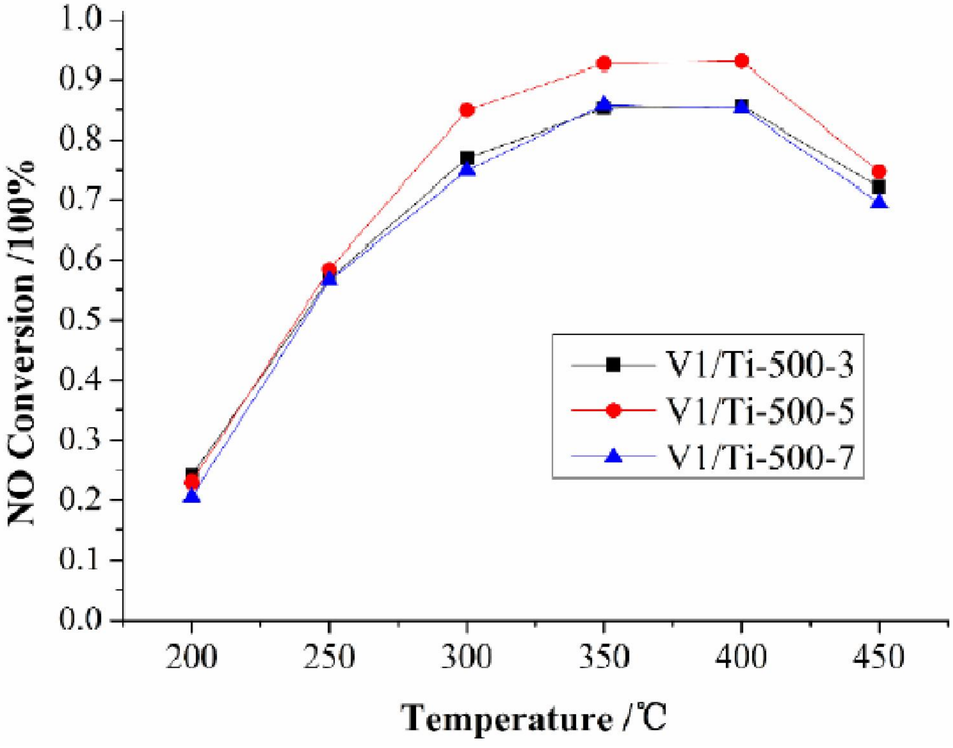


Figure 4 : DeNO*x* efficiency of catalysts calcined at different time

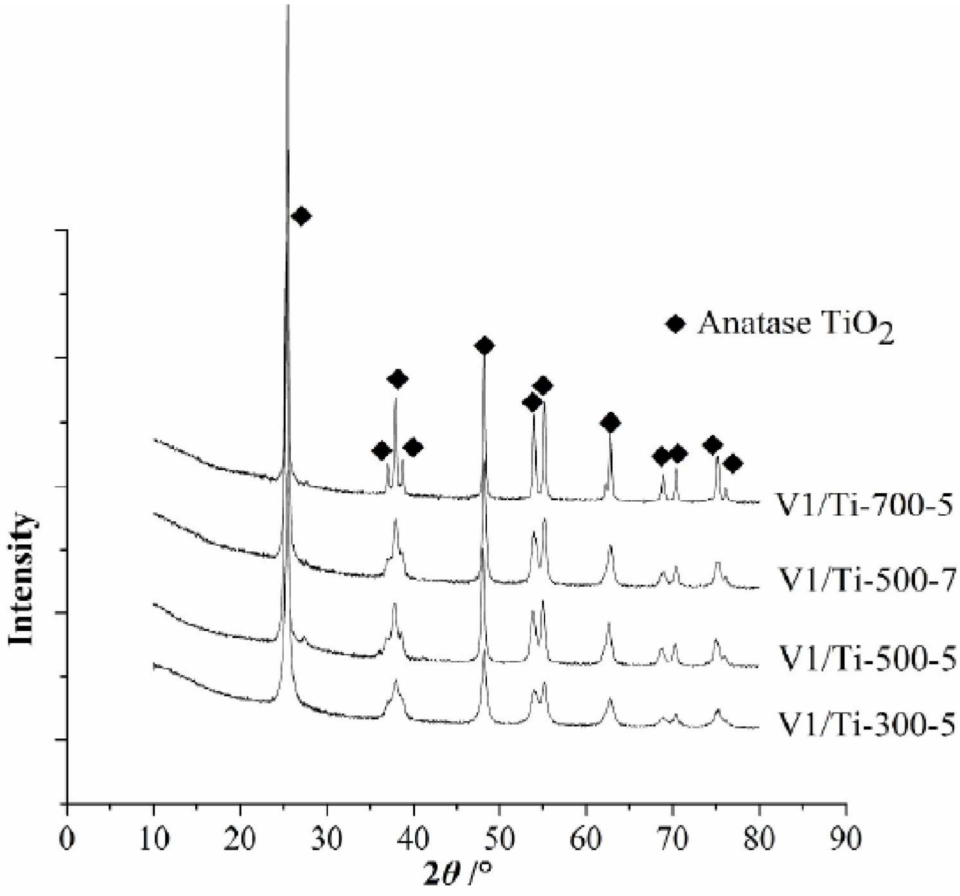


Figure 5 : XRD map of catalysts calcined at different conditions

ture was below 250 °C. However, when the reaction temperature rose above 250 °C, both V1/Ti-500-3 and V1/Ti-500-7 performed a little poorly than V1/Ti-500-5. But obviously, the influence of calcining time on the DeNO*x* efficiency was weaker than that of calcining temperature.

