BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 716—721 (1968)

A Study on Mixed Vanadium Catalysts for the Ammoxidation of Xylene

Masatomo ITO, Hazime TANAKA and Akira MATSUMOTO

The Central Research Laboratory, Showa Denko K. K., Tamagawa, Ohta-ku, Tokyo

(Received September 23, 1967)

The phase composition and the physicochemical properties of an antimony-vanadium catalyst and a chromium-vanadium catalyst for the ammoxidation of xylene were studied by X-ray diffraction method, differential thermal analysis, infrared absorption analysis and ESR measurement. An antimony-vanadium catalyst consisted essentially of $SbVO_4$ which contained no double covalent bond V=O, while a chromium-vanadium catalyst consisted essentially of a chemical compound which was different from $CrVO_4$. $SbVO_4$ and $CrVO_4$ were hard to be reduced with ammonia at 400°C, while a chemical compound in the chromium-vanadium system was reducible. The activity and the selectivity of reaction were affected by the nature and the distribution of metal ions and oxygen ion on surface.

The kinetic study of the vapor-phase ammoxidation of xylene over a vanadium oxide catalyst and mixed vanadium catalysts, an antimony-vanadium catalyst and a chromium-vanadium catalyst, showed that the rate and the selectivity of the reaction were affected by the adsorbability and the reactivity of related reactants.1) A basic study on mixed vanadium catalysts for the ammoxidation of xylene was, therefore, of interest in order to gain a better understanding of the reaction processes which take place on the catalyst surface.

The present study is an attempt to clarify the physicochemical properties of mixed vanadium catalysts for the ammoxidation of xylene.

Experimental

Sample Preparation. Catalyst samples, which were free of carrier, were prepared by mixing a solution of vanadyl oxalate with a solution of chromium oxalate or a solution of vanadyl tartarate with a solution of antimonyl tartarate in the desired proportions. After evaporating the mixture to dryness on a steam bath the sample was calcinated in air for periods up to 2 days.

Physical Measurement. The powder-type X-ray diffraction patterns of samples were recorded using a Rigaku Denki model D-2F Geigerflex with a copper target.

The infrared absorption spectra of samples were recorded using a JASCO model IR-S infrared spectrophotometer and preparing the samples in the form of KBr pressed discs (1 mg sample in 0.5 g KBr).

The differential thermal analysis curves for the samples were run in air heating at a rate of 10°C/min using a Shimadzu model DT-1A differential thermal analyzer.

The ESR absorption spectra of samples were measured at room temperature by using the same apparatus and procedure employed in a previous work.2)

---

1) M. Ito and K. Sano, This Bulletin, **40**, 1321 (1967).

2) H. Tanaka and A. Matsumoto, *ibid.*, **39**, 876 (1966).

The oxygen loss during the reduction of samples with ammonia was determined at 400°C by using a Shimadzu thermal balance. Weighed powdered sample (0.3 g) was heated to 400°C in a nitrogen atmosphere and ammonia was then introduced at a rate of 200 cc/min.

Results

Antimony-Vanadium System. The differential thermal analysis curves of the mixtures of an antimonyl tartarate and a vanadyl tartarate are shown in Fig. 1. Taking account of the X-ray diffraction patterns (Fig. 2) of samples which were treated in air at desired temperature for 4 hr, they were interpreted in the following way. The endothermic peak in the range from 100 to 200°C and the following exothermic peak in the range from 200 to 300°C were ascribed to the dehydration and the decomposition of tartarates respectively. Two exothermic peaks at 300 and 420°C in an antimonyl tartarate were seemed to indicate the formation of antimony trioxide(cubic type) and tetraoxide (orthorombic type) respectively. In mixed tartarate samples a new crystal phase was formed below 300°C. This new crystal phase was in good agreement with one which was prepared by treating the equimolar mixture of antimony trioxide and vanadium pentoxide in a sealed Pt tube at 700°C.[3] The exothermic peaks near 400°C were seemed to be ascribed to the crystallization of this chemical compound and the temperature at the last peak was regarded the melting point.

