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Technical Information

The Effect of Promoters Addition on NOx Removal by NH_3 over V_2O_5/TiO_2

Keon Joo Lee
Department of Environmental Engineering, Sangji University, Wonju, 220-702, Korea

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Abstract

The selective catalytic reduction (SCR) reaction of promoter catalysts was investigated in this study. A pure anatase type of TiO_2 was used as support. Activation measurement of prepared catalysts was practiced on a fixed reactor packing by the glass bead after filling up catalysts in 1/4 inch stainless tube. The reaction temperature was measured by K-type thermocouple and catalyst was heated by electric furnace. The standard compositions of the simulated flue gas mixture in this study were as follows : NO 1,780 ppm, NH_3 1,780 ppm, O_2 1% and N_2 as balance gas. In this study, gas analyzer was used to measure the outgassing gas. Catalyst bed was handled for 1hr at 450°C, and the reactivity of the various catalyst was determined in a wide temperature range. Conversion of NH_3/NO ratio and of O_2 concentration was practiced at 1, 1.5 and 2, respectively. The respective space velocity were as follows : 10,000, 15,000 and 17,000 hr^{-1}. It was found that the maximum conversion temperature range was in a 50°C. It was also found toi be very sensitive at space velocity, O_2 concentration, and NH_3/NO ratio. We also noticed that the maximum conversion temperature of (W, Mo, Sn)-V_2O_5/TiO_2 catalysts was broad. Specially $WO_3-V_2O_5/TiO_2$ catalyst appeared nearly 100% conversion at not only above 300°C but also below 250°C. At over 300°C, NH_3 oxidation decreased with decrease of surface excess oxygen. In addition, $WO_3-V_2O_5/TiO_2$ catalyst did not appear to affect space velocity, O_2 concentration, and NH_3/NO ratio.

Key words : Oxidation, Activation, Space velocity, surface activity, conversion

1. INTRODUCTION

NOx is known as a source of urban photochemical smog and is treated as a pollutant in air pollution management (Ronald, 1994; Jeong, 1988). Table 1 and 2 show that NOx emission increases continuously and that approximatelly 30% of total NOx was emitted from stationary sources (Kim, 1985). NOx is classified into three types: thermal NOx, prompt NOx and fuel NOx. Thermal NOx formation in gas, oil and coal fired devices results from thermal fixation of atmospheric nitrogen in the combustion air. The NOx formed from the reaction of the fuel nitrogen with oxygen is termed as fuel NOx. Flue gas treatment is classified into wet and dry method. A low solubility NO is oxidized to liquid or gas conditionand oxidized NO_2 is absorbed and reduced by the absorption tower.

Combustion modification concludes off-stoichiometric, staged combustion, low-NOx burner, flue gas recirculation and used for thermal NOx.

Flue Gas Treatment (Kim, 1985) is classified into wet and dry method. In first NOx that was absorbed by the liquid ferrous chelating reduce to NO or N_2O,

* Corresponding author.
E-mail : kjoolee@mail.sangji.ac.kr

Table 1. Annual emission of major air pollutants. (unit: ton/year)

Year \ Pollutant	Total	SO_2	NOx	TSP	CO	HC
'90	5,169,119	1,610,960	926,065	420,318	1,991,065	220,711
'91	4,869,959	1,597,780	878,389	431,375	1,759,505	199,910
'92	4,867,637	1,613,549	1,067,001	392,243	1,630,378	164,466
'93	4,583,839	1,571,700	1,186,697	389,750	1,290,527	145,165
'94	4,526,250	1,602,764	1,191,533	429,398	1,156,464	146,091
'95	4,349,606	1,532,320	1,152,765	405,526	1,109,097	149,898
'96	4,424,546	1,500,260	1,257,993	423,694	1,088,788	153,811

Table 2. Air pollutant exhaust amount by source. (unit: ton/year)

