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Effect of preparation methods on DeNO*x* efficiency of CeO_2/TiO_2 catalysts

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Abstract : The $DeNO_x$ performance of catalysts is a key part in the selective catalytic reduction process. In this study, CeO_2/TiO_2 catalysts were prepared by the impregnation method and the sol-gel method, and the $DeNO_x$ performance of the catalysts was tested on a self-built experimental system. The efficiency difference due to the two preparation methods was analyzed by X-ray diffraction technology and Brunauer-Emmett-Teller method. The experimental results showed that CeO_2/TiO_2 catalysts prepared by the sol-gel method had a larger surface area and the $DeNO_x$ activity was higher than the catalysts prepared by the impregnation method, when the temperature was below 350 °C. For CeO_2/TiO_2 catalysts prepared by the impregnation method, the crystal form of CeO_2 could be seen, when CeO_2 content was 10%. However, if CeO_2 content was more than 3%, the catalyst had relative high activity suitable for industrial application.

Keywords : CEO_2; TIO_2; DENO*X* EFFICIENCY; SCR

INTRODUCTION

The emission of nitrogen oxides during coal combustion is great harmful to the environment[1-3]. As an important part of nitrogen oxides removal technology, selective catalytic reduction (SCR) has been adopted in many power plants[4-6]. In SCR technology, the performance of the catalysts is the focus for researchers. Vanadium-titanium catalyst has received a lot of attention and been widely used in SCR technology, while the common method is to load V_2O_5 on TiO_2 and add different amounts of WO_3 or MoO_3[7-10]. In addition, other metal oxides, such as Fe, Cu, Cr, and Mn, have been widely studied as active ingredients[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 the research for the effect of different loadings on SCR catalysts has been carried out for years, little work has been done to study the effect of preparation methods on the DeNO*x* efficiency. In this study, CeO_2/TiO_2 catalysts were prepared by the impregnation (IM) method and the sol-gel (SG) method, and different amounts of CeO_2 were loaded in TiO_2 to determine the optimal loading amount of active substance. The microstructure of the catalysts was investigated to explore the reasons for the differences of DeNO*x* performance by X-ray diffraction (XRD) technology and Brunauer-Emmett-Teller (BET) method.

EXPERIMENTAL SECTION

Experimental system

The experimental system is as shown in Figure 1. In the experiments, the mixed gas of NO, O_2 and N_2 was simulated flue gas, NH_3 was used as a reducing agent, wherein the NO content was 500 ppm, the same as NH_3. O_2 content was about 4%, and N_2 was used

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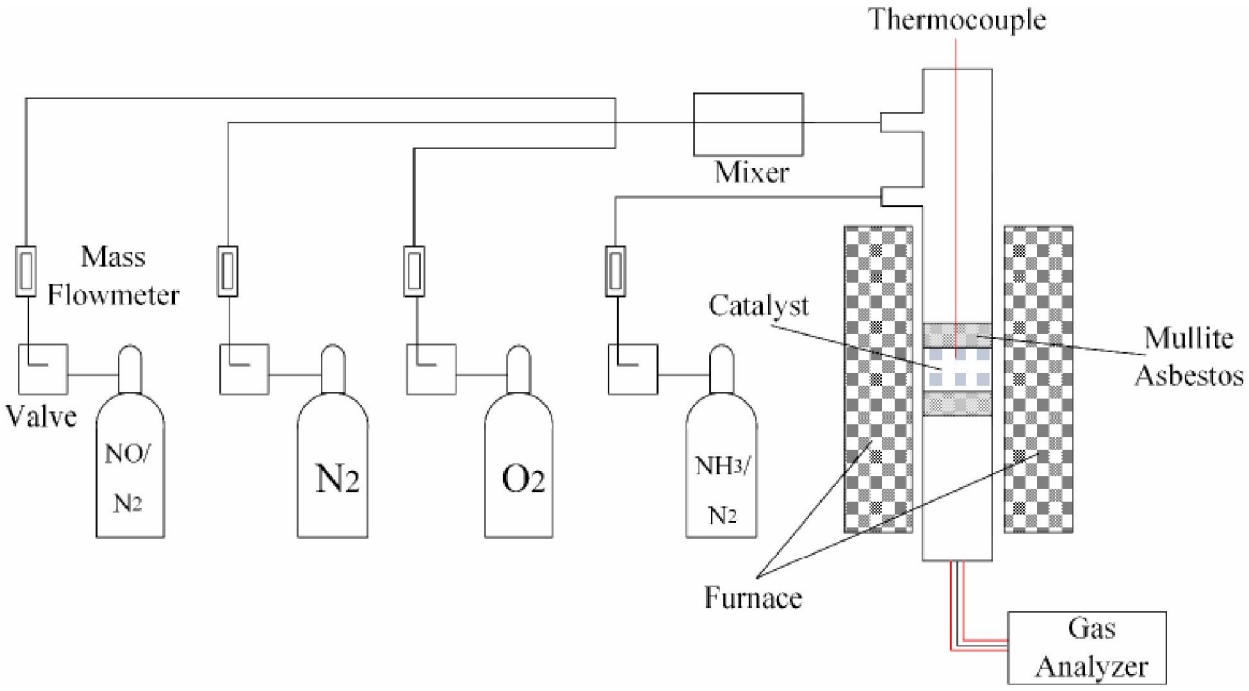

