

WO₃ AND MoO₃ ADDITION EFFECT ON V₂O₅/TiO₂ AS PROMOTERS FOR REMOVAL OF NO_x AND SO_x FROM STATIONARY SOURCES

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Abstract—As an attempt to improve the catalytic activity at higher reaction temperatures between 300-450°C, various mole ratios of WO₃ were added to V₂O₅/TiO₂ catalytic systems. And also, in order to suggest a new mixed oxide catalyst system for simultaneous removal of NO_x and SO_x from stationary sources, MoO₃-V₂O₅/TiO₂ catalysts were prepared by a conventional impregnation method together with a newly introduced method of surface fixation (non-aqueous solution method). In case of WO₃ addition, at higher reaction temperature range (300-450°C), WO₃ and WO₃-V₂O₅/TiO₂ catalysts showed significant high conversion in NO reduction with NH₃ while V₂O₅/TiO₂ catalyst showed a significant change in selectivity mainly due to the excess side reaction of NH₃ oxidation. This difference in selectivity due to NH₃ oxidation at high temperature is supposed to be associated with the difference in values of surface excess oxygen between WO₃ and V₂O₅ on titania. The surface acidities of tested catalysts were relatively well correlated with the % conversion of NO at 400°C. In case of MoO₃ addition, the catalytic activity for the simultaneous removal of NO_x and SO_x were quite enhanced by the addition of MoO₃ into V₂O₅/TiO₂ catalysts. The enhanced activities were responsible for the formation of Mo=O bond on the intermediate species produced by solid solutions on MoO₃-V₂O₅/TiO₂ (aqueous). However, in the case of MoO₃-V₂O₅/TiO₂ (non-aqueous), the exact source of active site was not able to detect in IR spectra in spite of more enhanced activity was obtained in this study. After SO₂ contact, VOSO₄ is newly formed on the surface of catalyst, which supposed to be associated with the activity enhancement.

INTRODUCTION

Among the commercialized catalyst system for S.C.R (Selective Catalytic Reduction) process, titania supported vanadium oxide catalysts are commercially used for its strong resistance to SO₂ poisoning as well as the excellent catalytic activities and selectivities for NO_x reduction at medium flue gas temperature conditions. However, the V₂O₅/TiO₂ catalyst system has some problems to solve further: the formation of ammonium sulfates, significant selectivity changes due to NH₃ oxidation at higher reaction temperature (over 350°C), the thermal stability, and the limitation of the use for simultaneous removal of NO_x and SO_x in a catalytic reactor-bed.

In these studies, **firstly** as an attempt to improve the catalytic activity at higher reaction temperatures between 300-450°C, various mole ratios of WO₃ were

added to V₂O₅/TiO₂ catalytic systems. It has been tried to find some correlations between the catalytic activities and the acidic properties of various WO₃-V₂O₅ catalysts on titania. **Secondly**, in order to suggest a new mixed oxide catalyst system for simultaneous removal of NO_x and SO_x from stationary sources, MoO₃-V₂O₅/TiO₂ catalysts were prepared by a conventional impregnation method together with a newly introduced method of surface fixation (non-aqueous solution method) as suggested by Teraoka et al. [1].

EXPERIMENTAL

1. Catalysts

TiO₂ (Aldrich Catalog No. 23-203-3) used as a support was purely anatase type. Catalysts were prepared in two main groups: the conventional aqueous impregnation method and non-aqueous method as shown in Table 1. The non-aqueous method for the preparation of V₂O₅/TiO₂ catalyst was same as that proposed by

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Table 1. Catalyst preparation

Group	Catalysts	Loading
I (aqueous)	V ₂ O ₅ /TiO ₂	5 mole%
	WO ₃ /TiO ₂	5 mole%
	V ₂ O ₅ -WO ₃ /TiO ₂	V ₂ O ₅ /WO ₃ mole ratio = 0.1, 0.2, 1, 2
	V ₂ O ₅ -MoO ₃ /TiO ₂	V ₂ O ₅ /MoO ₃ wt. ratio = 1 Atomic mole ratio [Mo/(V + Mo)] = 0.385
II (non-aqueous)	V ₂ O ₅ /TiO ₂	10 wt%
	V ₂ O ₅ -MoO ₃ /TiO ₂	V ₂ O ₅ /MoO ₃ wt. ratio = 1 Atomic mole ratio [Mo/(V + Mo)] = 0.385
		V ₂ O ₅ /MoO ₃ wt. ratio = 2 Atomic mole ratio [Mo/(V + Mo)] = 0.241

Teraoka et al. [1].

