

(Scientific Note)

Reduction of NO by NH₃ over Composite Catalysts

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ABSTRACT

Composite catalysts V₂O₅/TiO₂/(modified zeolite supports) were prepared by mixing modified zeolites (H-Y, Cu-Y, DAY) with n-hexane solutions of isopropyl orthotitanate and ammonium monovanadate. The activity of the composite catalysts prepared by the reflux method was higher than that by impregnation. The effect of TiO₂ on NO conversion was dependent on the type of catalyst and the method of preparation. Furthermore, pretreatment of a composite catalyst with SO₂ did not decrease its activity.

Key Words: composite catalyst, reflux, impregnation, reduction, NO

I. Introduction

One of the major methods of reducing NO concentration in flue gas is selective catalyst reduction (SCR). Commercialized catalysts for SCR include base metal/metallic plate (Babcock Hitachi), base metal/ceramic monolith (Hitachi Zosen), zeolite (Steuler) and noble metal/metallic plate (Camet/Grace) (Bosch and Jannsen, 1987). V₂O₅/TiO₂ has high activity and good selectivity (Handy *et al.*, 1992; Miyamoto *et al.*, 1982; Takagi *et al.*, 1977; Went *et al.*, 1992). In addition, it is SO₂ resistant. However, its surface area is low compared to that of other catalysts. On the other hand, the activity of Y zeolite for NO reduction decreases dramatically when SO₂ is present in the flue gas (Mizumoto *et al.*, 1979). However, its operating window is wider (Bosch and Jannsen, 1987), and it has large NH₃ storage capacity (Seiyama *et al.*, 1977). Moreover, NO conversion over Y zeolites modified by ion exchange with copper and/or dealumination is very high. Therefore, it is hoped that a better catalyst which has the advantages of both V₂O₅/TiO₂ and Y zeolite can be prepared.

In this study, composite catalysts which consist of modified Y zeolites and V₂O₅/TiO₂ were prepared. The activity of these catalysts for NO reduction by NH₃ in the presence of O₂ and/or SO₂ was investigated.

II. Experimental

(1) Preparation of DAY (dealuminated Y zeolite):

Five grams of Na-Y powder (Strem Chemicals,

framework Si/Al: 2.1) were treated with 200 mL, 0.005-0.01M HCl solution at 40°C for 10 h. DAY thus obtained was then washed with deionized water for several times and dried at 60°C (Lee and Ress, 1987).

(2) Preparation of H-Y:

One gram of Na-Y powder was treated with 40 mL, 0.05 M NH₄Cl solution at room temperature for 6h. NH₄-Y (76% exchange level) obtained was then washed with deionized water for several times and dried at 60°C. The exchange level of NH₄-Y was defined as $x/(x+y)$, where x and y are from (NH₄)_xNa_y-Y (Wang *et al.*, 1991). H-Y was prepared by treating 0.5 g pelletized NH₄-Y (40-60 mesh) with Ar at 500°C for 12 h. The flow rate of Ar was 120 mL/min.

(3) Cu⁺² ion exchange:

Six grams of powdered catalyst (Na-Y, TiO₂/H-Y or DAY) were treated with 300 mL, 0.05 M Cu(NO₃)₂ solution at 80°C for 24 h. They were then washed with deionized water and dried at 60°C. The exchange level of Cu-Y was defined as $2x/(2x+y)$, where x and y are from Cu_xNa_y-Y (Jacobs *et al.*, 1977).

(4) Preparation of TiO₂/zeolite (H-Y, DAY or Cu-Y):

Both reflux and impregnation methods were used to prepare TiO₂/zeolite. Reflux method: The powdered zeolites were treated with 150 mL n-hexane solution containing various concentrations of isopropyl orthotitanate at 64°C for 20 min. They were then washed with n-hexane for several times, dried at 60°C, and calcined by air at 500°C for 2 h. Impregnation method: The powdered zeolites were treated with 25 mL n-hexane solution containing various concentrations of isopropyl orthotitanate at room temperature for

one hour. They were then washed with 5 mL n-hexane, dried at 60°C, and calcined by air at 500°C for 2 h (Wauthoz *et al.*, 1991).