Figure 1 : Experimental system

as the balance gas. There were three parts in the experimental system: the gas supply system, the reaction system and the measurement system.

The gas supply system provided simulated flue gas and reducing agent, and the gas flow was controlled by mass flow meter. The reaction system contained the reactor and temperature controller. As one-dimensional tube furnace, the reactor was made from quartz glass, filled with cotton insulation. The catalysts loaded in the reactor and were fixed by mullite asbestos in the position, in which a thermocouple was set to monitor temperature. The measurement system was mainly composed of flue gas analyzer (GASMET FTIR Dx4000), which was applied to record the concentration of NO and NH_3.

Catalyst preparation

The methods of catalyst preparation in the laboratory are mainly sol-gel method, precipitation method, ion exchange method and impregnation method. By Isometric impregnation method solution can just immerse all carrier particles to avoid the recovery steps of filtering and impregnating solution. In this work, CeO_2/TiO_2 catalysts was prepared by IM method. Preparation process of granular CeO_2/TiO_2 catalysts is shown in Figure 2.

Step-by-step SG preparation method is as follows:

(1) Take appropriate amount of butyl titanate and anhydrous ethanol (volume ratio is 4:1), then mix and stir fully to give a uniform and transparent light yellow solution, which is denoted by solution A.

(2) Take a suitable amount of deionized water, ethanol, nitric acid (volume ratio is 1:1:0.2) and weigh a certain amount of cerium nitrate. Then mix the above solution, dissolve cerium nitrate and stir sufficiently to give a solution, which is denoted by solution B. And then different amounts of cerium nitrate can produce different CeO_2/TiO_2 catalysts supporting different amount of CeO_2.

(3) Place solution B in a water bath of magnetic stirrer and control a certain water bath temperature and stirring speed, at the same time drip the solution A through the burette slowly into the solution B to form a mixed solution that can hydrolyze. After dripping the solution A, stirring is continued for a period of time to give a pale yellow transparent sol and finally become wet gel.

(4) Put wet gel in drying oven under 110 °C for 24 h, calcine in the muffle furnace for 5 h under 500 °C and fresh CeO_2/TiO_2 catalyst is prepared. Finally, the catalyst is milled to 40 to 60 mesh to test its DeNO*x* efficiency.

The catalysts was named Ce*x*/Ti(IM) or Ce*x*/Ti(SG) in this study, and *x* means the mass percentage of CeO_2 in the catalyst.