Source year		Total	Heating	Industry	Power plant	Transport
NOx	'91	878,389	58,547	221,582	152,139	446,121
	'92	1,067,001	64,993	234,083	201,724	566,201
	'93	1,186,697	62,194	288,715	190,975	644,813
	'94	1,191,533	58,996	329,733	129,086	673,718
	'95	1,152,765	64,606	344,683	136,977	606,499
	'96	1,257,993	70,048	380,568	191,335	616,152

second NO of a low solubility is oxidized to liquid or gas condition, and NO_2 is absorbed and reduced by the absorption tower, third NOx is absorbed with as absorbent and is converted into NO_3^- and finally NO is oxidized to NO_2 pass through gas phase oxidization reaction and is absorbed with as absorbent. However wet method is difficult to practice, so it has problem such as the waste water treatment and the high cost of equipment. Dry method is the greatest practical and bright technique among the NOx removal method. Selective catalytic reduction (SCR) of dry method get accomplished in large number of technical development. In this study, the effect of promoter (W, Mo, and Sn) addition on catalyst was observed to solve such problem.

2. THEORETICAL BASE

2. 1 SCR reaction mechanism

SCR reaction mechanism can be described as follows:

NOx Reduction

$$4NO+4NH_3+O_2 \rightarrow 4N_2+6H_2O \quad (1)$$
$$4NO+4NH_3+3O_2 \rightarrow 4N_2+6H_2O \quad (2)$$
$$6NO+4NH_3 \rightarrow 5N_2+6H_2O \quad (3)$$
$$6NO+8NH_3 \rightarrow 7N_2+12H_2O \quad (4)$$

NH_3 Oxidation

$$4NH_3+3O_2 \rightarrow 2N_2+6H_2O \quad (5)$$
$$4NH_3+4O_2 \rightarrow 2N_2O+6H_2O \quad (6)$$
$$4NH_3+5O_2 \rightarrow 4NO+6H_2O \quad (7)$$
$$4NH_3+7O_2 \rightarrow 4NO_2+6H_2O \quad (8)$$

SO_2 Oxidation

$$2SO_2+O_2 \rightarrow 2SO_3 \quad (9)$$

Side Rections

$$2NH_3+8NO \rightarrow 5N_2O+3H_2O \quad (10)$$
$$2NH_3+H_2O+2NO_2 \rightarrow NH_4NO_3+NH_4NO_2 \quad (11)$$

2. 2 The reaction mechanism of V_2O_5/TiO_2

The SCR reaction by NH_3 can be explaned in Figure 1. NOx reduction is indispensable to SCR as major reaction and NH_3 oxidation reaction that occur in high temperature must be restrained. Reaction 6 was not known as occur when moisture full, reactions 7 and 8 are most unfavorable to SCR and increase according as temperature rises. Reaction 5 has not a direct influence on SCR, but needlessly consume NH_3. Sulfate or nitrate formed by side reaction can stop up reactor or break catalyst. Reactions 10 and 12 can be prevented by that operating temperature remained as approximately 150 and 200°C.

Reactions 1 and 7 are the main reaction of SCR.

