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Oxidation of Propylene over Vanadium and Molybdenum Oxide Catalysts

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The oxidation of propylene with a large amount of propylene has been studied over vanadium and molybdenum oxide catalysts in a flow system. The reaction temperature was 470°C; the partial pressure of oxygen was kept at 0.1 atm, while that of propylene was varied from 0.1 to 0.8 atm. The main oxidation products were carbon monoxide, carbon dioxide, and acrolein. In the oxidation with a pure vanadium oxide catalyst, the yield of acrolein increased with the propylene partial pressure, and the selectivity to acrolein was about 30% at the propylene partial pressure of 0.8 atm. The extrapolated values of the selectivity to various reaction products at the contact time of 0 sec did not change even though the propylene partial pressure was changed from 0.1 to 0.8 atm. X-ray patterns of the catalysts used (free of carriers) show the presence (of V_2O_4 or a mixture) of V_2O_4 and V_2O_3 according to the partial pressure of propylene. It is concluded that acrolein undergoes a secondary reaction more severely when a vanadium oxide catalyst is in the higher oxidative state, that is, when it is richer in V_2O_4. In the system of vanadium-molybedenum oxides, the three mixed catalysts, containing 10, 18 and 30 mol% MoO_3, acted in a similar way and raised the selectivity to acrolein to some extent in comparison with a pure vanadium oxide catalyst, whatever was partial pressure of propylene. In the mixtures containing more than 50 mol% MoO_3, MoO_3 had a dilution effect on the catalytic activity. A pure molybdenum oxide catalyst scarcely oxidized propylene at all at 470°C. It has thus been found that the catalytic activity of this system is closely related with the formation of solid solutions of MoO_3 in V_2O_5.

Vanadium oxide catalysts have been extensively studied since these catalysts are the most efficient agents for the oxidation of aromatic hydrocarbons into valuable organic compounds. However, as compared with the number of studies of the oxidation of aromatic hydrocarbons over vanadium oxide, there have been a relatively small number of works on the oxidation of olefins over the same oxide.

A series of fundamental studies of the oxidation of olefins over vanadium oxide have, however, been made in the USSR. Andrianova and Roginskii[1] have shown that the oxidation of propylene over a vanadium pentoxide catalyst yields large amounts of carbon monoxide and carbon dioxide, along with small amounts of aldehydes and acids. Margolis *et al.*[2] have also shown that vanadium oxide on alumina gives some aldehydes and acids, but mainly carbon monoxide and carbon dioxide. In addition, they have studied the kinetics of the oxidation of propylene over vanadium pentoxide on silica.[3]

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1) T. I. Andrianova and S. Z. Roginskii, *J. Gen. Chem. USSR,* **24**, 606 (1954).

2) L. Ya. Margolis, S. Z. Roginskii and T. A. Gracheva, *ibid.,* **26**, 1541 (1956).

3) L. Ya. Margolis, E. P. Malyarova and S. Z. Roginskii, *Izv. Akad. Nauk USSR, Otd. Khim. Nauk,* **1954**, 958.

The rate of the formation of various products was shown to be first order in oxygen and independent of the propylene concentration; the activation energies were also given. They have also investigated the reaction mechanism by means of studying the ^{18}O distribution among the various products.[4] With respect to the oxidation of butylenes, Bretton *et al.*[5] have established quantitative methods of analysis for the reaction products and have explained the composition of the products in terms of a free radical mechanism.

As has been remarked above, complete oxidation occurs dominantly; accordingly, a poor amount of organic compounds containing oxygen are produced when the oxidation of olefins is carried out with a small amount of olefin over vanadium oxide. However, as for the oxidation of olefins with a large amount of olefin over vanadium oxide, only a few reports have been presented. Margolis *et al.*[6] have investigated the kinetics of the oxidation of propylene on vanadium and molybdenum catalysts with an approximately 5-fold excess of propylene to oxygen and have observed that in each case the selectivity to acrolein was less than 30%. However, they did not inquire into the effect of the propylene partial pressure on the formation of acrolein.