The difference of the preparation process of the two catalyst group is summarized as block diagrams as shown in Fig. 1.

2. Activity Measurement

For the measurement of catalytic activity of each prepared catalyst, the "simulated flue gas and catalytic

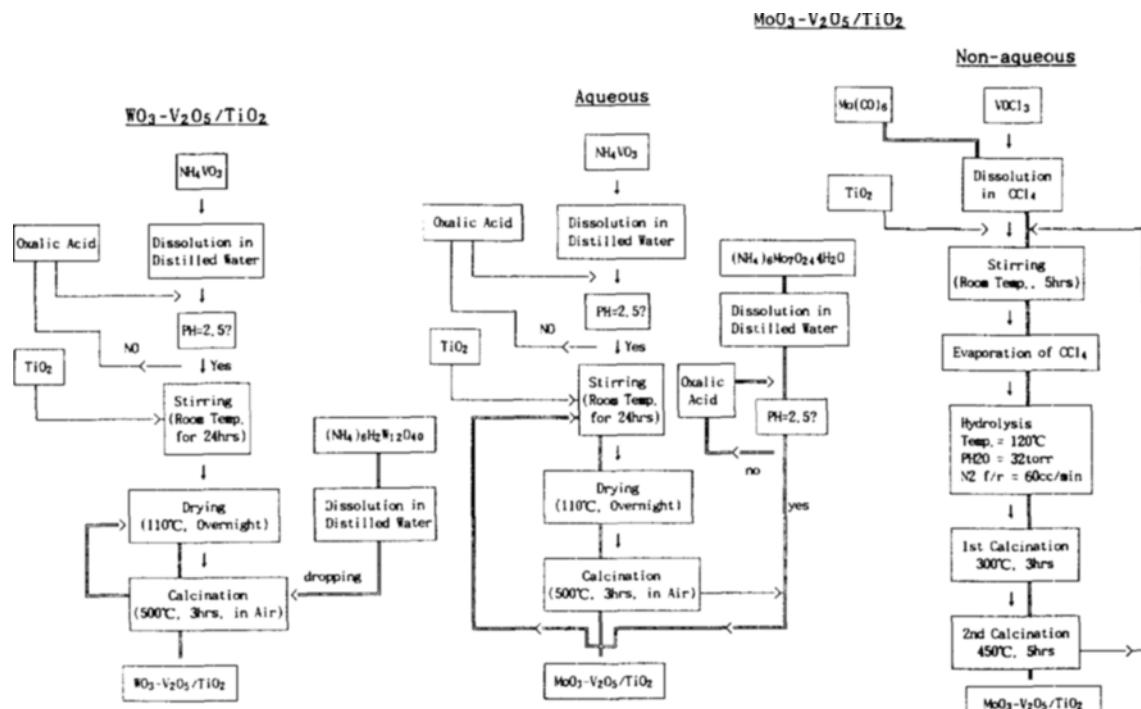
reactor system" suggested by Kato et al. [2] was used in this study.

The catalytic reactor was a quartz tube with the O.D. 12.7 mm, I.D. 10.7 mm and 300 mm length. The catalyst bed was located in the middle of the reactor for about 10 mm length, and the remaining part of the reactor was charged with quartz beads. The space velocity was about 60,000 hr⁻¹, and the reaction temperature was controlled by a closed loop temperature controlling system. The standard composition of the simulated flue gas mixture in this study was as follows: NO_x 500 ppm, SO_x 1100 ppm, NH₃ 2600 ppm, O₂ 2 vol%, and N₂ as a balance gas (for the case of simultaneous removal of NO_x and SO_x). In the case of activity measurement of WO₃-V₂O₅/TiO₂ for NO_x removal only, the standard composition of reactant was NO_x 600 ppm, NH₃ 600 ppm, O₂ 2 vol% in N₂ balance gas.

For the analysis of each gas, chemiluminiscent NO_x analyzer, SO₂ analyzer and oxygen digital meter were used, which were verified by the calibration process using wet analysis methods in ref. (3). Ammonia was collected in boric acid solution, and was titrated.

