

Structural Study on Promoting Actions of Titanium Dioxide and Stannic Oxide on Vanadium Pentoxide Catalysts

Satohiro YOSHIDA, Tomoaki MURAKAMI, and Kimio TARAMA*

Received June 13, 1973

Promoting actions of TiO_2 and SnO_2 on vanadium oxide catalysts have been investigated from structural point of view. Though X-ray diffraction revealed the crystal structure of vanadium oxide to be the same as pure vanadium oxide, infrared spectra and magnetic susceptibility showed the increase of four valent vanadium ions in the catalysts in the case of TiO_2 promoted catalysts. On the other hand, in the case of SnO_2 promoted catalysts, infrared spectra showed the existence of weakened $\text{V}=\text{O}$ bonds. The promoting actions of the two oxides have been discussed on the basis of the results mentioned above.

INTRODUCTION

Promoted vanadium oxide (V_2O_5) catalysts are widely used for the oxidation of organic compounds. As the promoters, a wide variety of compounds such as MoO_3 , WO_3 , K_2SO_4 , P_2O_5 and so on are reported. We have been investigated the promoting actions of some oxides mentioned above from the structural point of view.¹⁾ Recently we have studied the promoting actions of TiO_2 and SnO_2 . Although they are used in the industrial manufacturing of phthalic anhydride by oxidation of naphthalene, fundamental studies of the promoting actions of them are very few.

Fabuss proposed that TiO_2 should be regarded as a structural promoter and SnO_2 as an adlineation promoter, though the basis of the proposal was not clear.²⁾ Sachtler *et al.* investigated V_2O_5 - SnO_2 catalysts in connection with their thermodynamic properties and concluded that catalytic activity and selectivity of the catalysts correlated with free energy and enthalpy change in reduction process of the catalysts.³⁾

In the present work, we investigated some physico-chemical properties of the V_2O_5 - TiO_2 and V_2O_5 - SnO_2 catalysts by means of X-ray diffraction, infrared spectroscopy and magnetic susceptibility measurements as well as reducibilities by propylene and discussed the promoting actions of TiO_2 and SnO_2 .

EXPERIMENTAL

2.1 Materials

V_2O_5 was prepared by thermal decomposition of extra pure grade ammonium metavanadate in dry air at 450°C . This V_2O_5 was mixed with extra pure grade

* 吉田郷弘, 村上知明, 多羅間公雄: Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University, Kyoto and Laboratory of Crystal and Powder Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

Table I. Samples

V_2O_5 - TiO_2			V_2O_5 - SnO_2		
V_2O_5 : TiO_2 mol ratio	Apparent state after heating	color of powder	V_2O_5 : SnO_2 mol ratio	Apparent state after heating	color of powder
100: 0	needle crystal	light orange	100: 0	needle crystal	light orange
95: 5	"	"	95: 5	"	"
85: 15	"	dark yellow brown	85: 15	"	"
75: 25	"	"	75: 25	needle crystal +briquette	"
67: 33	"	"	67: 33	"	"
50: 50	briquette	"	50: 50	briquette	"
33: 67	"	"	33: 67	powder	"
25: 75	"	"	25: 75	"	"
10: 90	powder	dark brown	10: 90	"	"
5: 95	"	dark gray	1: 99	"	yellowish white
3: 97	"	gray	0:100	"	white
1: 99	"	white			
0:100	"	"			

TiO_2 (anatase) or SnO_2 in a given ratio and melted in a crucible at 700°C for 30 min.* After cooling, the obtained samples were apparently homogeneous porous masses when promoters were contained less than 50 mol%. While, apparent powder briquettes were obtained for the samples containing promoters 50–70 mol% and when promoters were mixed in much higher concentration, the obtained samples were in the state of powder. All samples were ground to powder in an agate mortar. The compositions of catalysts samples are tabulated in Table I.

Propylene (C_3H_6) from a commercial bomb (99% pure) was used for reduction of the catalysts.

2.2 Apparatus and Procedure

X-ray diffraction experiments were carried out by a Shimadzu GX-III B X-ray diffractometer with Cu target at room temperature. Magnetic susceptibilities were measured by a Shimadzu MB2B recording magnetic balance according to Faraday method. Infrared spectra of samples dispersed in KBr disks were recorded on a Jasco IRA-2 spectrometer with in the wave number range of 4000–400 cm^{-1} .