In this paper, the oxidation of propylene will be studied with regard to the formation of acrolein over a vanadium oxide catalyst with a high propylene concentration and, accordingly, with a low oxygen concentration. In addition, for the purpose of examining the effect of promoters on the catalytic activity over vanadium oxide, a vanadium-molybdenum oxide system will be investigated; this is one of the most typical mixed catalysts for the oxidation of aromatic hydrocarbons.[7]

Experimental

The vapor-phase oxidation of propylene with a small amount of oxygen was carried out over vanadium-molybdenum oxide catalysts in a flow-type reaction system at atmospheric pressure. A gas mixture, consisting of propylene, oxygen and nitrogen in the desired concentrations, in the gas storage area was fed into the converter through a capillary-type flow meter, a dehydrator, and a gas-sampling cock. The converter was a Pyrex-glass tube (1.8 or 1.0 cm i. d.) with an axially-positioned thermocouple tube inside. This converter was immersed in a molten salt bath, the temperature of which was controlled to within ±1°C of the desired temperature. The gas stream leaving the converter was directed to the gas-sampling cock, traps, a washing bottle, a dehydrator, and a gas meter, and then discharged in the air.

When acrolein was introduced into the reaction zone, the nitrogen stream was directed into an evaporator containing acrolein. The nitrogen-acrolein mixture thus obtained was mixed with the nitrogen-oxygen-propylene mixture on the way to the converter, and a feed gas composed of the two mixtures was then directed into the converter.

The catalysts used in the experiments were of two systems: one was of 6 wt% vanadium pentoxide supported on silicon carbide granules, while the other was an unsupported system composed of vanadium oxide, molybdenum oxide, and mixtures of these two components. The former system was prepared by impregnating 12-mesh silicon carbide granules with a solution of ammonium metavanadate, after which they were melted in a muffle furnace at 700°C for one hour. The latter system was prepared using a solution of ammonium metavanadate and ammonium molybdate at the desired vanadium pentoxide to molybdenum trioxide ratio without any carrier. The solution was evaporated to dryness, leaving vanadium oxides

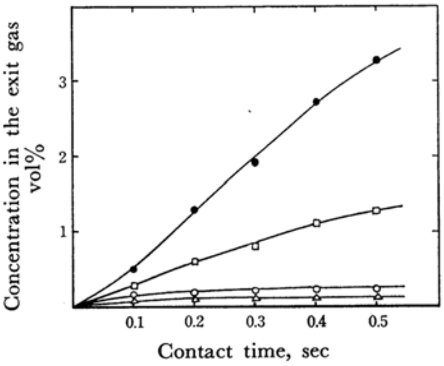

Fig. 1A. The concentration of reaction products in the exit ga.
470°C, $P_{C_3H_6}=0.1$ atm; $P_{O_2}=0.1$ atm;
$P_{N_2}=0.8$ atm
● CO, □ CO_2, ○ $CH_2=CHCHO$
△ CH_3CHO

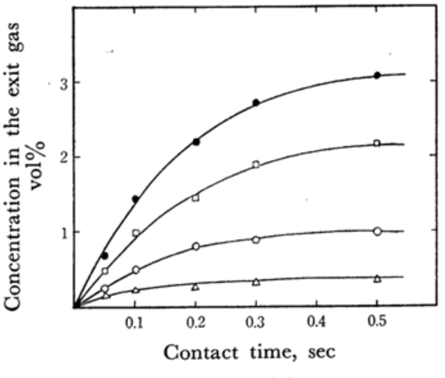

Fig. 1B. 470°C, $P_{C_3H_6}=0.8$ atm
$P_{O_3}=0.1$ atm
$P_{N_2}=0.1$ atm

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[4] L. Ya. Margolis and E. G. Plyshevskaya, *ibid.*, **1953**, 697.

[5] R. H. Bretton, S. W. Wan and B. F. Dodge, *Ind. Eng. Chem.*, **44**, 594 (1952).

[6] L. Ya. Margolis and L. N. Kutseva, *J. Gen. Chem. USSR*, **32**, 100 (1962).

[7] I. I. Ioffe, Z. I. Ezhkova and A. G. Lyubarskii, *Kinetics and Catalysis*, **3**, 165 (1962).

and molybdenum oxides, and the solid thus obtained was melted at 700°C for one hour. The melted substance was then cooled in the air, and crushed to 16- to 20-mesh.