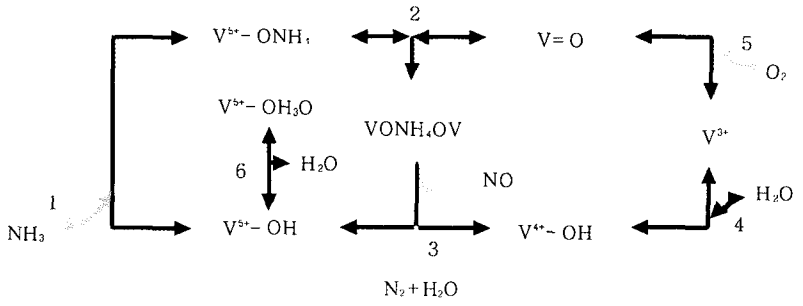
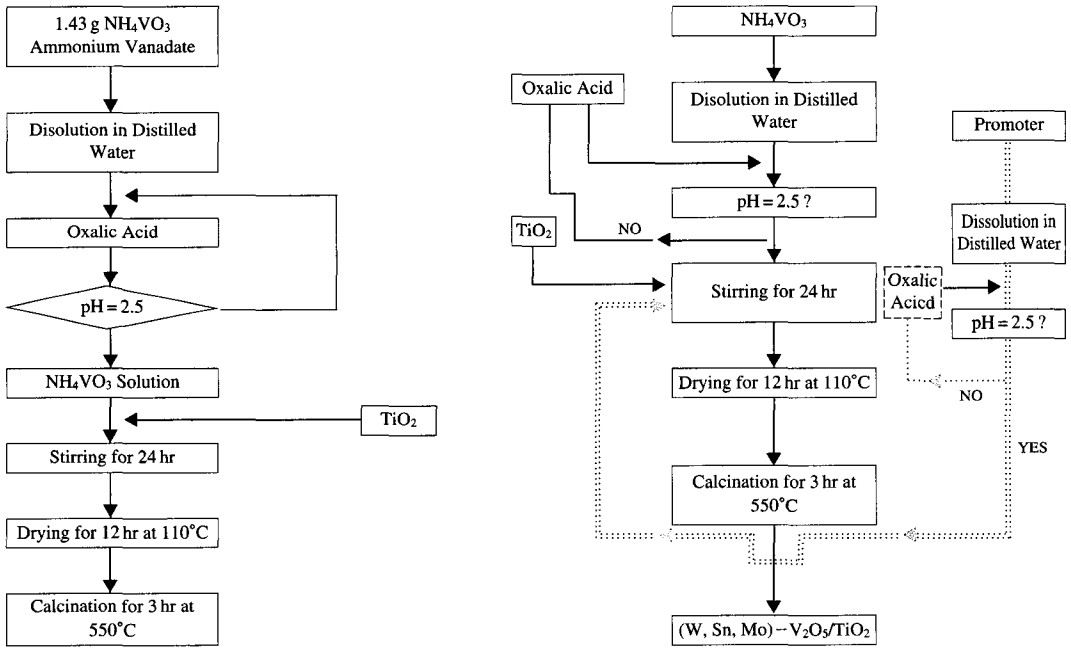


Fig. 1. A schematic representation of catalytic cycle for the SCR reaction over acid sites ($V^{5+}-OH$) and redox sites (V = O).



(a) V_2O_5/TiO_2 (b) (W, Mo, Sn) - V_2O_5/TiO_2

Fig. 2. A schematic diagram of the catalyst preparation.

Takagi *et al.* (1977) proposed a Langmuir-Hinshilwood reaction between adsorbed NO_2 and adsorbed NH_4. However Inomata *et al.* (1980) did not observe oxidation of NO to NO_2 by O_2 in dilute gas mixtures typical of industrial reaction condition. Bosch *et al* (1986) proposed a redox mechanism, which is supported by Janssen *et al.* where V^{+5} is first reduced by NH_3 and is subsequently reoxidized by NO. Inomata *et al.* (1980) suggested that NO reacts with NH_3 adsorbed on dual sites comparised of V-OH and on adjacent V = O species which assists in the activation of NH_3. Ramis *et al.* (1976) proposed an oxidation/reduction mechanism in which the reaction takes place between strongly adsorbed ammonia and gaseous or weakly adsorbed NO. Fig. 2 presents a schematic diagram of the catalytic cycle for the SCR reaction, which is supported by Topsoe *et al.* (1990). Steps 1 and 2 are the ammonia absorption and activation step. Gaseous or weakly adsorbed NO reacts in steps 3 with surface species $V-HNH_3-V_4-OH$ to form N_2 and H_2O by Israe (1996). The removal of surface hydroxyl group to know water is described in step 4. Step 5 represents reoxidation of the catalyst by O_2.