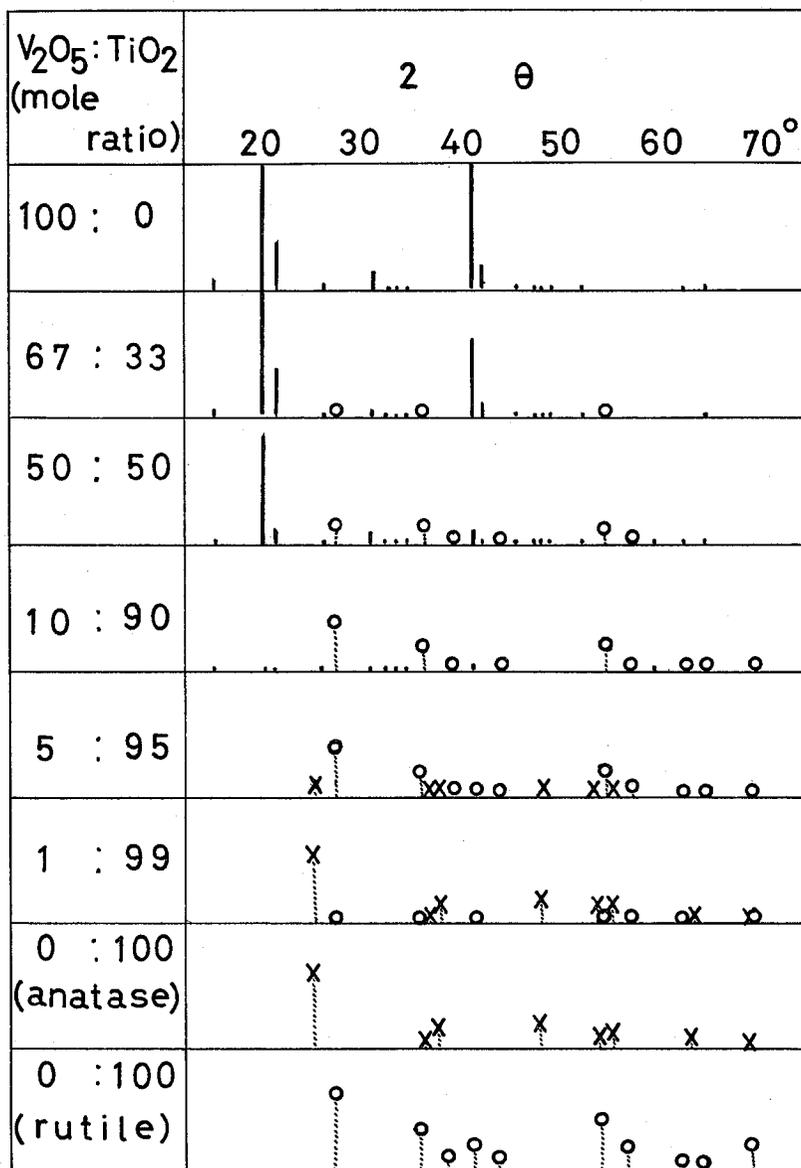
The reduction process of a catalyst by C_3H_6 was followed by measuring the weight decrease of the sample. For this purpose, a Shimadzu MTB-50 micro electrothermal balance was used under following conditions; amount of a sample, 50 mg; feed rate of C_3H_6 , 100 ml/min; temperatures, 300, 315 and 330°C. The sample was heated to a temperature mentioned above in air and after the weight of the sample reached a constant value, a stream of dry nitrogen was passed through the apparatus to displace the air for 15 min and then C_3H_6 gas made to flow.