3. Characterization

A conventional gas volumetric adsorption system

**Fig. 1. Flow chart of catalyst preparation.**

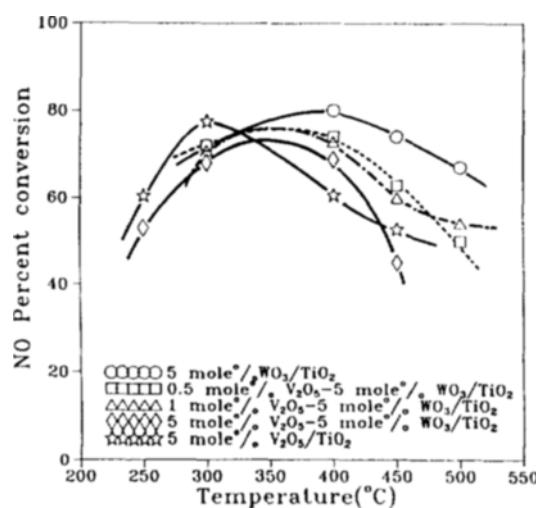


Fig. 2. Temperature dependencies of NO reduction for various catalysts.

was used for the BET surface area measurement from the N_2 adsorption data at -196°C . For the XRD pattern, X-ray diffractometer (Rigaku Model RAD-3A) was adopted using a $\text{CuK}\alpha$ as a target. The acidity measurement was followed by the "calorimetric titration method" which was verified by Tanabe et al. [4].

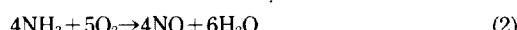
To check the acid site distribution, the NH_3 TPD experiments were also carried out. To monitor the differences in surface properties of catalysts before and after SO_2 contacts, the IR (Nicholet HX-1) study was carried out. And the morphology of catalyst was monitored from SEM measurements.

RESULTS AND DISCUSSION

1. WO_3 Addition Effects

1-1. Activity Measurement Results

Fig. 2 shows the temperature dependency in NO reduction activities (% conversion of NO) of each catalyst for the temperature range from 250°C to 500°C . Each catalyst shows maximum position of activity in the temperature range. This is obviously due to the excessive NH_3 oxidation at higher temperature range:



Among them, the WO_3/TiO_2 catalyst shows its maximum at 400°C , while $\text{V}_2\text{O}_5/\text{TiO}_2$ has its maximum at 300°C . Depending upon the mixing ratio of $\text{V}_2\text{O}_5/\text{WO}_3$, the maximum activity positions in temperature shifted

Table 2. Acidities of various catalysts

Catalysts	Acidities (m-mol/g·cat)
TiO_2	0.39
5 mole% $\text{V}_2\text{O}_5/\text{TiO}_2$	0.51
$\text{V}_2\text{O}_5/\text{WO}_3 = 2$	
1	0.77
0.2	0.82
0.1	0.92
5 mole% WO_3/TiO_2	1.01

from 400°C to 300°C . Consequently the position of temperature at maximum activity maybe adjusted by controlling the mixing ratio of $\text{V}_2\text{O}_5/\text{WO}_3$ properly depending upon the flue gas temperatures. The reason why WO_3 shows 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. [5]. According to Morikawa et al., the rate of NH_3 oxidation at higher temperature region is strongly dependent upon the surface excess oxygen of the active component of supported catalyst. That is, V_2O_5 has more surface excess oxygen which could contribute the side reaction of NH_3 oxidation to make NO or N_2O at high temperature over 300°C than that of WO_3 . And it causes the worse NO_x reduction efficiency on V_2O_5 than WO_3 in high temperature region.

1-2. Acidic Properties of Catalysts and its Relation to Activity

Table 2 summarized the results in surface acidity (total acid amount) measurements for various catalysts using an amine titration method.

As shown in Table 2, the acidity of WO_3/TiO_2 is almost double when it was compared with that of $\text{V}_2\text{O}_5/\text{TiO}_2$. Also, as the mole ratios of $\text{V}_2\text{O}_5/\text{WO}_3$ in $x\text{V}_2\text{O}_5-y\text{WO}_3/\text{TiO}_2$ catalysts are increased from 0.1 to 2, the values of acidities are approaching from that of WO_3/TiO_2 to that of $\text{V}_2\text{O}_5/\text{TiO}_2$. This fact suggests that the V_2O_5 species on the surfaces is less susceptible than WO_3 to the formation of new acid sites during the catalyst preparation process.