(5) V_2O_5 /support (Cu-Y, Cu-DAY, TiO_2 /Cu-Y or TiO_2 /Cu-DAY):

The catalyst support was impregnated with an aqueous solution of ammonium monovanadate (V_2O_5 /support: 6 wt%) at room temperature for 6 h, dried at 120°C, and calcined by air at 500°C for 2 h.

(6) SO_2 treatment:

Catalysts were treated with a mixture of 1800 ppm NH_3 , 15% O_2 , 2000 ppm SO_2 , and balance Ar at 400°C for 1 h. The flow rate of the gas mixture was 180 mL/min (Nam *et al.*, 1986).

(7) Measurement of the activity of the catalysts:

The reduction reaction was conducted in a fixed bed reactor made with a quartz tube. The reaction temperature was measured by a thermocouple inserted in the catalyst bed. The temperature of the reactor was raised from room temperature to the reaction temperature by 2 °C/min. NO conversions over the catalyst measured seven minutes and one hour after the temperature reached the reaction temperature were defined as transient state and steady state conversion, respectively, due to the fact that NO conversion remained the same after one hour. The concentration of NO, N_2 , and O_2 in the inlet and outlet gas was measured by a gas chromatograph with TCD. The gas chromatographic column contained a molecular sieve 13X in 0.32 cm o.d. by 3 m long stainless steel tubing and was maintained at 60°C. This column could separate N_2 , O_2 and NO. Argon was used as the carrier gas. The formation of N_2O was also measured by the same method except that Porapak Q was used as the column packing. The reaction conditions are shown in Table 1. It should be noted that the formation of N_2O under the reaction conditions used in this study was negligible. Thus, the main product of the SCR reaction was N_2 .

III. Results and Discussion

The effect of the catalyst preparation method on NO conversion at steady state over TiO_2 /H-Y is shown in Fig. 1. The activity of the catalyst prepared the

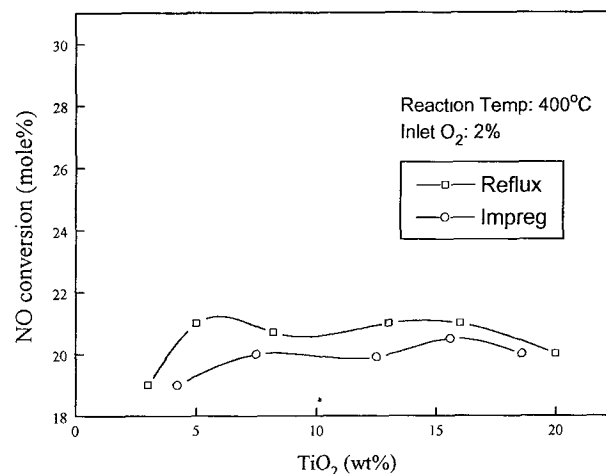


Fig. 1. Effect of catalyst preparation method on steady state NO conversion over TiO_2 /H-Y.

reflux method was higher than that by prepared by the impregnation method. This is due to the fact that TiO_2 disperses more uniformly in the catalyst made by the reflux method (Wauthoz *et al.*, 1991). Also shown in this figure is that the activity of TiO_2 /H-Y made by the impregnation or reflux method was not significantly affected by the amount of TiO_2 in the catalyst.

Figure 2 shows the effect of inlet oxygen concentration on NO conversion at steady state over TiO_2 /DAY prepared by the reflux method. As shown in this figure, the activity of TiO_2 /DAY at a low oxygen concentration was lower than that at a high oxygen concentration. Also shown in this figure is that the reaction temperature had a negligible effect on the activity of the catalyst at a low oxygen concentration. However, its effect was dramatic at a high oxygen concentration. Note that the treatment time for the reflux method could not exceed one hour; otherwise, the catalyst became amorphous (from XRD) and was not suitable for catalyst support.

The effect of catalyst preparation method on NO conversion at transient state over Cu- TiO_2 /H-Y is shown in Fig. 3. Again, the activity of Cu- TiO_2 /H-Y prepared by the reflux method was higher than that prepared by the impregnation method. Also shown in this figure is that NO conversion decreased as the amount of TiO_2 increased. This is due to the low exchange level of active Cu^{+2} for the catalyst with high TiO_2 content as shown in Table 2.