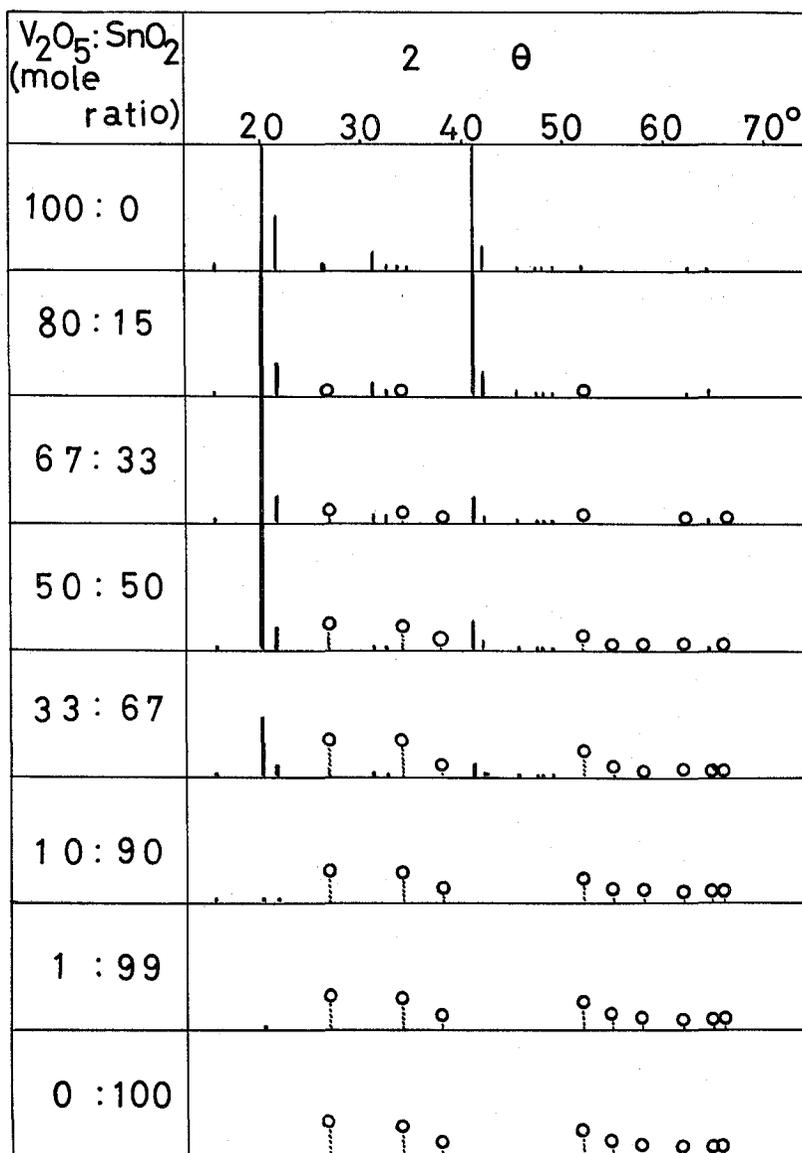
* Melting points of V_2O_5 , TiO_2 and SnO_2 are 690°, 1640° and 1127°C, respectively.

EXPERIMENTAL RESULTS

3.1 X-ray diffraction

X-ray diffraction diagrams of V_2O_5 - TiO_2 and V_2O_5 - SnO_2 catalysts of various compositions are shown in Fig. 1 and Fig. 2, respectively. In the both figures, the diffraction peaks due to V_2O_5 did not change in its position but decreased in the relative intensities by addition of TiO_2 and SnO_2 . This fact differs from the results obtained in V_2O_5 - MoO_3 or V_2O_5 - WO_3 systems.⁴⁾ In the figures, the diffraction peaks due to the other components, TiO_2 or SnO_2 , can be found and it should be

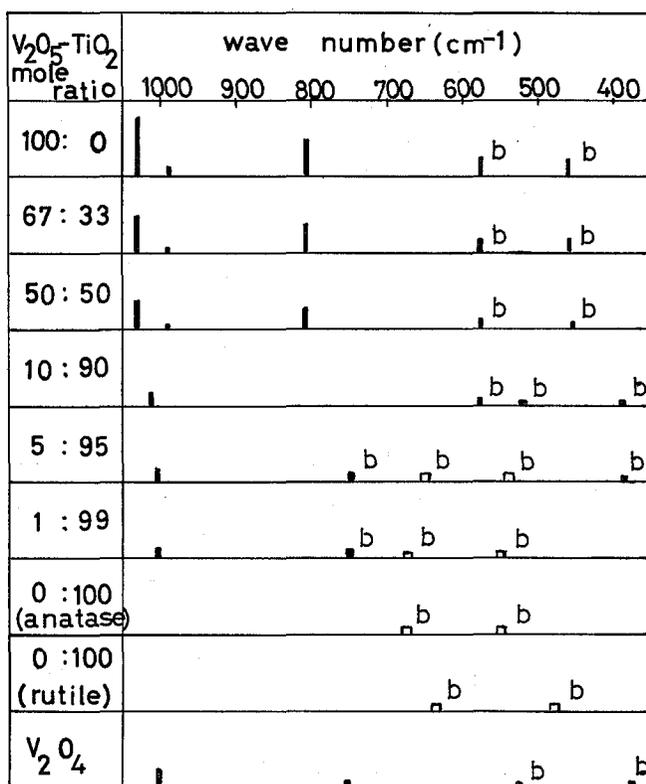
Fig. 1. X-ray diffraction diagrams of V_2O_5 - TiO_2 .

