Effect of Component on Performance of Titania-Supported Selective Catalytic Reduction Denitrification Catalyst

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Selective catalytic reduction of nitrogen oxides remains as a widely used technology scheme for reducing NO_x in the flue gas from stationary sources. Investigation of the influence of composition on the performance of selective catalytic reduction flue gas denitrification (DeNO_x) catalyst has great significance as catalyst technology is the core of the selective catalytic reduction process. In this research, the DeNO_x activity and selectivity of different titania-supported catalysts were tested in a small-scale experimental system. Titanium dioxide, tungsten oxide and molybdenum oxide all had denitrification effect, but the activity of these species was low and activation temperature was high. The deposition of sulfate radical led to an increase in the NH_3 adsorption but only slightly in catalytic activity. Higher vanadium loading increased the DeNO_x activity of titania-supported vanadia catalyst and lowered the activation temperature. However, more N_2O was observed with the increasing of vanadium which showed that the selectivity decreased. Catalysts supported on different species of titanium dioxide had certain differences in DeNO_x performance. $\text{FeSO}_4/\text{TiO}_2$ was a good alternative denitration catalyst with a high DeNO_x efficiency and in the temperature range of 330-420 °C, the NO conversion rate reached 93.56-99.25 % under the topical testing condition with a FeSO_4 loading of 16 (wt.) %.

Keywords: Selective catalytic reduction, DeNO_x , N_2O , Catalyst component.

INTRODUCTION

NO_x emission has been a seriously environmental problem in recent years. In combustion of fossil energy in boilers, more than 95 % of NO_x is NO and the other 5 % is NO_2 . To reduce the pollution from NO_x , NH_3 -based selective catalytic reduction technology has been widely used in power plants¹. In selective catalytic reduction process, the performance of denitrification (DeNO_x) catalysts, such as activity and selectivity, is the most concerned part. Moreover, there is more or less N_2O generated in the selective catalytic reduction process, which leads to significantly serious greenhouse effect.

The typical chemical reaction of selective catalytic reduction is reaction (1):

The result of isotope label method also shows that in reaction (1), one of the two N atoms comes from NH_3 and the other comes from NO.

If there is NO_2 existing in the reaction and the ratio of NO_2 and NO is less than 1:1, the chemical reaction takes place as follows^{2,3}:

At the same temperature, the rate of reaction (2) is much higher than that of reaction (1)⁴. Additionally, if the ratio of

NO_2 and NO is more than 1:1, redundant NO_2 reacts with NH_3 as reaction (3):

In the absence of oxygen, the chemical reaction of NH_3 and NO takes place as follows:

In the selective catalytic reduction process, side reaction (5) also takes place to generate N_2O :

At high temperatures, NH_3 could be oxidized as reaction (6), (7), (8):

As is well known, catalysts composed of different components have different DeNO_x activity and selectivity. Shi *et al.*⁵ comparatively explored the catalyst performance of fresh and hydrothermally aged Fe-ZSM-5 in standard and fast selective catalytic reduction reactions. Gao *et al.*⁶ studied the reaction kinetics of Cu-SSZ-13 catalysts with various Cu loadings. The adhesion and surface characteristics of monolithic Cr-V/TiO₂/

cordierite catalysts were investigated for low-temperature NH_3 -selective catalytic reduction reactions by Huang *et al.*⁷.

Although much work has been done on the influence of catalyst states on DeNO_x performance, but little attention has been paid to the impact of each component and the synergistic effect between them. In the experiments reported here, we explored the effect of different titania-supported catalytic components and the interaction effect between various components.

EXPERIMENTAL

Fig. 1 illustrates the experimental setup used in this study. Primary composition of the flue gas was supplied by cylinders containing NO/N_2 , NH_3/N_2 , O_2 and N_2 . The relative parameters of the cylinder gas are given in Table-1. The gas flow rate is controlled by mass flowmeter and mass flowmeter was corrected by soap film flowmeter. The exhausted gas after DeNO_x reaction flew into a gas analyzer through a PTFE pipe, which was heated to 105-120 °C. The flue gas analyzer (GASMET FTIR D_x4000) measures the concentrations of gases (NO , NO_2 , N_2O , *etc.*) to be as low as 0.2-2 ppm and the measurement accuracy is $\pm 2\%$.