The results of NO- NH_3 - O_2 reaction at steady state over V_2O_5 / TiO_2 /Cu-Y are shown in Fig. 4. As shown in this figure, the activity of V_2O_5 / TiO_2 /Cu-Y was higher than that of V_2O_5 /Cu-Y. Roozeboom *et al.* (1980) pointed out that the reaction of TiO_2 with V_2O_5 produced an active solid solution; however, without the TiO_2 stable monolayer V_2O_5 on Al_2O_3 and crystalline

Table 1. Reaction Conditions

Weight of catalyst	0.2 g
Size of catalyst	40-60 mesh
Concentration of NO and NH_3	1500 ppm
Flow rate of gas mixture	150 mL/min
Reaction temperature	90-400°C
Reaction pressure	1 atm
Gas hour space velocity	75000 h ⁻¹

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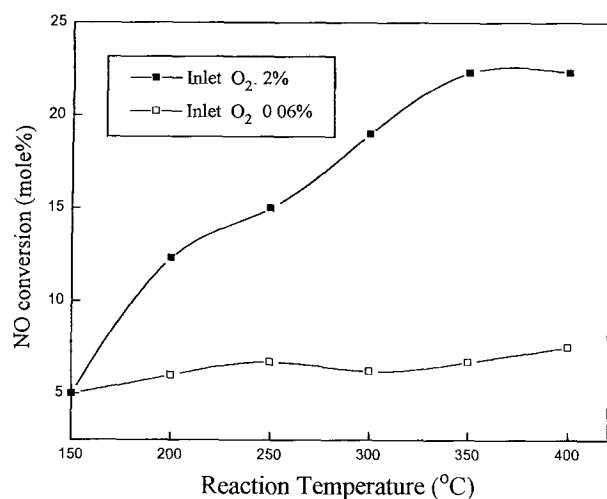


Fig. 2. Effect of oxygen concentration on steady state NO conversion over TiO₂(16wt%)/DAY.

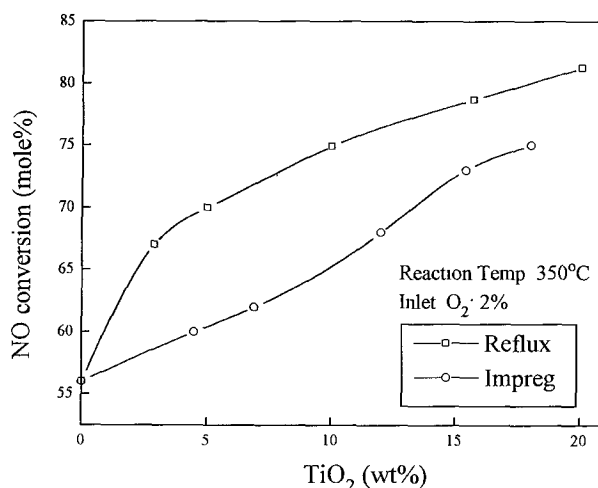


Fig. 4. Effect of catalyst preparation method on steady state NO conversion over V₂O₅(6wt%)/TiO₂/Cu-Y.

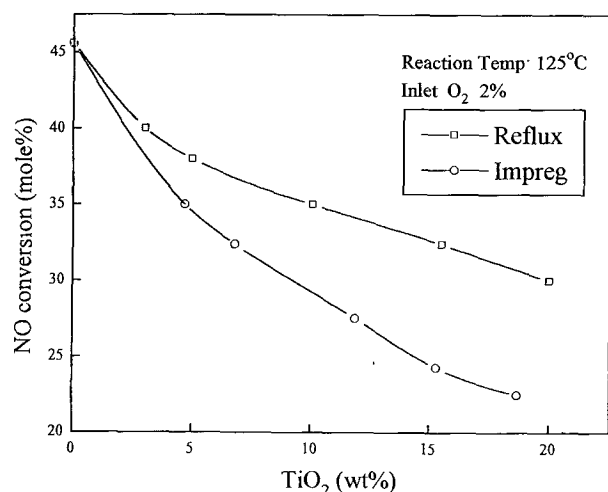


Fig. 3. Effect of catalyst preparation method on NO conversion over Cu-TiO₂/H-Y.