Fig. 2. X-ray diffraction diagrams of V₂O₅-SnO₂.

noticed that in the case of V₂O₅-TiO₂, peaks due to "rutile" TiO₂ were observed in the samples of wide range of composition (TiO₂, 15-99 mol%), while peaks due to "anatase" TiO₂ which was the starting material are found only in the sample containing TiO₂ more than 95 mol%. X-ray diffraction measurements showed that no modification occurred in pure "anatase" TiO₂ by heating at 700°C for 30 min.

3.2 Infrared absorption spectra

Figure 3 and Fig. 4 are diagrammatic presentation of infrared spectra of V₂O₅-TiO₂ and V₂O₅-SnO₂ catalysts, respectively. It is interesting that in the case of

Fig. 3. IR absorption diagrams of V₂O₅-TiO₂. b: broad peak

V₂O₅-TiO₂ system, the spectra of samples containing TiO₂ less than 75 mol% are essentially the same as the spectrum of V₂O₅, while the samples containing TiO₂ more than 90 mol% give the absorption peaks due to V₂O₄ and "rutile" TiO₂. The peaks due to "anatase" TiO₂ can be observed only in the spectrum of 99 mol% TiO₂ sample.

In the case of V₂O₅-SnO₂ system, the very similar spectra to each other were obtained for the samples containing SnO₂ 0-67 mol%. The peaks due to SnO₂ can be observed in the samples containing SnO₂ more than 75 mol%. It is noteworthy that the absorption band of 1025 cm⁻¹ (assigned as V=O stretching vibration mode) shifted to lower frequency side (to 1005 cm⁻¹), when the content of SnO₂ was more than 50 mol%. In this system, absorption peaks due to V₂O₄ can not be observed.

Though X-ray diffraction peaks due to promoters were observed for the samples of wide range of composition, infrared spectra showed the existence of promoters in the samples containing promoters more than 70-80 mol%. This contradiction should arise from the difference of penetrating power of X-ray and infrared ray into solid, and infrared spectra can contain the information about surface much more than the information about bulk phase. The same phenomena mentioned above have been observed previously.⁵⁾ So, it can be concluded that these samples were not homogeneous and vanadium oxide was much rich in the surface phase compared with composition as a whole.

V ₂ O ₅ :SnO ₂ (mole ratio)	Wave number (cm ⁻¹)						
	1000	900	800	700	600	500	400
100:0						b	b
85:15						b	b
67:33						b	b
50:50						b	b
33:67						b	b
10:90						b	b b
1:99						b b	b
0:100						b b	b