Fig. 1. Experimental setup

TABLE-1
GAS USED IN THE EXPERIMENTS

Gas	Purity (%)	Gas	Molar ratio (%)
N_2	99.999	NO/N_2	5
O_2	99.990	NH_3/N_2	5

The flow rate of the total gas was kept 1L/min (STP, the same below), which contains 4 % O_2 , 24 mmol/L NH_3 and 24 mmol/L NO with the balance N_2 .

Catalyst preparation: The catalysts tested in the experiments were sieved to 40-65 mesh particles after steeped in the same column of water, dried, calcined and ground. Usually, the mass of catalyst used in each experiment was 1 g.

There were four kinds of titanium dioxide in the first tested group, namely 6001, 6002, 6003 and 6009 and corresponding parameters are given in Table-2.

TABLE 2
CORRESPONDING PARAMETERS OF
THE FOUR KINDS OF TITANIUM DIOXIDE

	6001	6002	6003	6009
TiO_2 content (wt. %)	90.5	85.5	88.5	95.8
WO_3 content (wt. %)	5.0	5.0	—	—
Fe_2O_3 content (ppm)	79	79	—	80
Na_2O content (ppm)	74	82	—	74
K_2O content (ppm)	29	36	—	21
SO_4^{2-} content (wt. %)	2.4	2.7	6.18	2.5
BaSO_4 content (wt. %)	—	—	6.8	—
SiO_2 content (wt. %)	—	4.9	—	—
Water content (wt. %)	1.6	1.6	—	1.3
Weight loss after ignition (wt. %)	1.5 ^a	1.4 ^a	—	4.3 ^b
Specific surface area (m^2/g)	90	102	88	93
Grain size (nm)	16.4	13	15.8	16.1

^aConditions: Dried for 2 h at 105 °C and ignition for 1 h at 600 °C

^bConditions: Ignition for 1 h at 900 °C

The second group of experimental materials were catalysts loading different content of V_2O_5 and 6009 and the mass ratios of V_2O_5 and TiO_2 were 0.2, 0.5, 1, 3, 5 and 10 %. The third group were catalysts loading 6009 and different content of WO_3 or MoO_3 . The mass ratios of WO_3 and TiO_2 were 0.5, 2, 5 and 10 %, while the mass ratios of MoO_3 and TiO_2 were also 0.5, 2, 5 and 10 %. The fourth group were different titania, 6001, 6002, 6003 and 6009, with the same V_2O_5 and the mass ratio of V_2O_5 and TiO_2 was always 1 %. The fifth group were 6009 catalysts with FeSO_4 as active ingredient, while the sixth group were 6009 with SO_4^{2-} as active ingredient.

Catalytic activity measurement: In this paper, catalytic activity and selectivity in the DeNO_x process were measured by comparing the different content of NO and N_2O before and after the process.

NO reduction efficiency X is defined as:

$$X = (\text{C}_{\text{NO}}^{\text{in}} - \text{C}_{\text{NO}}^{\text{out}}) / \text{C}_{\text{NO}}^{\text{in}} \times 100\% \quad (8)$$

where $\text{C}_{\text{NO}}^{\text{in}}$ and $\text{C}_{\text{NO}}^{\text{out}}$ refer to the NO concentrations at the entrance and exit of the experimental setup in a experiment condition.

The catalytic selectivity of selective catalytic reduction was measured by the generation of N_2O in this research.

RESULTS AND DISCUSSION

The main component of titania is TiO_2 . As a kind of metal oxide, TiO_2 itself has catalytic action in selective catalytic reduction reaction⁸⁻¹². From Fig. 2, it could be seen that the DeNO_x activity of 6001 and 6002 was extremely similar at different temperatures and it was better than that of 6003 and 6009. As the temperature increased from 320 to 420 °C, the activity of all the four catalysts increased greatly. Compared with 6001, 6002 contains 4.9 (wt.) % SiO_2 , but the activity remained almost the same, which suggests that SiO_2 is inert component in the selective catalytic reduction process. There is 5 (wt.) % WO_3 in 6001 and 6002, while there is not WO_3 in 6003 and 6009, so the difference of the reduction activity is mainly due to WO_3 . It is clear from Fig. 2 that the reduction activity of 6003 was a little different from that of 6009. There is more SO_4^{2-} and BaSO_4 but less Fe_2O_3 , Na_2O and K_2O in 6003 than in 6009 and the result here shows that BaSO_4 has a low reduction activity in this experimental condition.