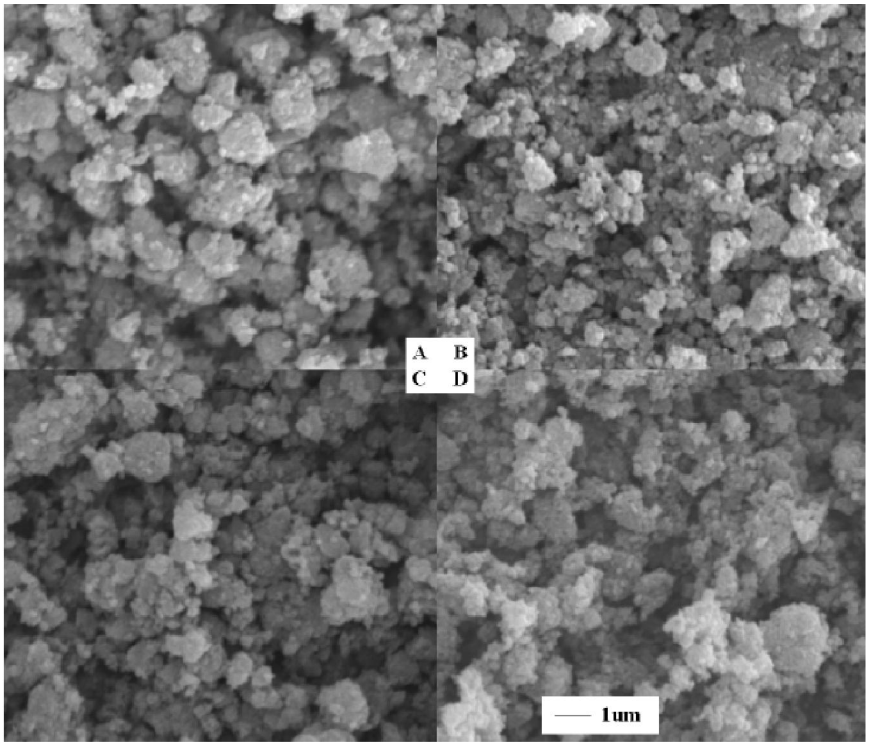
Microscopic properties of catalysts

The XRD map of catalysts is shown in Figure 5, from which we could see that for different types of catalysts, there were only diffraction peaks of TiO_2 found in the map but not V_2O_5. Therefore, these data imply that the V_2O_5 loading on TiO_2 existed in the state of equiaxed aggregate, which was beneficial to the DeNO*x* efficiency of catalysts. From Figure 5 we could also conclude that as the calcining temperature increased, the intensity of the diffraction peaks of TiO_2 rose significantly. Moreover, there were more diffraction peaks in the XRD map of V1/Ti-700-5, and the crystal form of TiO_2 became much sharper and more obviously. These findings confirm that as the calcining temperature increased from 300 °C to 700 °C, the crystalline grain of TiO_2 gradually grew up and it became much easier to be sintered. As is well known to us all, if the SCR catalyst is sintered, the DeNO*x* efficiency would decrease greatly and the catalyst would lose its efficiency, so we must avoid it carefully in industries. By comparing the XRD map of V1/Ti-500-5 with the map of V1/Ti-500-7, it could be found that there was little difference between them, which suggests that the crystal form of V1/Ti-500-5 and V1/Ti-500-7 did not differ much at the same calcining temperature of 500 °C. Therefore, we could conclude that the effect of calcining time on the crystal form of catalysts was much weaker than that of calcining temperature, which could explain why the influence of calcining time on the DeNO*x* efficiency was not as obvious as that of calcining temperature.

To explore the variation of the catalyst grain sizes at different calcining temperature quantificationally, the grain sizes of V1/Ti-300-5, V1/Ti-500-5 and V1/Ti-

TABLE 1 : Grain size of catalysts

Catalyst	V1/Ti-300-5	V1/Ti-500-5	V1/Ti-700-5
Grain size (nm)	21.1	23.5	31.9



A: V1/Ti-300-5 B: V1/Ti-500-5 C: V1/Ti-500-7 D: V1/Ti-700-5

Figure 6 : SEM photographs of catalysts calcined at different conditions