Fig. 4. IR absorption diagrams of V₂O₅-SnO₂. b: broad peak

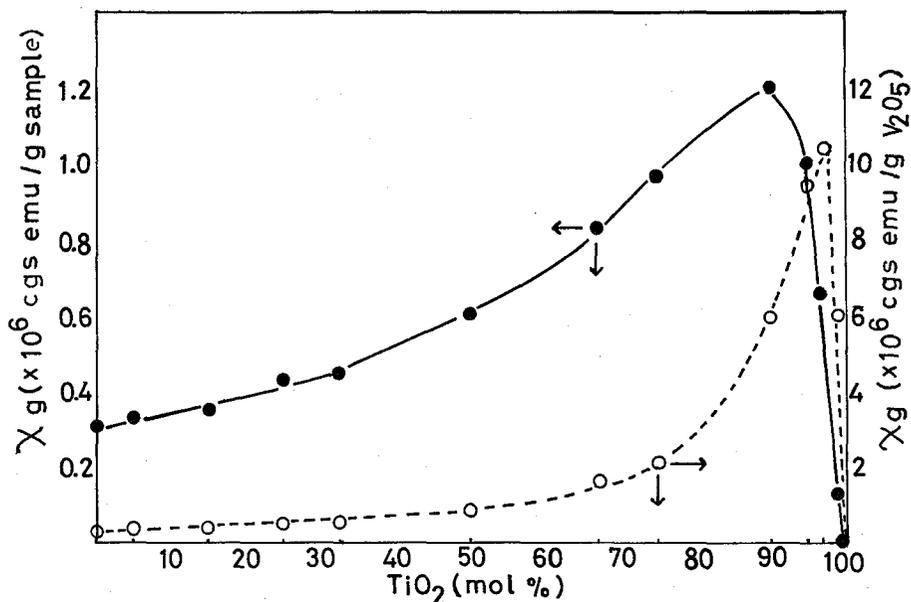


Fig. 5. Magnetic susceptibility of V₂O₅-TiO₂. The solid line is magnetic susceptibility per 1 g sample and the dotted line is magnetic susceptibility per 1 g V₂O₅ contained in a sample.

Promoting Action of TiO₂ and SnO on V₂O₅

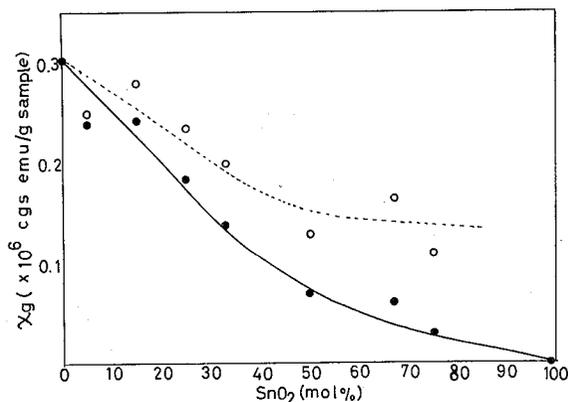


Fig. 6. Magnetic susceptibility of V₂O₅-SnO₂. The solid and dotted lines have the same meanings as in Fig. 5.

3.3 Magnetic susceptibility

In an earlier paper,⁶⁾ we reported that a melted V₂O₅ has a paramagnetic susceptibility (χ_g) corresponding to 0.7 atom% of V⁴⁺ ions in the sample. The χ_g can be used as a quantitative index of V⁴⁺ (3d¹ electron configuration, paramagnetic ion) concentration in V₂O₅ catalysts. Figures 5 and 6 show variation of χ_g with composition. Dotted lines in the figures show χ_g , per 1 g of V₂O₅ ($\chi_{gV_2O_5}$) calculated from the composition of samples.

From the Fig. 5, ratio of V⁴⁺ to total V ions increased gradually in a range of TiO₂ 0–50 mol% and remarkably in the samples containing TiO₂ more than 50 mol%.

On the other hand, in V₂O₅-SnO₂ system, $\chi_{g \text{ sample}}$ decreased gradually with increase of SnO₂ content as shown in Fig. 6. In this case, $\chi_{gV_2O_5}$ also decrease to the sample of V₂O₅ : SnO₂ = 1 : 1 and then become constant.

3.4 Reduction by propylene

Reduction of V₂O₅-Al₂O₃ or -SiO₂ by benzene vapor has been reported.⁷⁾ The qualitative feature of reduction curve of V₂O₅-TiO₂ and V₂O₅-SnO₂ are the same as V₂O₅-Al₂O₃, that is, weight decrease with time followed parabolic curve.

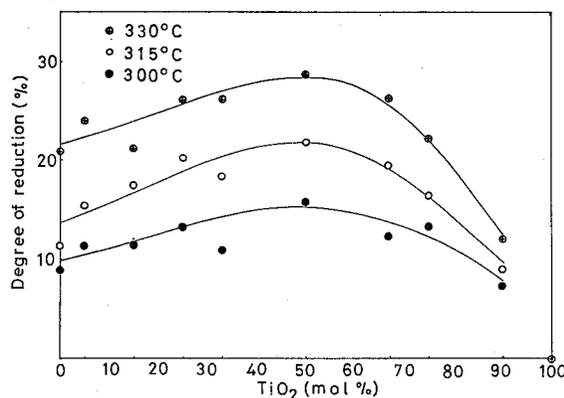


Fig. 7. Reducibility of V₂O₅-TiO₂: the degree of reduction at 50 min.