It was tried to correlate the acidities of $x\text{V}_2\text{O}_5-y\text{WO}_3/\text{TiO}_2$ catalysts with the activities in % conversion of NO_x at high temperature of 400°C . As a result, as shown in Fig. 3, it could be found that this correlation is relatively well matched up to equal molar ratio of $\text{V}_2\text{O}_5/\text{WO}_3$. This result strongly suggests that the reason of higher activity of WO_3 than that of V_2O_5 at 400°C is due to the low value of surface excess oxygen of WO_3 , which results in the compressing of

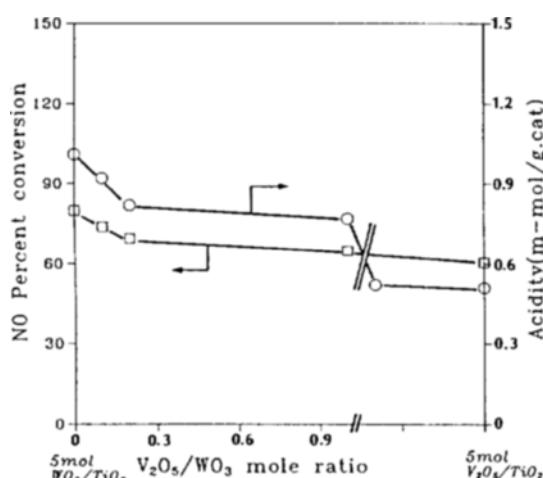


Fig. 3. Correlationship between catalyst acidities and activities (400°C).

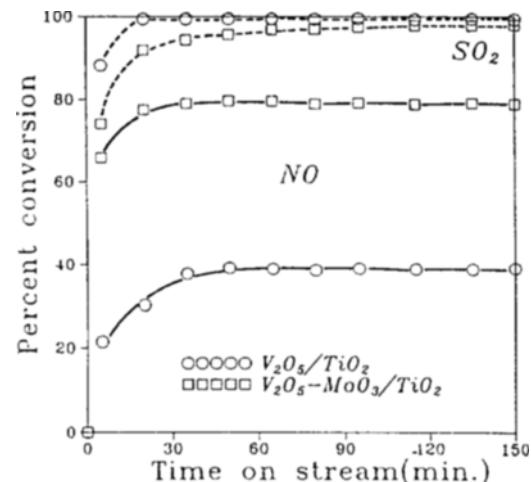


Fig. 4. Activities for MoO₃-V₂O₅-TiO₂ (non-aqueous) at 350°C.

NH₃ oxidation, might be explained by the susceptibility to the formation of acid site through the dehydration of hydroxyl groups on metal site by heating during the drying and calcination steps in catalyst preparation process.

2. MoO₃ Addition Effects

2-1. Activity Measurement Results

Table 3 shows the results of simultaneous removal of NO_x and SO_x on catalysts prepared by aqueous and non-aqueous methods in NO-NH₃-SO₂-O₂ system at reaction temperature of 350°C, and Fig. 4 shows that for non-aqueous catalyst. In the case of V₂O₅/TiO₂ catalysts almost similar activities could be found (about 39-42% conversion of NO_x) without regarding the types of preparation method. And as expected, when 10 wt% MoO₃ added to the 10 wt% V₂O₅/TiO₂ catalyst system, striking activity enhancement could be found for both types of catalyst [from 39 to 71% conv. of NO for type A catalyst (aqueous), from 42 to 81% conv. of NO for type B (non-aqueous)]. For same loading of MoO₃-V₂O₅/TiO₂ catalysts, type B catalyst (non-aqueous) showed relatively higher activity enhancement than type A cat-

alyst (aqueous). The enhancement effect by the addition of MoO₃ could be explained by the formation of solid solution. According to the results on surface characterization of unsupported V₂O₅-MoO₃ catalysts by Satsuma et al. [6], there were strong signs of the formation of solid solution up to 30 mole % of MoO₃ [equivalent to Mo/(V+Mo)=0.18]. By the addition of MoO₃ on bulk V₂O₅, the redox sites of surface V=O species are newly formed on the various crystal plane of solid solution, and also the surface Mo=O species on the intermediate compounds are activated under the effect of V₂O₅ to act as redox sites. Another reason of enhancement in activity could be found from the suggestion by Tarama et al. [7, 8] that there is an qualitative change in active site, i.e., weakening of the V=O bond by the addition of MoO₃ into V₂O₅. Therefore, it could be summarized that addition of MoO₃ into V₂O₅/TiO₂ catalysts results in the enhancement of redox sites of V=O and Mo=O species as well as the weakening of V=O bond, and thereby the catalytic activity enhancement for NO_x reduction could be obtained. The higher activity on MoO₃-V₂O₅/TiO₂ cata-