700-5 were calculated according to the Scherrer formula[16] and the results are listed in TABLE 1. As the calcining temperature rose, the grain size increased gradually and the grain size of V1/Ti-700-5 was much larger than that of V1/Ti-500-5.

The SEM photographs of catalysts V1/Ti-300-5, V1/Ti-500-5, V1/Ti-700-5 and V1/Ti-500-7 are shown in Figure 6, and the magnification of the SEM is 10000. From Figure 6 it could be seen that the catalyst particles of V1/Ti-300-5 were evenly distributed but the particle size was large. That was mainly because the precursor compound of vanadium in the catalyst was not completely decomposed at the calcining temperature of 300 °C, and there was only part of the total vanadium playing the role of the active center. From Figure 6 we could also see that the particles of V1/Ti-500-5 were tiny and evenly distributed, which showed that vanadium well dispersed in the catalyst and it benefited the process of the DeNO*x* reaction. Resulting from the long calcining time, the catalyst particles of V1/Ti-500-7 became larger, which led to the decrease of the DeNO*x* efficiency. Seen from the XRD map in Figure 5, TiO_2 in V1/Ti-700-5 did not change from anatase type to rutile type, but the diffraction peaks obviously became much sharper. Combined with the SEM photograph, it could be found that the particles on the V1/Ti-700-5 surface already reunited and the specific surface area decreased, which resulted in the reduction of the DeNO*x* efficiency.

CONCLUSION

The DeNO*x* efficiency of catalysts prepared under different calcining conditions was tested and analyzed in this research. The experimental results show that the efficiency of the catalysts prepared under different calcining temperature all increased with the reaction temperature, but it dropped when the reaction temperature exceeded 400 °C. The particles of V1/Ti-500-5 were tiny and evenly distributed, so it performed greater efficiency than others. The influence of calcining time on the DeNO*x* efficiency of V_2O_5/TiO_2 was less than that of calcining temperature, which was mainly because that the effect of calcining time on the crystal form of catalysts was much weaker.

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