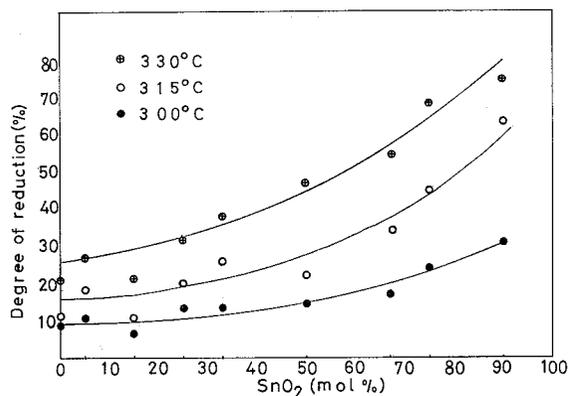


Fig. 8. Reducibility of V_2O_5 - SnO_2 : the degree of reduction at 50 min.

As a measure of reducibility of samples the degree of reduction at 50 min in a reduction curve was adopted. Degree of the reduction was defined as % of V^{4+} to total V ions, that is, V_2O_4 is regarded as 100% reduced sample.

The results are shown in Fig. 7 and Fig. 8. In the case of V_2O_5 - TiO_2 , the reducibility changed with composition as volcano type and maximum reducibility was obtained at 50 mol% TiO_2 sample. On the other hand, the reducibility of V_2O_5 - SnO_2 samples increased monotonously with increase of SnO_2 content. TiO_2 (anatase) itself did not show weight decrease under the same condition. Although SnO_2 was reduced to very small extent (weight decrease of about 1% was observed by 50 min reduction), it seemed to be negligible and it is assumed that both TiO_2 and SnO_2 themselves were not reduced in the mixed catalysts.

DISCUSSION

Although TiO_2 and SnO_2 have been used as promoters of vanadium oxide catalysts, the promoting effects are mainly cited in patents and the mechanism of the promoting actions have not been clarified. Fabuss reported that maximum efficiency of the TiO_2 corresponded to a 1 : 1 mol ratio of V_2O_5 and TiO_2 , while the SnO_2 promoter was effective in a much wider concentration range, from 10 to 55 mol%.²⁾ And he concluded that the TiO_2 promoter apparently stabilized the structure of the catalyst coating, while at the same time the SnO_2 promoter acted possibly as an adlineation promoter, significantly increasing the number of lattice defects in the catalyst coating.

His concluding based on the reduction rate measurement of only three mixed samples for each promoters and experimental background seems to be unsatisfactory. We attempted to discuss the promoting effects of these promoters on the basis of experimental results mentioned above section from structural point of view.

From the results of X-ray diffraction measurements, no evidence of formation of a new compound was obtained, as each diffraction peak of samples can be assigned to V_2O_5 or promoters. Further, peak positions (diffraction angle, 2θ) in the diffraction patterns agreed very closely with the values of pure V_2O_5 or promoters and signif-

icant shift can not be observed.

In the case of V₂O₅-MoO₃ system, significant shifts were observed in diffraction peaks of V₂O₅, when content of MoO₃ was less than 25% and this fact was regarded as an evidence of formation solid solution.¹⁾ The present result of X-ray diffraction measurements seems to show that V₂O₅ was only dispersed in promoters as small crystallites. Effect of TiO₂ or SnO₂ on crystal structure of V₂O₅ can not be discussed from the X-ray diffraction measurements.

The remarkable result clarified by X-ray diffraction study is that "anatase" TiO₂ is modified to "rutile" TiO₂ at a low temperature. Though the mechanism of the easy modification is not clear at present, V ions should act as a kind of catalyst for the modification.

In TiO₂ crystals, a Ti ion was surrounded by six oxygen ions and each bond length between Ti and oxygen are almost identical and TiO₆ unit forms almost regular octahedron in "rutile" TiO₂, while in "anatase" TiO₂ the octahedron is distorted.⁸⁾ SnO₂ is also a rutile type crystal. In V₂O₅ a V ion was also surrounded by six oxygen ions, but in this case, one oxygen ion is placed very closely to V ion and VO₆ unit forms square bipyramid.

Therefore, the stable crystal structure of V₂O₅ differs significantly from that of TiO₂ and SnO₂, so the formation of solid solution between V₂O₅ and TiO₂ or SnO₂ would be impossible.

On the other hand, infrared spectra exhibited the existence of V₂O₄ in V₂O₅-TiO₂ samples. The existence of V⁴⁺ ions in high concentration was also revealed by the results of magnetic susceptibility for the samples of high TiO₂ content. As TiO₂ has a high melting point, during the sample preparation, TiO₂ does not melt and melted vanadium oxide was deposited on the TiO₂.