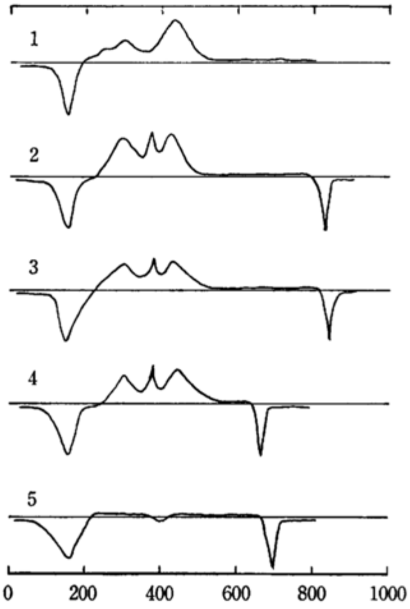

Fig. 1. Differential thermal analysis curve of the mixture of antimonyl tartarate and vanadyl tartarate.
Sb/V ratio: 1) 1/0, 2) 2/1, 3) 1/1, 4) 1/2, 5) 0/1

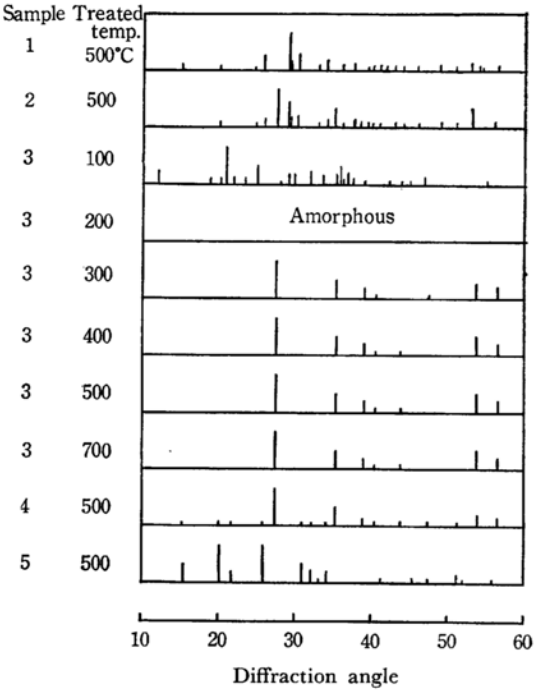

Fig. 2. X-Ray diffraction pattern of antimony-vanadium sample.
Sb/V ratio: 1) 1/0, 2) 2/1, 3) 1/1, 4) 1/2, 5) 0/1

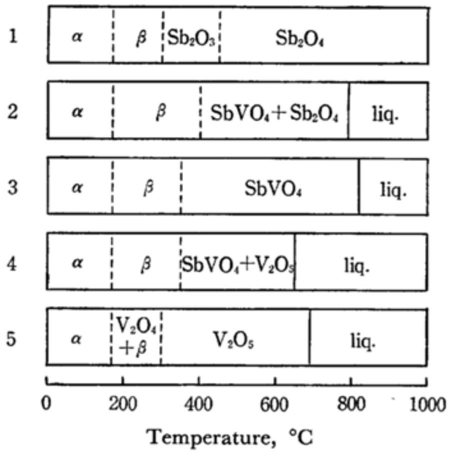

Fig. 3. Phase diagram in antimony-vanadium system.
Sb/V ratio: 1) 1/0, 2) 2/1, 3) 1/1, 4) 1/2, 5) 0/1

In view of above results, the phase diagram in this system is presented in Fig. 3. The α-phase was the crystalline of tartarates and the β-phase was the amorphous intermediate.