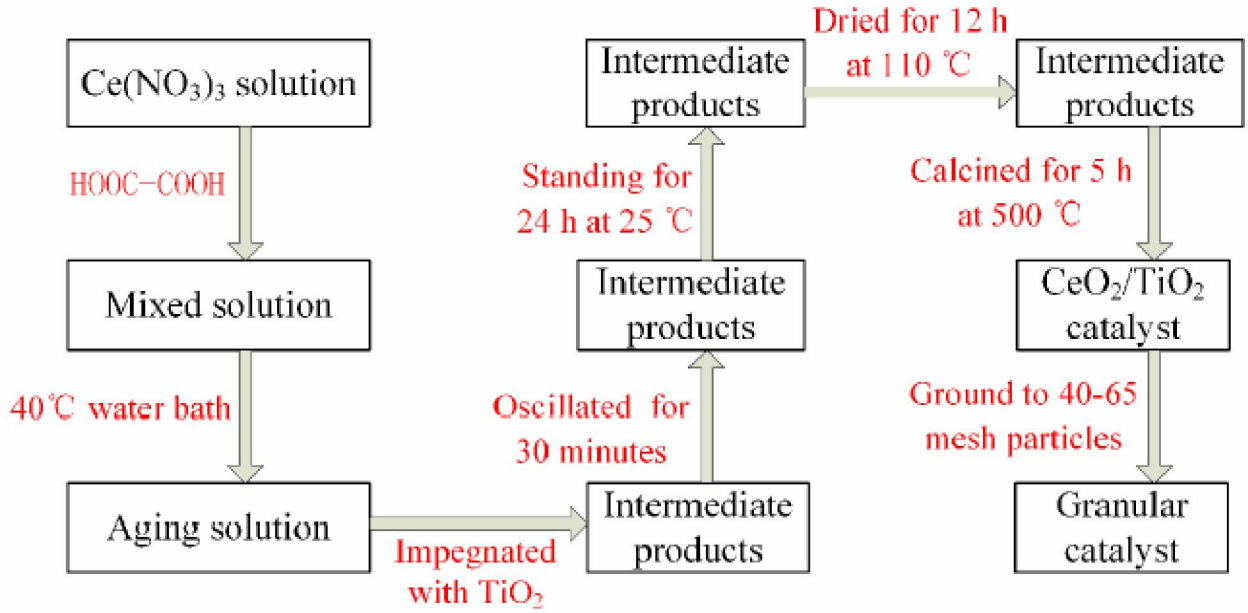

Figure 2 : Preparation process of granular CeO_2/TiO_2 catalysts by IM method

RESULTS AND DISCUSSION

DeNO*x* of CeO_2/TiO_2 catalysts

Figure 3 shows that DeNO*x* efficiency of CeO_2/TiO_2 catalysts prepared by IM method versus temperature. As can be seen from the Figure 3, when CeO_2 content was between 0.5% and 2%, the DeNO*x* efficiency of CeO_2/TiO_2 catalysts was relatively low. When CeO_2 content was 5% and 10%, CeO_2/TiO_2 catalyst DeNO*x* efficiency was significantly high, and under 250 °C the DeNO*x* efficiency reached more than 93.4%. When CeO_2 content was 0.5%, in the temperature range of 200-300 °C the DeNO*x* efficiency was very low (between 9.7%-14.9%); under 350 °C and 400 °C the DeNO*x* efficiency was significantly increased to 48.1% and 98.9%. When CeO_2 content was 1%, the DeNO*x* efficiency had the same rules with Ce0.5/Ti (IM), the DeNO*x* efficiency increased slightly. Thus, the CeO_2/TiO_2 catalysts DeNO*x* efficiency had a great relationship with CeO_2 content.

Figure 4 shows that DeNO*x* efficiency of CeO_2/TiO_2 catalysts prepared by SG method versus temperature. As can be seen from Figure 4, compared with Ce0.5/Ti-4 (IM), the DeNO*x* efficiency of CeO_2/TiO_2 catalysts was generally low when CeO_2 content is 0.5% below 400 °C. But when the temperature is higher than 400 °C, the efficiency greatly improved, and the