The partial pressure of oxygen was kept at 0.1 atm throughout the experiments, while that of propylene was changed from 0.1 atm to 0.8 atm. The total pressure was kept at 1 atm using nitrogen.

The reaction temperature was defined as the average value of the temperature of the inlet and the maximum temperature in the reaction zone; it was kept at 470°C throughout the experiments.

The difference between the maximum and minimum temperatures in the catalyst bed was not larger than 40°C. The contact time was defined as the ratio of the catalyst volume (m*l*) to the flow rate (at 25°C), which was kept at 5 m*l*/sec; the contact time was changed by either increasing or decreasing the amount of catalyst in the converter. The catalytic activity became constant about one hour after the catalyst had been placed in the current of the feed gas, and the experimental data were obtained in the stationary state.

The reaction products were analyzed by a gas-chromatographic method.

Results and Discussion

The Pure Vanadium Oxide Catalyst (Supported). The main oxidation products were found to be carbon monoxide, carbon dioxide and acrolein, along with small amounts of acetaldehyde, formaldehyde and acids when propylene was oxidized with a small amount of oxygen over the vanadium oxide catalyst. The concentration of acrolein in the exit gas increased as the partial pressure of propylene in the feed gas was increased. Figures 1A and 1B show the relationship between the contact time and the concentrations of various products in the exit gas when the molar ratio of propylene to oxygen (R. P. O.) in the feed gas was 1 : 1 and 8 : 1. The acrolein concentration was 0.20 vol% in the exit gas at the contact time of 0.5 sec when the R. P. O. was 1 : 1, while that of acrolein was 0.95 vol% at the same contact time when the R. P. O. was 8 : 1. The value obtained at R. P. O. of 8 : 1 was approximately five times as large as that obtained at R. P. O. of 1 : 1.

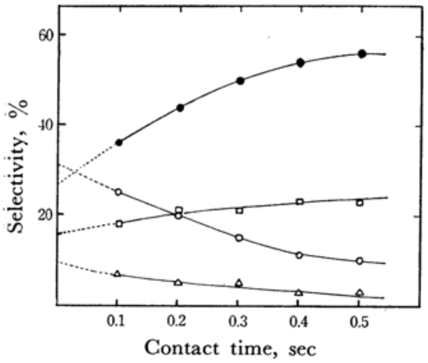

Fig. 2A. The relationship between selectivity and contact time.
470°C, $P_{C_3H_6}=0.1$ atm; $P_{O2}=0.1$ atm
$P_{N_2}=0.8$ atm
● CO, □ CO_2, ○ CH_2CHCHO,
△ CH_3CHO

$$S_{CO}=\frac{1}{3}\times\frac{\text{moles of CO formed}}{\text{moles of propylene reacted}}\times 100$$

$$S_{CO_2}=\frac{1}{3}\times\frac{\text{moles of CO}_2\text{ formed}}{\text{moles of propylene reacted}}\times 100$$

$$S_{CH_3CHO}=\frac{2}{3}\times\frac{\text{moles of acetaldehyde formed}}{\text{moles of propylene reacted}}\times 100$$

$$S_{CH_2=CHCHO}=\frac{\text{moles of acrolein formed}}{\text{moles of propylene reacted}}\times 100$$