Fig. 2. DeNO_x activity of titania

As shown in Fig. 3, the N₂O production of 6001 raised the most at about 370 °C, while the N₂O production of 6003 and 6009 raised the most at about 430 °C. Below 400 °C, 6001 generated more N₂O than 6003 and 6009, but it generated less above 400 °C. That's mainly because that there is 5 (wt.) % WO₃ in 6001, while there is not WO₃ in 6003 and 6009, which indicates that although WO₃ has a good reduction activity, its selectivity is poor. It can also be seen from Fig. 3 that N₂O generation of the three types of titanium dioxide decreased at high temperatures (above 420 °C). The possible reason is that as temperature rises in the reaction, the path of N₂O generation is restrained, or there are other competitive reaction paths to restrict N₂O generation.

Fig. 3. DeNO_x selectivity of titania

The absorption isotherms of the four kinds of titania is shown in Fig. 4, from which we could conclude that there was little difference between them and 6003 could absorb more at high pressure. Moreover, when they were close to saturated absorption isotherms, there was not any absorption limitation. The pore volume of the four types of titania were tested and the differential distribution curves of logarithmic pore volume are shown in Fig. 5. Compared with 6009, there is 5 (wt.) % WO₃ in 6001 and there is 5 (wt.) % WO₃ and 4.9 (wt.) % SiO₂ in 6002, but there is not much difference in the pore size distribution of them. That shows in the range of 1-100 nm, loading WO₃ or SiO₂ has little influence on the pore structure.

Fig. 4. Adsorption isotherms of titania

Fig. 5. Differential distribution curves of logarithmic pore volume of titania

Fig. 5 showed that the pore volume of 6003 is quite different from the others since there is 6.8 (wt.) % BaSO₄ in it. However, the DeNO_x activity of 6003 and 6009 was similar in our experiments, which shows that the pore structure in this range did not have much effect on the DeNO_x activity.

Effect of different V₂O₅ content: Oxides of V, Cu, Fe, Co, Ni, La, Mn, W, Nb, Cr, etc perform a certain catalytic activity at different temperature ranges in the selective catalytic reduction process^{13,14}. Among them, V₂O₅ shows the best activity and selectivity¹⁵. As shown in Fig. 6, the NO conversion rate of titania loading V₂O₅ increased much than titania alone. Moreover, at low temperatures (< 350 °C), the NO conversion rate increased as the V₂O₅ content increased. When the temperature rose above 360 °C, catalyst of 1 % V₂O₅/TiO₂ performed the greatest activity, while the activity of catalysts loading higher V₂O₅ fell down quickly.

However, the N₂O production of titania loading V₂O₅ also increased much at high temperatures and more V₂O₅ promoted more N₂O production. From Figs. 6 and 7, it could be concluded that V₂O₅ had a perfect reduction activity and selectivity at low reaction temperatures, but as the temperature rose the selectivity became worse and worse. The result of isotope labeling shows that the two N atoms of some N₂O

Fig. 6. DeNOx activity of titania loading V_2O_5 Fig. 7. DeNOx selectivity of titania loading V_2O_5

molecules come from the reaction of NH_3 and NO (reaction (5)). The oxidation of NH_3 also generates N_2O [reaction (7)], but it was quite weak in this condition because of other competitive reactions. Another N_2O production source was the NO conversion from the inlet gas and it was 0.2455 mmol/m^3 in this experimental condition. At the same temperature, more V_2O_5 led to more N_2O , indicating that the greater polymerization degree of V_2O_5 on TiO_2 made for the more N_2O generation in selective catalytic reduction process.