Table 3. Simultaneous removal of NO_x and SO_x (Steady-state activity)

Types of catalyst	Catalysts	Loading (%)		Steady-state % conversion at 350°C (NO + SO ₂ + NH ₃ + O ₂)		
		V ₂ O ₅	MoO ₃	NO	NH ₃	SO
Type A (aqueous)	V ₂ O ₅ /TiO ₂	10	-	39	85	97
	MoO ₃ -V ₂ O ₅ /TiO ₂	10	10	71	95	93
Type B (non-aqueous)	V ₂ O ₅ /TiO ₂	10	-	42	87	97
	MoO ₃ -V ₂ O ₅ /TiO ₂	10	5	68	93	95
	MoO ₃ -V ₂ O ₅ /TiO ₂	10	10	81	96	96

Table 4. Physical properties of various catalysts

Preparation method	Catalysts	Loading (wt%)		Surface area (m ² /g)
		V ₂ O ₅	MoO ₃	
Aqueous	V ₂ O ₅ /TiO ₂	10	-	130.0
	V ₂ O ₅ -MoO ₃ /TiO ₂	10	10	121.3
Non-aqueous	V ₂ O ₅ /TiO ₂	10	-	142.0
	V ₂ O ₅ -MoO ₃ /TiO ₂	10	10	144.2

lyst prepared by non-aqueous solution method seems associated with the new formation of VOSO₄ on the surface of catalyst by the contact of SO₂ as suggested by Teraoka et al. [9]. For SO₂ conversion in this study on various catalysts showed exceptionally high % conversion without regarding the types of catalyst (from 90-98% conv.). In general, the SO₂ conversion increases as the reaction temperature increases, and the relatively high reaction temperature of 350°C at present studies might result in high values of SO₂ conversion. However, considering that some of ammonium sulfate formation could be found in the down-stream of reactor system, the values of SO₂ conversion might be somewhat over-estimated.

2-2. Characterization

2-2-1. Surface Area and XRD Analysis

In order to estimate the difference in surface properties between the catalysts prepared by different methods, the BET surface areas and XRD patterns are examined.

Table 4 summarized the BET areas for two different types of catalysts. While the BET areas of catalyst prepared by conventional aqueous method were reduced by the addition of MoO₃, those of catalysts prepared by non-aqueous method showed almost same values. And the values of BET areas of catalyst prepared by aqueous method were 10-20% less than those of catalysts prepared by non-aqueous method. This implies that the conventional aqueous impregnation method had severe pore plugging phenomena than that of non-aqueous one through the catalyst preparation process.

Fig. 5 shows the XRD patterns for aqueous and non-aqueous catalyst systems. In V₂O₅/TiO₂ catalyst system, there were no peaks of V₂O₅ except TiO₂ of anatase regardless of catalyst preparation method. It means that V₂O₅ supported on TiO₂ is armorphous state with very small particle size. In contrast with that, when MoO₃ was added into V₂O₅/TiO₂ system, there were remarkable changes of XRD patterns with regard to catalyst preparation method. In aqueous catalyst, a large number of bulk MoO₃ were detected

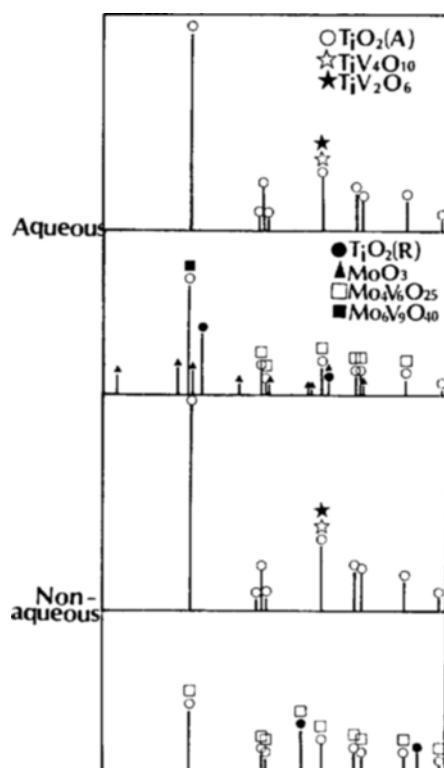


Fig. 5. XRD patterns for V₂O₅-TiO₂ (aqueous, non-aqueous) and MoO₃-V₂O₅-TiO₂ (aqueous, non-aqueous).