3. EXPERIMENTAL

3. 1 Catalyst preparation

TiO_2 (Yamuri Pure Chemicals Co: Japan) used as a support was pure anatase (see Table 3). The wet impregnation method that proposed by Bosch *et al.* was applied in this work (see Fig. 3). The preparation of the catalysts are summarized in fig. 2. BET surface area of catalyst was examined by ASAP2010 using N_2 gas at 77 k (see Table 4).

3. 2 Evaluation of reactivity

Activation of prepared catalysts was prepared in a

Table 3. Specification of raw materials for catalyst preparation.

Reagent	Company	Molecular weight (g)
TiO_2 (anatase)	Yakuri pure chemicals Co. (Japan)	79.9
NH_4VO_3	Kizuda pure chemicals Co. (Japan)	116.98
Oxalic acid	Duksan chemicals Co. (Korea)	126.27
$SnCl_2/2H_2O$	Duksan chemicals Co. (Korea)	225.63
$(NH_4)6Mo_7O_2/4H_2O$	Dongyang chemicals Co. (Korea)	1235.86
$(NH_4)10W12O41/5H_2O$	Wako prue chemical industries (Japan)	3132.62

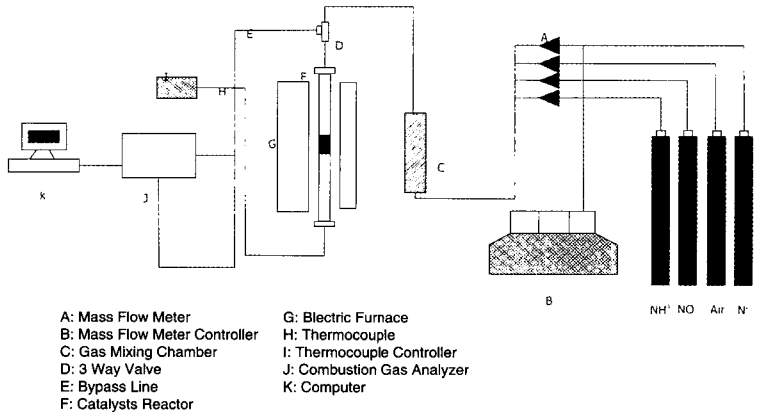


Fig. 3. A schematic diagram of the experimental apparatus for measuring the catalytic activity.

Table 4. BET surface area of various catalysts.

	TiO_2	V_2O_5/TiO_2	$MoO_3-V_2O_5/TiO_2$	$SnO_2-V_2O_5/TiO_2$	$WO_3V_2O_5/TiO_2$
BET surface area (m^2/g)	17.1318	12.106	21.6724	15.8003	10.7716

fixed reactor packing by the glass bead after fill up catalysts in 1/4 inch stainless tube (see Fig. 3). The reaction temperature was measured using K-type thermocouple and the catalyst was heated by electric furnace. The standard composition of the simulated flue gas mixture in this study was as follows: NO 1,780 ppm, NH_3 1,780 ppm, 1% O_2, and N_2 as balance gas. In this study, combustion gas analyzer was used to measure the outlet gas concentration. Catalyst bed was reacted for 1hr at 450°C, and the reactivity of the various catalyst was measured in a wide temperature range. Conversion of NH_3/NO ratio was practiced at 1, 1.5, and 2 respectively. Then the conversion of O_2 concentration was measured and the space velocity was as follows: 10,000, 15,000 and 17,000 hr^{-1} respectively.

The surface area of catalyst was calculated using ASAP 2010. After outgassing the gas, the pressure was maintained under 0.002 mmHg and the BET surface area was calculated by adsorption and desorption of N_2 gas as change the pressure. The crystalization of catalyst was obtained using XRD (GE XRD410). The target was CuKα which use Ni filter and was calculated using $\theta-2\theta$ scan. The BET surface area of various catalysts were shown in Table 4.