Infrared absorption spectra of the samples are shown in Fig. 4. The mixed sample in the atomic

---

[3] R. S. Roth and J. L. Waring, *Am. Mineral.*, **48**, 1348 (1963).

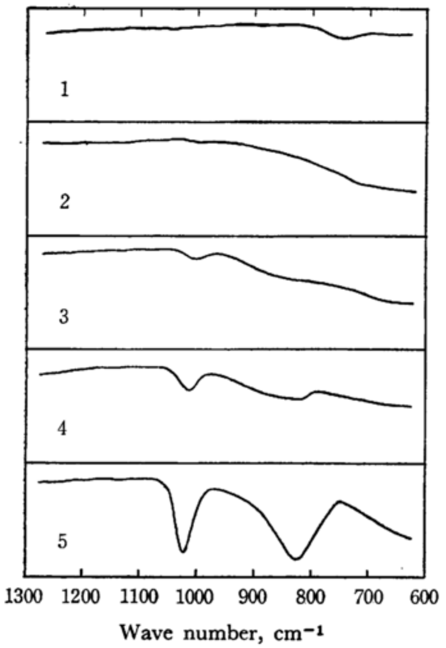

Fig. 4. Infrared absorption spectrum of antimony-vanadium sample heat-treated at 500°C for 4 hr.
Sb/V ratio: 1) 1/0, 2) 2/1, 3) 1/1, 4) 1/2, 5) 0/1

ratio of 1 : 1 had only a very weak absorption near 1000 cm^{-1}. This indicates that $SbVO_4$ contains no double covalent bond V=O.

The heat-treated samples of this system except Sb_2O_4 gave a single broad ESR absorption spectrum. Figure 5 shows the variation of the ESR intensity of the sample in the atomic ratio of 1 : 1 with heat treatment. The intensity of ESR signal decreased with an increase in treated temperature, while the width increased. The *g*-value, *ΔHmsl* and relative intensity of ESR signal of samples heat-treated at 480°C are listed in Table 1. The signal intensity passed through a maximum at the atomic ratio of 1 : 1. Further details on the ESR study in this system will be reported in a separate paper.

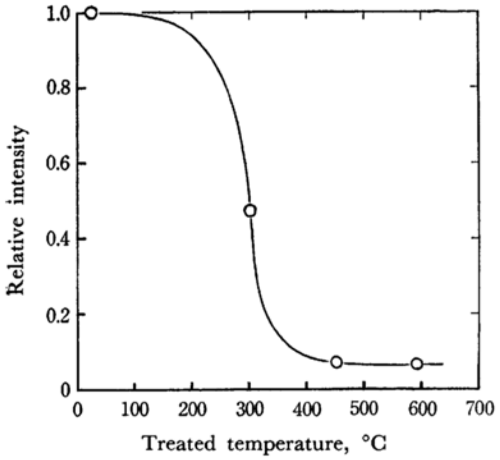

Fig. 5. Variation of the ESR intensity of antimony-vanadium sample in the atomic ratio of 1:1 with heat treatment.

TABLE 1. ESR CONSTANTS OF ANTIMONY-VANADIUM SAMPLE HEAT-TREATED AT 480°C

Sb/V Ratio	*g*-Value	Width *ΔHmsl*	Relative signal intensity[b]
98/2	1.96	240 gauss	
10/1	1.97	270	0.00008
2/1	a	500	0.0023
1/1	1.98	500	0.04
1/2	1.96	500	0.007
1/10	1.98	95	
0/1	1.98	85	0.0008

a : very broad signal
b : relative intensity to vanadyl tartarate

Chromium-Vanadium System. The differential thermal analysis curves of the mixtures of a chromium oxalate and a vanadium oxalate are shown in Fig. 6. The X-ray diffraction patterns of samples, which were treated in air at desired temperature for 4 hr, at shown in Fig. 7. The endothermic and the following exothermic peaks near 400°C were seemed to be the decomposition of oxalates. The exothermic peaks in the mixed oxalate sample in the range from 500 to