V₂O₅ on SiO₂ were formed and were inactive. Therefore, NO conversion over V₂O₅/TiO₂/Cu-Y was higher than V₂O₅/Cu-Y. Furthermore, the activity of V₂O₅/TiO₂/Cu-Y increased as the amount of titanium increased. This is in contrast to that for Cu-TiO₂/H-Y as shown in Fig. 3. This is due to the fact that V₂O₅ could be dispersed more uniformly over TiO₂ at a high

TiO₂ content. Thus, the activity of V₂O₅/TiO₂/H-Y containing more TiO₂ was higher.

A comparison of NO conversions over Cu-Y, V₂O₅/TiO₂, and V₂O₅/TiO₂/Cu-DAY is shown in Fig. 5. As shown in this figure, the activity of V₂O₅(6wt%)/TiO₂(16wt%)/Cu-DAY (63% copper exchange level and Si/Al: 5.8) was higher than that of V₂O₅(6wt%)/TiO₂ or Cu-Y (78% copper exchange level and Si/Al: 2.1). Figure 5 also shows the effect of SO₂ treatment on steady state NO conversion over V₂O₅(6wt%)/TiO₂(16wt%)/Cu-DAY (63% copper exchange level and Si/Al: 5.8). It is seen in this figure that pretreatment of the catalyst with SO₂ did not decrease its activity. Thus, it was SO₂ resistant.

IV. Conclusions

Composite catalysts consisting of modified zeolites (H-Y, Cu-Y, DAY, Cu-DAY), V₂O₅, and TiO₂ were prepared in this study. NO conversions over these catalysts were measured experimentally. It was found that:

- (1) NO conversion over the catalysts synthesized by the reflux method was higher than that by impregnation.
- (2) NO conversion increased with increasing oxygen concentration or reaction temperature.

Table 2. The Copper Ion Exchange Level of Cu-TiO₂/H-Y

		Reflux				Impregnation			
TiO ₂ (wt%)		0	5	10	15.5	0	6.8	15.3	18.7
Copper ion exchange level		78	60	55	43	78	45	37	35

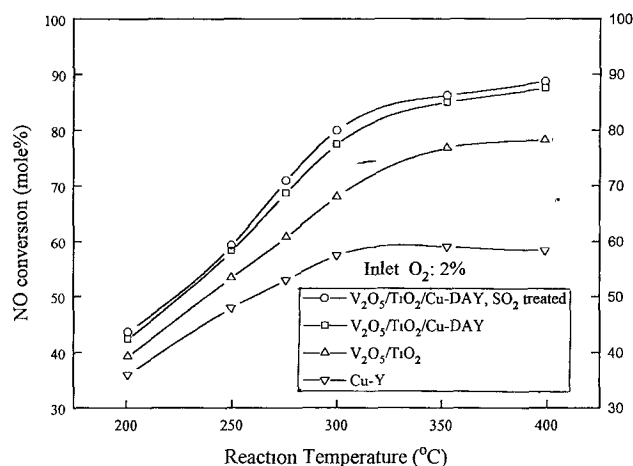


Fig. 5. Effect of reaction temperature on steady state NO conversion over V₂O₅ (6wt%)/TiO₂ (16wt%)/Cu-DAY, V₂O₅ (6wt%)/TiO₂ and Cu-Y (78%).

- (3) NO conversion over the composite catalysts could be raised by the addition of copper or vanadia.
- (4) The effect of TiO₂ on NO conversion was dependent on the type of catalyst used and its preparation method.
- (5) The composite catalysts were SO₂ resistant.

Acknowledgments

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沸石與V₂O₅/TiO₂之混合觸媒應用於以NH₃還原NO反應

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摘 要

改質沸石（H-Y，Cu-Y，DAY）與含有機鈦之n-hexane溶液及NH₄VO₃水溶液混合以製備V₂O₅/TiO₂/（改質沸石），以回流法製備之複合觸媒之活性高於以含浸法製備之複合觸媒，TiO₂對NO轉化率之影響取決於觸媒之種類及其製備方式，經SO₂前處理之複合觸媒其活性並未降低。