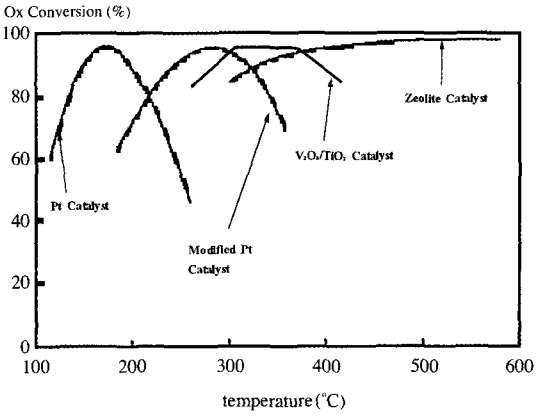


Fig. 4. Operation temperature windows for different SCR catalyst formulaions (ref; Ronald M. 'Catalytic Air Pollution Control').

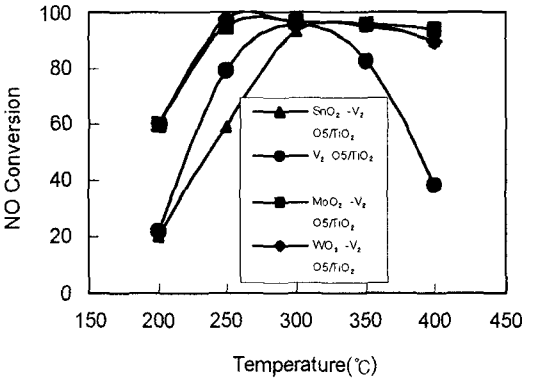
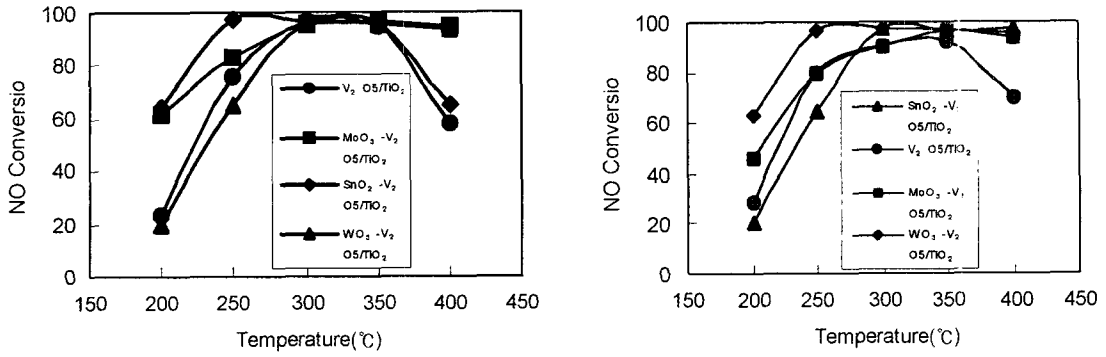


Fig. 5. Effect of temperature on NO conversion over various catalysts. Flux: 200 ml/min, NO; 1,780 ppm, NH_3: 1,780 ppm, O^2: 1%, SV: 10,000 hr^{-1}

4. EXPERIMENTAL RESULTS

4. 1 Effect of temperature

It is known that operating temperature is most important and is wide different as the properties of catalyst. The catalysts usually can be expressed as low temperature, medium temperature and high temperature catalyst by operating temperature (see Fig. 4). In this study V_2O_5/TiO_2 catalyst is most compatible in economic and commercial aspect. However V_2O_5/TiO_2 catalyst has several kinds problem. The effect of promoter is shown in Fig. 5. Conversion of NOx decreased about 70% at near 400°C however the catalysts were not changed as adding promoter. It was also observed that as adding W and MO, almost 100% conversion of NOx was obtained in not only high temperature but also near 250°C. From this results, it can be considered as the NOx conversion was affected by adding W and MO to the catalysts.