In melted state, V₂O₅ lose some oxygen and V⁴⁺ were formed.⁶⁾ When the vanadium oxide becomes to be deposited on TiO₂ in cooling procedure, the crystal growing on the textile of TiO₂ will tend to form a resemble structure of TiO₂ by epitaxy phenomena. V₂O₄ has a similar crystal structure to "rutile" TiO₂, the V⁴⁺ ions will be stabilized as V₂O₄ when the deposited layer is thin, that is, the content of V₂O₅ is small. The same phenomena have been observed in V₂O₅-Al₂O₃ and -SiO₂ systems.⁷⁾

On the other hand, in V₂O₅-SnO₂ system, no evidence for the formation of V₂O₄ or low valent vanadium ions was obtained by X-ray diffraction, infrared spectroscopy and magnetic susceptibility measurements, though SnO₂ has also a "rutile" type structure. The difference of structure of vanadium oxide on TiO₂ and SnO₂ will be resulted from the difference of oxidation ability between TiO₂ and SnO₂. SnO₂ itself has oxidation ability and in the present work, SnO₂ was reduced by C₃H₆, even if to small extent. Ozaki and Morooka adopted $-\Delta H_f^0$ (heat of formation divided by the number of oxygen atoms of metal oxide) as a measure of bond strength of oxygen to metal ion and the larger catalytic activity of oxidation by the metal oxides is observed, the smaller value of $-\Delta H_f^0$.⁹⁾ Heats of formation of TiO₂ and SnO₂ are reported as 218 kcal/mol and 139 kcal/mol, respectively.¹⁰⁾ Following Ozaki's observation, SnO₂ has more oxidation ability than TiO₂. Therefore, V⁴⁺ will be oxidized to V⁵⁺ on the surface of SnO₂, before it is stabilized as V₂O₄.

On the reduction by C₃H₆, it was found that the sample of 1 : 1 mol ratio of V₂O₅

and TiO_2 had a maximum reducibility in TiO_2 promoted catalysts and this is consistent with Fabuss' results. In connection with promoting effect of SnO_2 it was found that the higher the content of SnO_2 is, the larger the reducibility become. Fabuss reported the same tendency of the change of reducibility for the $\text{V}_2\text{O}_5\text{-SnO}_2$ catalysts containing SnO_2 to 50 wt% (55 mol%).

As mentioned above section, reduction curves followed generally parabolic curves. This suggests that the slowest step in reduction is the diffusion step of oxygen through the bulk phase. To ascertain the role of diffusion step on reduction rate, applicability of Jander equation was tested.

Jander equation has been derived for solid phase reaction, in which mass transfer occurs by diffusion process.

$$[1 - (1 - \alpha)^{1/3}]^2 = kt$$

where α is degree of reaction.¹¹⁾

Two examples of Jander plot are given in Fig. 9 and Fig. 10. In the case of $\text{V}_2\text{O}_5\text{-TiO}_2$, all samples for which measurable weight decrease were observed, obey Jander

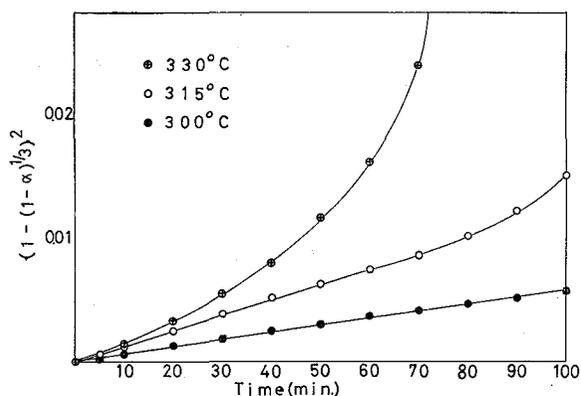


Fig. 9. Jander plot for the reduction of a $\text{V}_2\text{O}_5\text{-TiO}_2$ sample (1 : 1 mol ratio). α : degree of reduction