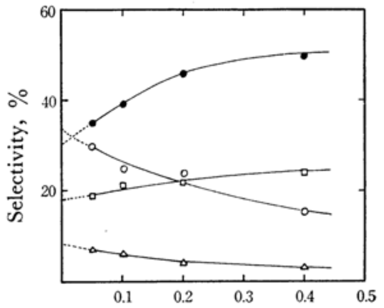

Fig. 2B. 470°C, $P_{C_3H_6}=0.2$ atm
$P_{O_2}=0.1$ atm
$P_{N_2}=0.7$ atm

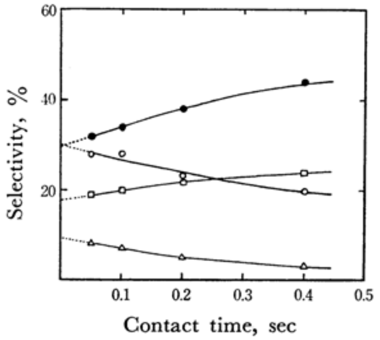

Fig. 2C. 470°C, $P_{C_3H_6}=0.4$ atm
$P_{O_2}=0.1$ atm
$P_{N_2}=0.5$ atm

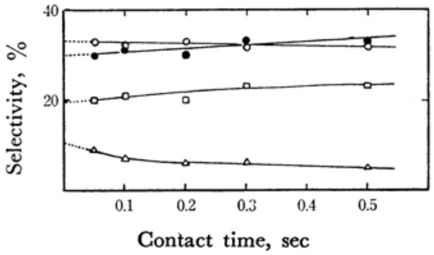

Fig. 2D. 470°C, $P_{C_3H_6}=0.8$ atm
$P_{O_2}=0.1$ atm
$P_{N_2}=0.1$ atm

The relationship between the contact time and

TABLE 1. THE EXTRAPOLATED SELECTIVITY OF VARIOUS REACTION PRODUCTS AT THE CONTACT TIME 0 sec

Partial pressure of propylene atm	Extrapolated selectivity, %			
	CO	CO_2	CH_3CHO	$CH_2{=}CHCHO$
0.1	27	16	9	32
0.2	30	18	8	34
0.4	30	18	9	30
0.8	30	20	10	33

the selectivity to each reaction product is shown in Fig. 2, which may clarify the difference between the two cases above. The values of the selectivities of various product formations were extrapolated to the contact time of zero seconds. The extrapolated values of carbon monoxide, carbon dioxide, acrolein, and acetaldehyde at the contact time of 0 sec, as given in Table 1, can be considered invariable over the entire range of the ratio of propylene to oxygen and independent of the gas composition; the average values in the four cases were 29, 18, 32 and 9% respectively. Those results suggest that the ratio of the rate of the initial formation of the oxidation products may be constant and independent of the partial pressure of propylene. From Fig. 2A it is evident that the acrolein formed by a primary reaction undergoes a further reaction to form some compounds such as carbon monoxide at R. P. O. of 1 : 1. When the R. P. O. is very high, that is, at 8 : 1, the selectivity to carbon monoxide, carbon dioxide, acrolein and acetaldehyde, as can be seen in Fig. 2D, remains almost constant over a wide range of contact times, indicating that the acrolein initially formed scarcely undergoes a further reaction. In conclusion, the maximum selectivity to acrolein proves to be no more than 35%.

Figure 3 shows X-ray patterns of vanadium oxide catalysts after they have been exposed to use. V_2O_5 was reduced to lower oxides because the gas composition was in the range of the reducing atmosphere. The catalyst used at R. P. O. of 1 : 1 is composed of a single phase of V_2O_4. However, the lines of another phase of V_2O_3 appear in the patterns and become sharp with an increase in the partial pressure of propylene in the feed gas. No phases other than V_2O_4 and V_2O_3 are detected in the catalysts used in the present experiments. The reduction of V_2O_4 thus seems to proceed to V_2O_3 directly, not through such intermediates as the $VO_{1.87}$, $VO_{1.86}$ and $VO_{1.84}$ observed by Schmitz.[8] From the point of view of the crystal structure,[9] V_2O_5 is not reduced to oxides lower than V_2O_3 under such reaction conditions; this is considered inactive for a oxidation catalyst. Hence, it is only by V_2O_4 that propylene is catalyzed under these reaction conditions; this offers a rational explanation of finding that the extrapolated selectivity at the contact time of 0 sec may be regarded as invariable over the large range of propylene partial pressures. Therefore, the authors call the extrapolated selectivity the "specific selectivity."