Effect of WO_3 and MoO_3 : As shown in Fig. 8, catalysts loading WO_3 could reduce NO efficiently, but the activation temperature was raised highly ($> 360^\circ\text{C}$). The NO conversion rate reached the highest at about 400°C , which was similar to titania but higher than V_2O_5/TiO_2 . It was found by Kobayashi and Motonobu that increasing the content of WO_3 could improve the reduction activity of WO_3/TiO_2 catalysts, which is consistent with the results here¹⁶. If the content of WO_3 is lower than 40 %, there is not WO_3 crystal existing in catalysts tested by X-Ray Diffraction, so WO_3 used in our experiments was in the single decentralized state on catalysts surface.

It could be seen from Fig. 9 that different contents of MoO_3 had quite different effects on the reduction efficiency and the reduction activity increase as the temperature increased. Especially, if MoO_3 content was lower, the activity was affected more by temperature. As the ratio of MoO_3 and TiO_2 increase, the activity at low temperatures increase significantly. Compared

Fig. 8. DeNOx selectivity of titania loading WO_3 Fig. 9. DeNOx selectivity of titania loading MoO_3

Figs. 8 and 9 with Fig. 6, it can be seen that the reduction activity of WO_3 and MoO_3 was much lower than that of V_2O_5 . Adding W to catalysts, new W-V-Ti oxide was formed on the V-Ti catalyst surface, so that W and V-Ti could have synergistic effect to raise the reduction activity in the selective catalytic reduction process¹⁷. Additionally, the Tamman temperature of WO_3 is high, so adding W could increase the temperature tolerance to adapt to variable working conditions¹⁸.

Effect of titania species in V/Ti catalysts: The result of the reduction activity of the fourth group (catalysts with the same V_2O_5 and different titania carrier) is shown in Fig. 10. The result of 6009 was put here for comparison, so we could see it clearly that the reduction activity of V/Ti was much better than that of 6009. Within the temperature range of $360\text{--}460^\circ\text{C}$, the activity difference of the four catalysts was very little and the NO conversion rate was in the range of 94–99 %. In the temperature range of $260\text{--}360^\circ\text{C}$, the activity of $V_2O_5/6001$ and $V_2O_5/6002$ was higher than that of $V_2O_5/6003$ and V_2O_5/TiO_2 , which was mainly because of the existence of WO_3 in 6001 and 6002.

In the temperature range of $260\text{--}460^\circ\text{C}$, N_2O generated from four kinds of V/Ti catalysts and 6009 was not much and N_2O from 6009 was a little less than from the four kinds of V/Ti catalysts. It can be seen from Fig. 11 that as temperature increased above 420°C , N_2O generation of 6009 decreased,

Fig. 10. DeNO_x activity of different titania loading the same V₂O₅

which differed greatly from the result of V/Ti catalysts. The tests showed that N₂O generation from catalysts containing WO₃ was great, because the reduction selectivity of WO₃ is poor. In this experiment, the carrier 6001 and 6002 both contain WO₃, but the N₂O generation amount of V₂O₅/6001 and V₂O₅/6002 was not more than that of V₂O₅/6003 and V₂O₅/TiO₂. This can account for that the active species of catalysts is vanadium and vanadium species promoted the reduction selectivity in 260-450 °C temperature region.

Fig. 11. DeNO_x selectivity of different titania loading the same V₂O₅

DeNO_x activity of titania-supported FeSO₄ catalyst:

The study of Fe-based compound for NO control includes the wet absorption method of FeSO₄ solution, catalysts of molecular sieve, Fe₂O₃/TiO₂ catalysts and so on¹⁹⁻²¹. Studies show that Fe-based catalysts have a good denitrification effect because Fe can form variable valence oxides and both polymeric Fe and monomer Fe have reduction activity in selective catalytic reduction process²². The reason for using FeSO₄ here was that the sulfate catalyst could increase the strength of acid sites on catalyst surface to promote the adsorption of ammonia and widen the temperature window of Fe-based catalyst to high-temperature region. As shown in Fig. 12, within the temperature range of 260-400 °C, 16 % FeSO₄/TiO₂ had the best reduction activity. However, as the temperature increased above 400 °C, 6 % FeSO₄/TiO₂ performed best in selective catalytic reduction process. The results showed that the most optimum ratio of FeSO₄ and TiO₂ was between 6 and 16 %.