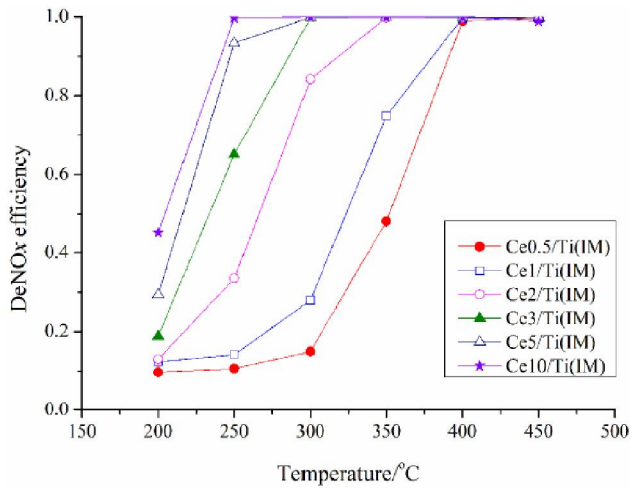

Figure 3 : DeNO*x* efficiency of CeO_2/TiO_2 catalyst prepared by IM method

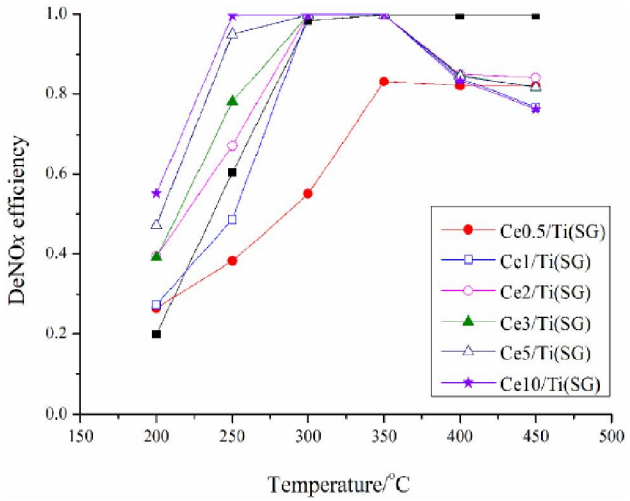

Figure 4 : DeNO*x* efficiency of CeO_2/TiO_2 catalyst prepared by SG method

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efficiency is 82.1%. When CeO_2 content continued to increase, the catalyst activity under low temperature continued to grow, but the catalyst DeNO*x* efficiency from different CeO_2 content decreased in the temperature range of 350-450 °C and both efficiency remained above 76.2%.

Microscopic properties of catalysts

The catalysts with different cerium contents were prepared in the experiments, by IM method and SG method. The specific surface area, pore volume, and pore diameter were listed in detail in TABLE 1. We can find that by SG method Ce3/Ti(SG) has a higher specific surface area of 97.211m^2/g, while Ce3/Ti(IM) has specific surface area of 74.520 m^2/g.

TABLE 1 : Microscopic properties of catalysts

catalyst	Specific surface area (m^2/g)	Pore volume (ml/g)	Pore diameter (nm)
Ce3/Ti(IM)	74.520	0.017	18.194
Ce3/Ti(SG)	97.211	0.027	19.237

Figure 5 shows that three kinds of XRD patterns of CeO_2/TiO_2(IM) catalysts, of which CeO_2 accounted for 0.5%, 3% and 10%. As can be seen from the figure, if the CeO_2 content increased from 0.5% to 3%, the diffraction peak position on the XRD patterns did not change significantly. However, the intensity of the characteristic peak became slightly smaller, indicating in CeO_2/TiO_2(IM) CeO_2 and TiO_2 were better together and TiO_2 grains of catalysts were smaller. All the catalysts only appeared anatase TiO_2 characteristic peaks, and no CeO_2 crystal phase, indicating that when