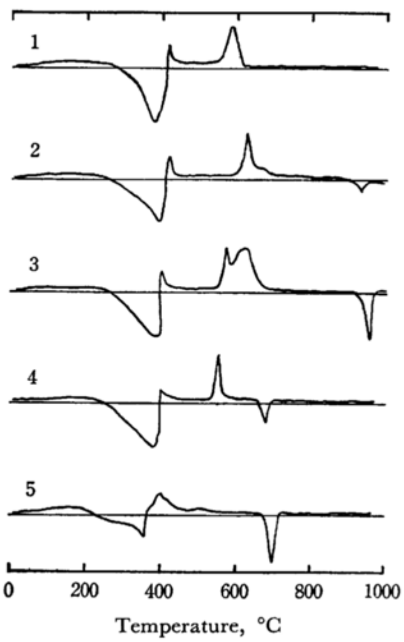

Fig. 6. Differential thermal analysis curve of the mixture of chromium-oxalate and vanadium oxalate.
Cr/V ratio: 1) 1/0, 2) 2/1, 3) 1/1, 4) 1/2, 5) 0/1

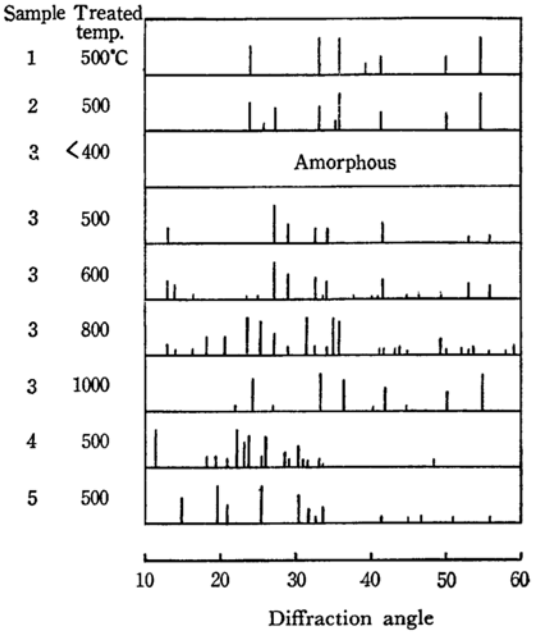

Fig. 7. X-Ray diffraction pattern of chromium-vanadium sample.
Cr/V ratio: 1) 1/0, 2) 3/1, 3) 1/1, 4) 1/3, 5) 0/1

620°C were seemed to be ascribed to the formation of x-phase compound which was in good agreement with $CrVO_4$ described by Brandt.[4] The last endothermic peak was regarded the melting point.

The X-ray diffraction pattern also showed that there were two new phase present in mixed samples. When the atomic ratio of chromium to vanadium was near 1 : 3, the y-phase was present in the range from 400 to 600°C. This phase could be obtained by the heat-treatment of chromium metavanadate[5,6] at 500°C. When the atomic ratio was near 1 : 1, the z-phase was present and was stable up to a higher temperature at the atomic ratio of 1 : 1. In view of above observation and the result by Amiel and his co-workers,[7] the phase diagram in this system is presented in Fig. 8.