with some intermediates of Mo₆V₆O₂₅ and Mo₉V₉O₄₀. But, in non-aqueous system, there was no bulk MoO₃ and all of the XRD patterns were intermediates except TiO₂ patterns. From these results, therefore, more enhancement of NO reduction activity on non-aqueous MoO₃-V₂O₅/TiO₂ is due to the vigorous formation of solid solution between V and Mo. A little transition of TiO₂ structure from anatase to rutile was found because of 2 stage calcination in the preparation of MoO₃-V₂O₅/TiO₂ catalysts.

2-2-2. IR Spectra Results

In order to monitor the surface redox sites (V=O and Mo=O) change depending upon the catalyst preparation method and upon the contacting of reactant such as SO₂, IR spectroscopic studies were performed. Fig. 6 shows the V=O stretching band of V₂O₅/TiO₂ and MoO₃-V₂O₅/TiO₂ catalysts prepared by aqueous and non-aqueous methods. V=O stretching band could be found at around 1016 cm⁻¹. Also by the addition of MoO₃, Mo=O stretching band was newly observed at 992 cm⁻¹, and the V=O band intensity was

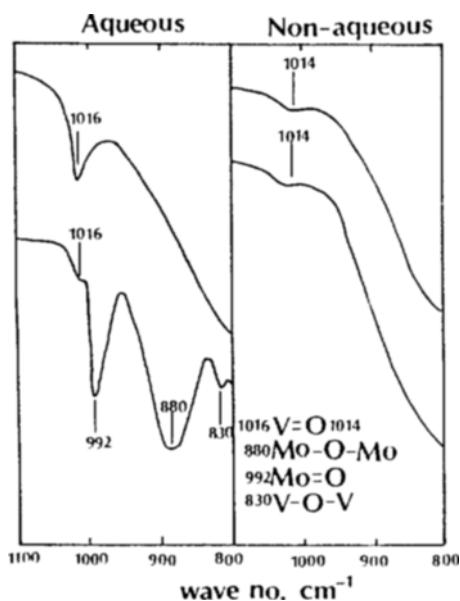


Fig. 6. IR spectra for fresh V₂O₅/TiO₂ (aqueous, non-aqueous) and MoO₃-V₂O₅/TiO₂ (aqueous, non-aqueous).

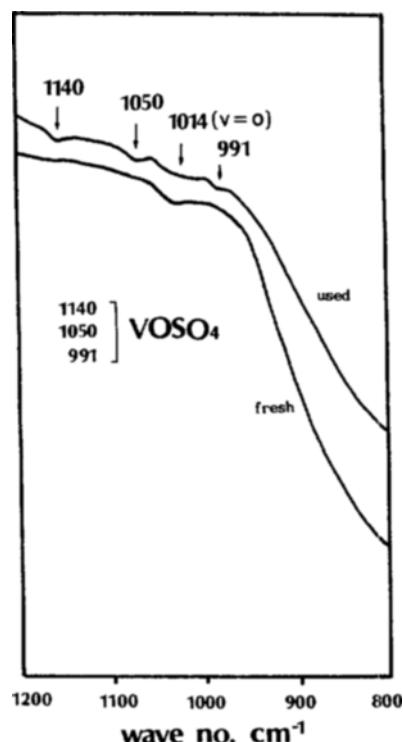


Fig. 7. IR spectra for fresh and used MoO₃-V₂O₅/TiO₂ (non-aqueous).