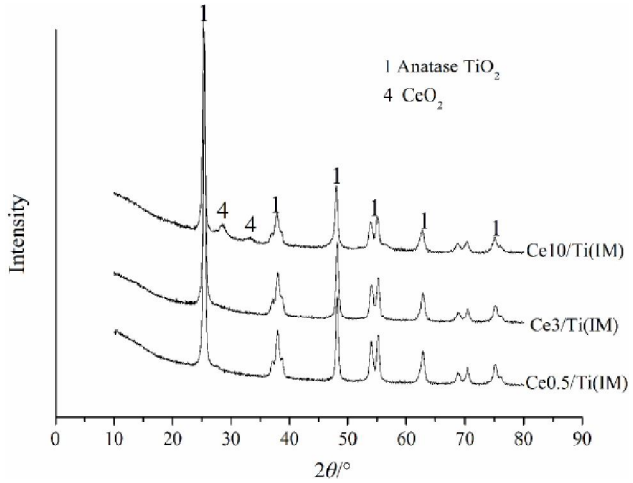

Figure 5 : XRD pattern of CeO_2/TiO_2 catalysts prepared by IM method

CeO_2 content was less than 3%, cerium was well dispersed on the surface. There was CeO_2 characteristic diffraction peaks (2θ=28.555°, 33.082°) in Ce10/Ti-4 (IM), indicating CeO_2 grains appeared in the catalyst and CeO_2 loading exceeded the saturation value of CeO_2 in the TiO_2 surface. CeO_2 grain is not active for SCR reaction, so it should be avoided in the preparation process.

Figure 6 shows that three kinds of XRD patterns of CeO_2/TiO_2(SG), of which CeO_2 accounted for 0.5%, 3% and 10%. As can be seen from the figure, when CeO_2 content was 0.5%, we can observe obvious anatase TiO_2 characteristic peaks, rutile TiO_2 diffraction peaks (2θ=27.508°, 36.159°) and brookite TiO_2 characteristic peaks, indicating that when catalyst was prepared by SG method, the TiO_2 appeared more changing. When CeO_2 content was 3%, the peak shape of anatase TiO_2 became incomplete, broad and diffuse. When CeO_2 content increased to 10%, the peak shape was more broad and low, indicating that the electronic interaction between CeO_2 and TiO_2 strengthened, and CeO_2 was dissolved in TiO_2 with highly dispersed or amorphous state. Meanwhile, rutile TiO_2 peaks disappeared, but brookite TiO_2 still existed with lower intensity. All these indicated the increase of CeO_2 content suppressed the transformation from anatase TiO_2 to rutile TiO_2.

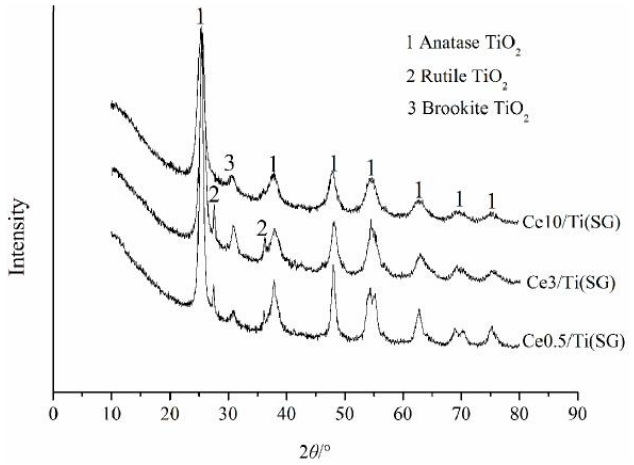

Figure 6 : XRD pattern of CeO_2/TiO_2 catalysts prepared by SG method

CONCLUSIONS

The specific surface area is an key factor that affected the DeNO*x* efficiency. The catalysts based on

CeO_2/TiO_2 made by SG method have greater specific surface area. XRD shows that the rutile and broolnte type of TiO_2 appeared in the catalysts prepared by SG method and the crystal form of CeO_2 did not show up. The crystal form of CeO_2 appeared as the concentration of CeO_2 was 10% in the catalysts prepared by IM method. It demonstrated that CeO_2 was not well dispersed on the surface of the carrier.

The CeO_2/TiO_2 catalysts prepared by IM method have relatively high DeNO*x* efficiency when the concentration of CeO_2 was 3% and that activity will not decline within a temperature range of 350-400 °C. The DeNO*x* efficiency of CeO_2/TiO_2 catalysts prepared by SG method turned out a litthle higher than that prepared by IM method when the temperature was below 350 °C.

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