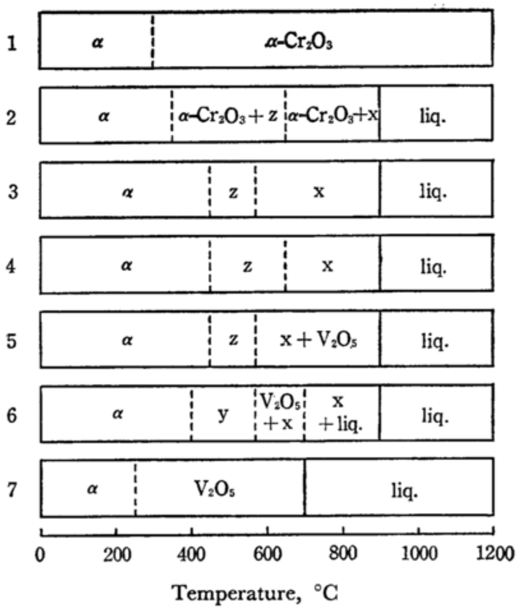

Fig. 8. Phase diagram in chromium-vanadium system.
Cr/V ratio: 1) 1/0, 2) 3/1, 3) 3/2, 4) 1/1, 5) 2/3, 6) 1/3, 7) 0/1

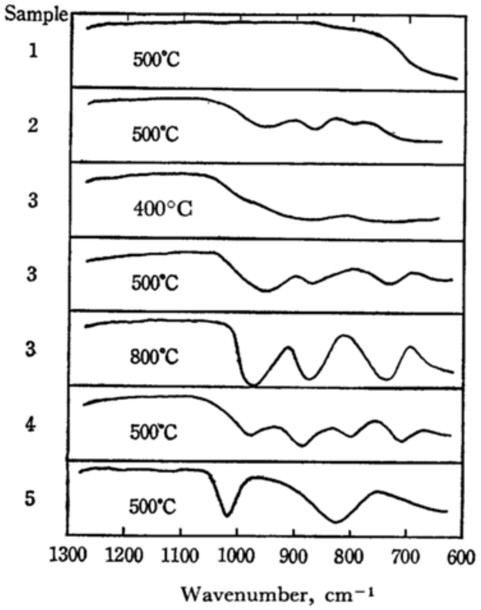

Fig. 9. Infrared absorption spectrum of chromium-vanadium sample heat-treated at desired temperature for 4 hr.
Cr/V ratio: 1) 1/0, 2) 3/1, 3) 1/1, 4) 1/3, 5) 0/1

Infrared absorption spectra of the heat-treated samples are shown in Fig. 9. The spectra of mixed samples differed from that of V_2O_5 and Cr_2O_3. In the atomic ratio of 1 : 1 the spectra showed remarkable change by the temperature of heat treatment. The spectrum of a brownish black amorphous material obtained by the heat treatment at 400°C was similar to one of chromium orthovanadate obtained by precipitating chromic nitrate solution with sodium orthovanadate and heating the precipitate at 400°C. In the spectrum of a grayish black crystal powder obtained by the heat treatment at 500°C three broad absorption bands were observed at 950, 870 and 740 cm^{-1}. The spectrum of a yellowish brown crystal powder obtained by the heat treatment at 800°C showed

---

[4] K. Brandt, *Arkiv. Kemi. Mineral Geo.*, **17A** (6), 1 (1943).

[5] J. Amiel, D. Olivier and M. Dessolin, *Compt. Rend.*, **264**, 1045 (1967).

[6] D. Olivier, *ibid.*, **264**, 1176 (1967).

[7] J. Amiel, D. Colaitis and D. Olivier, *ibid.*, **263**, 224 (1966).

three very strong absorption bands at 970, 880 and 740 cm^{-1}. This observed change in the spectra is seemed to be ascribed to the formation of the chemical compounds, in good agreement with phase analysis described above.

The heat-treated samples in this system gave a single broad ESR absorption spectrum. Figure 10 shows the variation of the ESR intensity of the sample in the atomic ratio of 1 : 1 with heat treatment. The intensity of ESR signal passed through a minimum at the sample heat-treated at 500°C, while the sample heat-treated at 800°C gave a very intense signal with a *g*-value of 1.98 and a width of 90 gauss. The *g*-value, $\Delta Hmsl$ and relative intensity of ESR signal of samples heat-treated at 500°C are listed in Table 2. The sample in the atomic ratio of 1 : 1 gave a broad signal with a weak intensity.