(a) NH_3 / NO ratio - 1.5 (b) NH_3 / NO ratio - 2

Fig. 6. Effect of NH_3/NO ratio on NO conversion over various catalysts. Flux: 200 ml/min, NO: 1,780 ppm, SV: 10,000 hr^{-1}, O_2: 1%

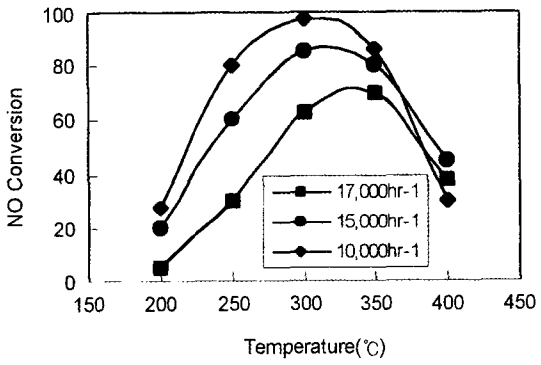


Fig. 7. Effect of space velocity on NO conversion over V_2O_2/TiO_2. Flux: 200 ml/min, NO: 1,780 ppm, NH_3: 1,780 ppm, O_2: 1%.

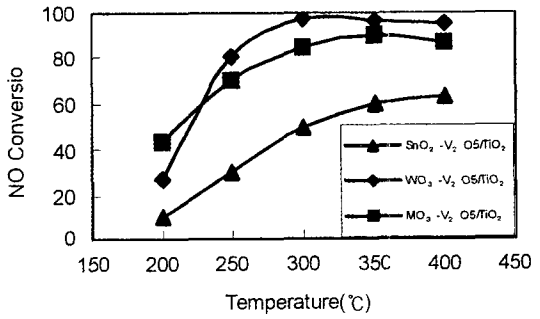


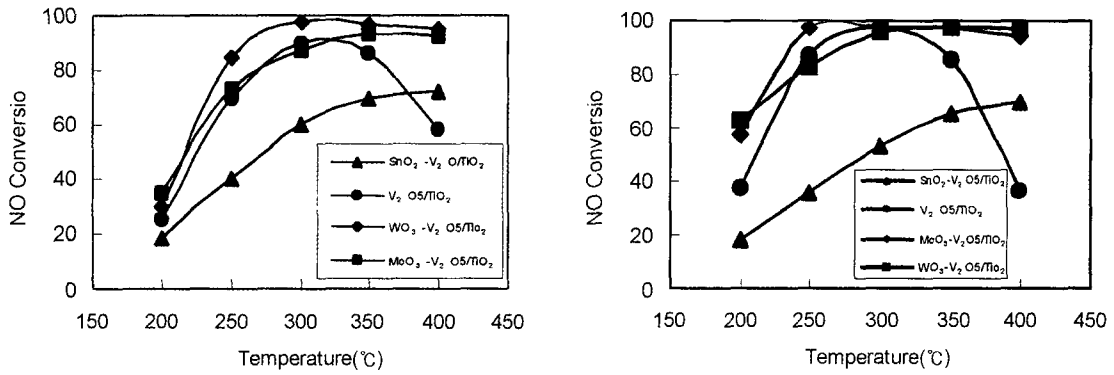
Fig. 8. Effect of space velocity on NO conversion over $(W_2MO_2Sn)-V_2O_2/Ti_2$. Flux: 200 ml/min, NO: 1,780 ppm, NH_3: 1,780 ppm, O_2: 1%.

4. 2 Effect of NH_3/NO mole ratio

In Fig. 6, it is compared the variable of conversion as adding the NH_3. When the NH_3/NO mole ratio was over 1, conversion of NOx was hardly changed. From this results, it is unnecessary to put NH_3/NO ratio over 1 will occurring the oxidation reaction at high temperature or will be emitted to the air without reaction.