Fig. 12. DeNO_x activity of titania-supported FeSO₄ catalyst

When the temperature was within 430-500 °C, the reduction activity of 16 % FeSO₄/TiO₂ and 32 % FeSO₄/TiO₂ dropped significantly and the possible reason was that NH₃ was oxidized to NO by FeSO₄/TiO₂ [reaction(8)].

Fig. 13 showed that little N₂O was generated by 16 % FeSO₄/TiO₂ and 32 % FeSO₄/TiO₂ below 430 °C, but the amount increased rapidly when the temperature was above 430 °C. The results showed that the reduction selectivity of FeSO₄ was better at lower temperatures, but it got worse as temperature increased.

Fig. 13. DeNO_x selectivity of titania-supported FeSO₄ catalyst

DeNO_x activity of catalysts loading SO₄²⁻: The testing results of sulfate radical supported catalysts are shown in Fig. 14, where it is observed that the activity of catalysts with SO₄²⁻ was slightly higher than that of 6009, but the difference was not big. It is also observed that impregnated in H₂SO₄, (NH₄)₂SO₄ or Ti(SO₄)₂ solution, the catalysts loading sulphate had a similar reduction activity. It was similar to catalyst loading 5 (wt. %) WO₃, but less than catalyst loading 5 (wt. %) MoO₃, letting alone with V/Ti catalysts.

Chen and Yang²³ reported that SO₄²⁻/TiO₂ catalysts by SO₂ treatment had a great denitrification activity at high temperatures (500-550 °C). But this study showed that although the activity

Fig. 14. DeNO_x activity of catalysts with SO₄²⁻

of catalysts with SO₄²⁻ was better than that of titanium dioxide, the activity remained weak. The existence of SO₄²⁻ increases the amount of acid sites on catalyst surface and the stability of acid sites at high temperatures, but no suitable reaction sites can not ensure a high denitrification activity.

Using the specific carrier, Choo *et al.*²⁴ found that the saturated amount of sulfate loading on the catalyst surface was 1-1.2 (wt. %) (calculated at S content). A number of investigators have reported that the final sulfate species were the same regardless of the loading mode²⁵⁻²⁷. This study also found that whether steeped in H₂SO₄, (NH₄)₂SO₄ or Ti(SO₄)₂ solution, the DeNO_x activity of catalysts loading sulfate remained almost the same.

Conclusion

The DeNO_x activity and selectivity of different titania-supported catalysts were tested in a small-scale experimental system. The results show that titania had a low catalytic activity of DeNO_x, but much N₂O was generated during the experiments. With V₂O₅, the activity of catalysts was enhanced greatly and the amount of N₂O decreased at the same DeNO_x activity as titania. Catalysts with WO₃ could reduce NO quite efficiently, but the activation temperature was raised highly (> 360 °C). Different contents of Mo had different effects on the DeNO_x efficiency. If Mo content was lower, the catalyst activity was affected more by the temperature.

By testing the activity of catalysts loading the same V₂O₅ and different titania, it could be concluded that within the temperature range of 360-460 °C, the activity difference of the four catalysts was very little and the NO conversion rate was in the range of 94-99 %. But within the temperature range of 260-360 °C, the activity of V₂O₅/6001 and V₂O₅/6002 was higher than that of V₂O₅/6003 and V₂O₅/TiO₂. For titania-supported FeSO₄ catalyst, the most optimum ratio of FeSO₄ and TiO₂ was between 6 and 16 %. Little N₂O was generated by FeSO₄/TiO₂ catalysts below 430 °C, but the amount increased rapidly when the temperature was above 430 °C. But impregnated in H₂SO₄, (NH₄)₂SO₄ or Ti(SO₄)₂ solution, the catalysts

loading sulphate had a similar reduction activity and it was similar to catalysts with 5 (wt. %) WO₃.

The tests showed that N₂O generation by catalysts containing WO₃ was great, because the DeNO_x selectivity of WO₃ is poor. In this experiment, the carrier 6001 and 6002 both contain WO₃, but the N₂O generation amount of V₂O₅/6001 and V₂O₅/6002 was not more than that of V₂O₅/6003 and V₂O₅/TiO₂. This can account for that the active species of catalysts is V and V species promoted the reduction selectivity in the temperature range of 260-450 °C.

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