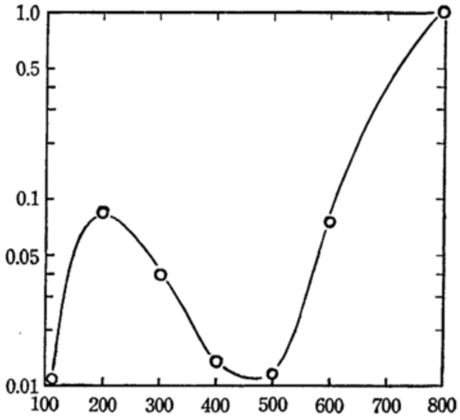

Fig. 10. Variation of the ESR intensity of chromium-vanadium sample in the atomic ratio of 1:1 with heat treatment.

TABLE 2. ESR CONSTANTS OF CHROMIUM-VANADIUM SAMPLE HEAT-TREATED AT 500°C

Cr/V Ratio	*g*-Value	Width $\Delta Hmsl$	Relative signal intensity[a]
1/0	1.97	600 gauss	0.004
3/1	1.97	260	0.05
1/1	1.98	600	0.01
1/3	1.98	250	0.05
0/1	1.98	70	0.0008

a : relative intensity to vanadyl oxalate

Permanganate titration indicated also that the sample heat-treated in the range from 400 to 500°C presented no vanadium in the V^{4+} state.

Reduction of Sample with Ammonia. In Fig. 11 the thermogravimetric analysis curves treated with ammonia at 400°C are shown. Vanadium pentoxide was very reducible under the given condition, while mixed samples were hard to be reduced. However the z-phase in the chromium-vanadium system was reducible. The phase analysis by X-ray diffraction method and infrared absorption analysis showed that each mixed sample treated with ammonia retained the original composition. These results indicate that mixed samples have no covalent double bond V=O to be easily reducible.

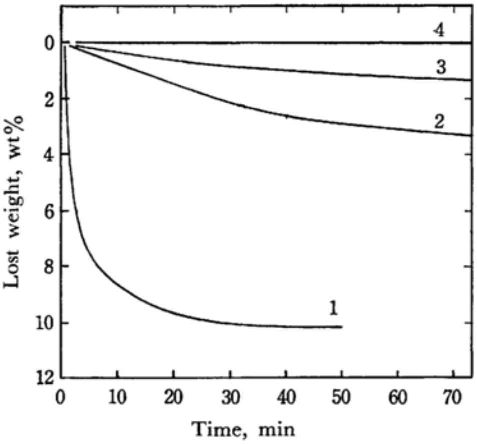

Fig. 11. Thermogravimetric analysis curve of sample in the treatment with ammonia at 400°C.
Sample:
1) V_2O_5
2) chromium-vanadium (1:1) treated at 500°C
3) antimony-vanadium (1:1) treated at 500°C
4) chromium-vanadium (1:1) treated at 800°C

Phase Composition of Used Catalysts. The fresh catalysts used for the ammoxidation of xylene[1] consisted essentially of V_2O_5, $SbVO_4$ and z-phase for a vanadium oxide catalyst, an antimony-vanadium catalyst and a chromium-vanadium catalyst respectively. X-Ray diffraction patterns for used catalysts showed that a vanadium oxide catalyst consisted essentially of V_2O_4, while mixed catalysts retained the original composition even after prolonged usage.

Discussion

Roth and Waring[3] and Brandt[8] have shown that $SbVO_4$ has the rutile structure with the metal ions randomly distributed. Taking account of the results for infrared absorption analysis, ESR measurement and reactivity with ammonia, it is suggested that the nature of vanadium ion in $SbVO_4$ is similar to one of V_2O_4.[9]

The chromium-vanadium system is more complicated. Brandt has shown that x-phase, that is $CrVO_4$, has a defect spinal structure having the vanadium atoms in tetrahedral coordination.[4]

---

[8] K. Brandt, *Structure Reports*, **9**, 178 (1942—4).
[9] K. Narita, *Nihon Butsuri Gakkaishi (J. Applied Phys. Japan)*, **20**, 748 (1965).