4. 3 Effect of space velocity

Space velocity is one of parameter of catalyst practice it is a measure that how much gas can be reacted. Fig. 7 show the results of NO conversion over V_2O_5/TiO_2 catalyst with various space velocity. As space velocity increased, the NO conversion was decreased, and the highest NO conversion moved from 300°C to near 350°C. The reason is that retention time is reduced as decreasing the space velocity. When the promoters were added to the catalysts, the similar phenomenon was obtained. Figure 8 show the results of NO conversion over promoter added to the catalysts with various space velocity. The $SnO_2-V_2O_5/TiO_2$ catalyst was similar with the result of V_2O_5/TiO_2 catalyst, however $WO_3-V_2O_5/TiO_2$ catalyst was no affected



(a) 0.5% O_2 concentration (b) 3% O_2 concentration

Fig. 9. Effect of O_2 concentration on NO conversion over various catalysts. Flux: 200 ml/min, NO: 1,780 ppm, NH_3: 1,780 ppm, SV: 10,000 hr^{-1}.

by the variation of space velocity.

4. 4 Effect of O_2 concentration

Fig. 9 shows the temperature dependency on conversion of NO of each catalyst for the oxygen concentration of 0.5 and 3%. From the Fig. 9, the conversion of NO decreased at 0.5% O_2 concentration except for $WO_3-V_2O_5/TiO_2$, however from figure 9-(b), as increased the oxygen concentration, the NO conversion was decreased in $SnO_2-V_2O_5/TiO_2$ catalyst. From this results, it can be considered the oxygen concentration does not affected the catalyst activity. It is proved that V_2O_5/TiO_2 catalyst was influenced by operating parameter, and it can be concluded that W was the most effected promoter. And also it can be considered that active sites were increased as addition the tungsten oxide on the preparation of catalyst. It is also suggested that the addition of the surface tungsten oxide promoter to the V_2O_5/TiO_2 catalyst has a dramatic influence on the surface Bronsted acidity of the catalyst. The reason why WO_3 show relatively higher NO reaction activity than V_2O_5 at a higher temperature region over 300°C can be explained by the "theory of surface excess oxygen", proposed by Morikawa *et al.* According to Morikawa *et al.* the rate of NH_3 oxidation at higher temperature region is strongly dependent on the surface excess oxygen of the active component of supported catalyst. V_2O_5 has more surface excess oxygen, which could contribute to the side reaction of NH_3 oxidation to make NO or N_2O at high temperature over 300°C than that of WO_3.

4. CONCLUSION

The main conclusions from the present study can be summarized as follows.

1. The NO conversion on V_2O_5/TiO_2 catalyst observed that the activation temperature range was narrowed, and was very sensible on NH_3/NO mole ratio, space velocity and oxygen concentration. As increasing the space velocity, the activation temperature range was moved from 300 to 350°C.

2. $SnO_2-V_2O_5/TiO_2$ catalyst effects to broad activation temperature range and this catalysts were very sensible reactivity as the change of space velocity and the oxygen concentration.

3. $MoO_3-V_2O_5/TiO_2$ catalyst was effective to improve the efficiency of V_2O_5/TiO_2 catalyst, and the maximum conversion temperature range was also affected by the $MoO_3-V_2O_5/TiO_2$ catalyst, however, the operating parameter was sensible below 300°C.

4. It was observed that almost 100% of NO conversion was obtained not only above 350°C but also 250 °C using $WO_3-V_2O_5/TiO_2$ catalyst, and it was hardly influenced on operating parameter (NH_3/NO ratio, O_2 concentration, space velocity) to obtain the maximum conversion temperature.

The increase of conversion efficiency by adding the W to the catalyst increases the active site. Hence, it can be concluded that the W is best promoters to increase the catalyst reactivity.

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