very weakened and slightly shifted to the lower wave range in the case of MoO₃-V₂O₅/TiO₂ (aqueous). Broad and large band at around 880 cm⁻¹ was assignable to the combination band of Mo-O-Mo stretching and lattice vibration. Also V-O-V stretching and lattice vibration band could be found at around 830 cm⁻¹. Those results are well consistent with the reports by Satsuma [6] and Teraoka [9]. Therefore it could be easily explained that the enhancement of activity by the addition of MoO₃ into the V₂O₅/TiO₂ catalyst prepared (aqueous) is contributed by the newly formed Mo=O species on intermediate compounds which acts as the redox site. However, in the case of catalyst prepared by non-aqueous method showed no significant evidence for the existence of V=O and Mo=O species. Same phenomenon was reported by Teraoka et al. [9]. However, since the activity for NO_x reduction on MoO₃-V₂O₅/TiO₂ catalyst (non-aqueous) was higher than the catalyst (aqueous), there must exist any kind of active sites. Teraoka postulated that the V=O band was not visible as a peak, probably it shifted to lower wave number to become a shoulder overlapping with the strong absorption of TiO₂. However, the speculation by Teraoka et al. [9] may not be probable since some trace of V=O band at 1014 cm⁻¹ was detected at present study. Another explanation of the more enhanced activity of the MoO₃-V₂O₅/TiO₂ (non-aqueous)

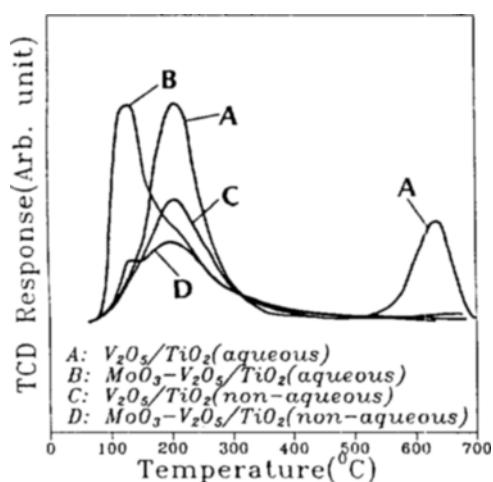


Fig. 8. NH₃ TPD patterns for various catalysts.

might be the growth of new band through the contacting of SO₂. The used catalyst, after contacting of SO₂, the growth of new band at 991, 1050 and 1140 cm⁻¹ were exhibited as shown in Fig. 7, which are assignable to vanadium oxisulfate (VOSO₄). Additional

activity on the basis of speculation by Teraoka et al. [9], the formation of VOSO_4 at present studies might be responsible to the enhanced activity for NO_x reduction, though the role of MoO_3 on the surface was not explained satisfactorily.

2-2-3. NH_3 TPD Results

To investigate the acid site distribution of aqueous and non-aqueous catalysts, Temperature Programmed Desorption (TPD) of chemisorbed NH_3 was carried out, and the results are shown in Fig. 8. In $\text{V}_2\text{O}_5/\text{TiO}_2$ (aqueous), there are two kinds of NH_3 desorption peaks at 200°C and 630°C. It means that aqueous $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst has both of weak and strong acid sites. But, when MoO_3 is added in that system, strong acid site disappeared with shifting of weak acid site to lower temperature (110°C), which is probably because of bulk MoO_3 . Remarkable changes of acid properties are progressed with the differences of catalyst preparation, and any correlations between catalyst activities and acidities could not be found.

CONCLUSION

1. WO_3 Addition Effects

At higher reaction temperature range (300-450°C), WO_3 and $\text{WO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$ catalysts showed a significant high conversion in NO reduction with NH_3 while $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst showed a significant decrease in selectivity mainly due to the excess side reaction of NH_3 oxidation. This difference in selectivity to NH_3 oxidation at high temperature is supposed to be associated with the difference in values of surface excess oxygen between WO_3 and V_2O_5 on titania.

The surface acidities of tested catalysts were relatively well correlated with the % conversion of NO at 400°C.

2. MoO_3 Addition Effects

From the activity measurements, the catalytic activity for the simultaneous removal of NO_x and SO_x were quite enhanced by the addition of MoO_3 into $\text{V}_2\text{O}_5/\text{TiO}_2$

catalysts. The enhanced activities responsible for the formation of $\text{Mo}=\text{O}$ bond on the intermediate species produced by solid solutions on $\text{MoO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$ (aqueous). However, in the case of $\text{MoO}_3\text{-V}_2\text{O}_5/\text{TiO}_2$ (non-aqueous), the exact source of active site was not able to detect in IR spectra in spite of more enhanced activity was obtained in this study. After SO_2 contact, VOSO_4 is newly formed on the surface of catalyst, which supposed to be associated with the activity enhancement.

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