The very intense absorption bands of infrared spectrum and the intense signal of ESR indicate also that octahedral chromium ion and tetrahedral vanadium ion are regularly distributed. The metal ions in $CrVO_4$ are also not reduced under reaction conditions.

The infrared absorption spectrum of amorphous phase was similar to one of amorphous chromium metavanadate. The amorphous phase is, therefore, seemed to have the polyanion of VO_3^-.

On the other hand X-ray diffraction pattern indicates that the structure of z-phase is quite different from one of x-phase. Ioffe and his co-workers(10,11) have obtained the similar compound by heat-treating the mixture of vanadyl oxalate and chromic acid at 400°C, but X-ray diffraction pattern is not in agreement with one of the z-phase of this work. The infrared absorption spectrum of z-phase was similar to one of x-phase rather than one of amorphous phase, but each absorption band of its spectrum was broad and considerably weak. The absorption band near $1000\ cm^{-1}$ also shifted to the longer wavelength than one of x-phase. The ESR absorption spectrum of 1 : 1 sample heat-treated in the range from 400 to 500°C was similar to one of Cr_2O_3 which had a single broad signal. Furthermore the z-phase was reducible with ammonia at 400°C differing from x-phase. The surface of the catalyst consisting of z-phase is seemed to become partially reduced under reaction condition. In view of above results, the z-phase is seemed to have the transitional structure with the elongated double convalent bond V=O.

A vanadium oxide catalyst, a chromium-vanadium catalyst and an antimony-vanadium catalyst had similar activity in the ammoxidation of xylene as described in the previous paper,(1) while a chromium-vanadium catalyst in which x-phase was one of major constituent of catalyst had a little catalytic activity in this reaction. These observations indicate that the nature and the distribution of metal ions and oxygen ion on catalyst surface affect the catalytic activity and the selectivity of reaction. It is difficult to expect the relationship between the adsorbability of reactant and the selectivity of reaction, but it may be assumed that the addition of more electronegative metal ions affects the electronic property of vanadium ion functioning as an adsorption center.(12,13)

Ioffe and his co-workers(10,11) showed that a chromium-vanadium catalyst in the atomic ratio of 1 : 1 had low activity and selectivity for the oxidation of benzene to maleic anhydride. An antimony-vanadium catalyst and a chromium-vanadium catalyst had an activity for the oxidation of *o*-xylene to phthalic anhydride, but the selectivity to phthalic anhydride showed less than 35%. Furthermore the relationship between the catalytic activity and the physical property of mixed catalysts for the ammoxidation of xylene are different from that for the oxidation of benzene.(11) These results suggest that the oxidative dehydrogenation is more significant than the formation of carboxylic acid for the mechanism of ammoxidation.(14)

The authers wish to thank Messrs. Hideo Ichinokawa, Tadashi Aoki, Nobuhisa Goto and Ken-ichi Sano for their valuable discussion.

---

10) I. I. Ioffe, Z. I. Ezhkova and A. G. Lyubarskii, *Kin.* & *Cat.*, **3**, 165 (1962).

11) Z. I. Ezhkova, I. I. Ioffe, V. B. Kazanskii, A. V. Krylova, A. G. Lyubarskii and L. Ya. Margolis, *ibid.*, **5**, 753 (1964).

12) L. Ya. Margolis, "Advance in Catalysis," Vol. 14 Academic Press Inc., London (1963), p. 429.

13) L. Ya. Margolis, A. V. Krylova and E. S. Aleksandrova, *Kin.* & *Cat.*, **7**, 59 (1966).

14) M. Ito and K. Sano, *Yuki Gosei Kagaku Kyokaishi (J. Soc. Org. Syn. Chem. Japan)*, **25**, 329 (1967).