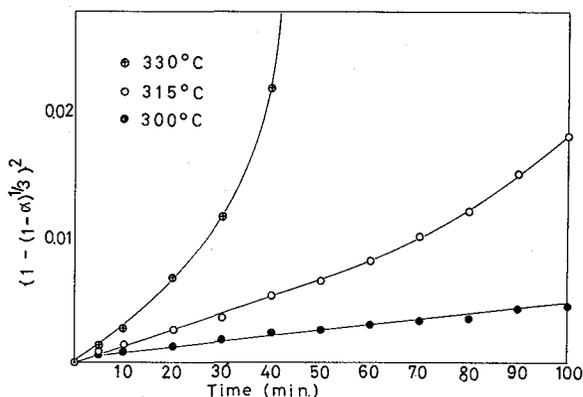


Fig. 10. Jander plot for the reduction of a $\text{V}_2\text{O}_5\text{-SnO}_2$ sample (1 : 1 mol ratio). α : degree of reduction

equation at 300°C . While, at 315°C the linearity became poor in the later period of reduction for the samples containing TiO_2 10–67 mol% and others also obeyed the equation. At 330°C , all samples except 90% TiO_2 sample did not obey the equation.

In the case of SnO_2 promoted catalysts, general feature was the same as V_2O_5 – TiO_2 catalysts. But in this case, the deviation from Jander equation was very significant at 315°C and all samples did not obey the equation at 330°C .

The fitness of reduction rate to Jander equation shows the rate determining step of the reduction is the diffusion process of oxygen through bulk phase. At 315°C , the reduction rate of promoted sample of higher reducibility than V_2O_5 did not obey the equation. Thus, in these catalysts, diffusion of oxygen is easier than unpromoted catalyst and should have a comparable to the surface reaction between oxygen ion and adsorbed C_3H_6 . In other words, oxygen ions should be more labile in promoted catalysts than in V_2O_5 .

The enhanced mobility of oxygen in promoted catalysts can be explained as follows.

In TiO_2 promoted catalysts, vanadium oxide has the same structure as V_2O_5 but it contains a larger amount of V^{4+} than pure V_2O_5 judging from χ_g measurement. This means the creation of oxygen defects in bulk phase. As oxygen ions diffuse in crystal through the oxygen defects, the increase of V^{4+} ions is favorable for oxygen diffusion.

On the other hand, in SnO_2 promoted catalysts, no evidence of increase of oxygen defects but infrared spectroscopy showed that $\text{V}=\text{O}$ bonds in the catalyst became weaker than in V_2O_5 . Therefore, oxygen of $\text{V}=\text{O}$ bond is more reducible in promoted catalysts than in V_2O_5 and after uptake of oxygen of $\text{V}=\text{O}$ bond by C_3H_6 , oxygen defects are created. Thus oxygen defects are created during reduction process.

As a conclusion, promoting action of TiO_2 can be attributed to the formation V^{4+} in the TiO_2 surface and to the creation of oxygen defects, while promoting action of SnO_2 to the weakening the $\text{V}=\text{O}$ bonds in V_2O_5 crystal.

REFERENCES

- (1) K. Tarama, S. Teranishi, S. Yoshida, and N. Tamura, "Proceedings of 3rd Int. Congress on Catalysis", North-Holland Pub. Co., Amsterdam (1965) p. 282; *This Bulletin*, **47**, 246 (1969).
- (2) B. M. Fabuss, "Actes 2eme Congres Int. Catalyst", Edition Technip, Paris (1961) p. 2561.
- (3) W. Sachtler, G. Dorgels, J. Fahrenfort, and R. Voorhoeve, *Recuel. trav. chim.*, **89**, 460 (1970).
- (4) K. Tarama, S. Teranishi, N. Tamura, and S. Yoshida, *Shokubai (Catalyst)*, **4**, 346 (1971).
- (5) K. Tarama, S. Teranishi, and S. Yoshida, *This Bulletin*, **46**, 185 (1968).
- (6) K. Tarama, S. Teranishi, S. Yoshida, N. Tamura, and S. Ishida, *Kogyo Kagaku Zasshi*, **68**, 1944 (1965).
- (7) S. Yoshida, T. Iguchi, S. Ishida, and K. Tarama, *Bulletin Chem. Soc. Japan*, **45**, 376 (1972).
- (8) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry" 2nd ed., Interscience Pub., New York (1966) p. 802.
- (9) A. Ozaki and Y. Morooka, *J. Catalysis*, **5**, 116 (1966).
- (10) National Bureau Standards Circular 500 "Selected Values of Chemical Thermodynamic Properties" **Part I** (1961).
- (11) W. Jander, *Z. anorg. u. allgem. Chem.*, **163**, 1 (1927).