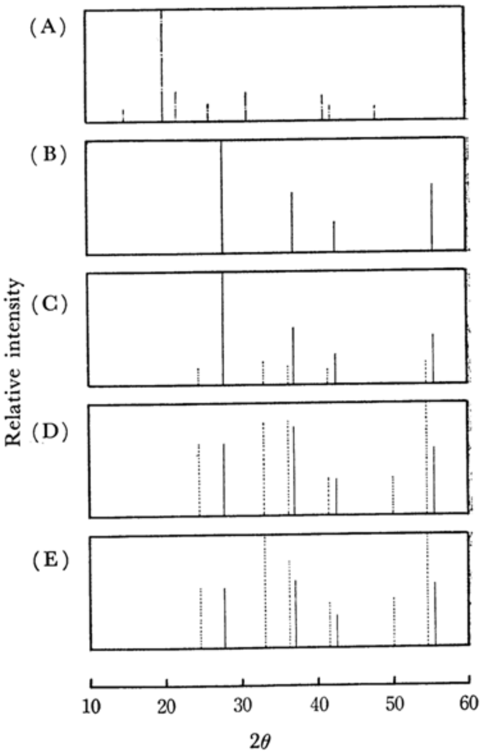

Fig. 3. X-ray patterns of the fresh catalyst and the used.
——— V_2O_5, —— V_2O_4, ---- V_2O_3
(A) Fresh catalyst
(B) Catalyst used at $P_{C_3H_6}=0.1$ atm
(C) Catalyst used at $P_{C_3H_6}=0.2$ atm
(D) Catalyst used at $P_{C_3H_6}=0.4$ atm
(E) Catalyst used at $P_{C_3H_6}=0.8$ atm

For the purpose of clarifying the effect of the ratio of propylene to oxygen on the secondary oxidation of acrolein, the oxidation of mixtures of propylene and acrolein was also investigated. The results are given in Table 2. In these runs, acrolein was fed into the reaction zone mixed with nitrogen. Each run was carried out under conditions such that the oxygen concentrations in the exit gas were as equal to each other as possible. As a result of this equalization of the oxygen concentrations, it is possible to neglect the influence of the oxygen concentration on the secondary oxidation of acrolein. At R. P. O. of 1 : 1 the acrolein concentration in the product gas was 0.14 vol% when no acrolein was introduced, while it was 0.31 vol% when 0.42 vol% of acrolein

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8) O. Schmitz and G. Woitas, *Z. Elektrochem.*, **63**, 122 (1959).

9) J. A. A. Ketelaar, *Nature,* **137**, 316 (1936).

TABLE 2. THE OXIDATION OF PROPYLENE-ACROLEIN MIXTURES

Reaction temp. °C	Composition of the feed gas, vol%			Introduced acrolein vol%*	Concentration in the exit gas, vol%				
	O_2	C_3H_6	N_2		CO_2	CO	CH_3CHO	CH_2=CHCHO	O_2
458	8.7	9.1	82.2	0	1.43	3.83	0.07	0.14	2.8
457	9.2	8.9	81.9	0.42	1.20	3.14	0.07	0.31	3.9
462	8.2	74.7	17.1	0	1.10	1.86	0.16	0.45	3.6
463	7.7	74.5	17.8	0.44	1.13	1.86	0.18	0.87	3.1

* Based on the total volume of propylene, oxgen and nitrogen in the feed gas.

was introduced into the feed gas. On the other hand, at R. P. O. of 8 : 1 the acrolein concentration was 0.45 vol% when no acrolein was introduced, while it was 0.87 vol% when 0.44 vol% of acrolein was introduced. These results indicate that acrolein undergoes a secondary reaction at R. P. O. of 1 : 1, while it scarcely does at R. P. O. of 8 : 1; these results are consistent with those observed in Figs. 2A and 2D.

As has been mentioned above, only V_2O_4 is active under such reaction conditions; V_2O_3 is inactive. Therefore, it is reasonable that the specific selectivity is invariable over a wide range of propylene partial pressures, and that the extent to which the acrolein primarily formed undergoes a secondary oxidation depends upon the amount of V_2O_4 present in the catalyst. Accordingly, it may be concluded that acrolein undergoes a further reaction more severely when the ratio of propylene to oxygen is smaller; that is, acrolein is more unstable when a vanadium oxide catalyst is richer in V_2O_4 during a reaction in this reducing atmosphere.

Vanadium - Molybdenum Oxide Catalysts (Unsupported). The products of propylene oxidation were almost the same as those of the oxidation with the pure vanadium oxide catalyst, though propylene was scarcely oxidized at all by the pure molybdenum oxide catalyst under the present reaction conditions.

The mole percentage of propylene reacted to the feed gas is shown in Fig. 4, which indicates that the pure vanadium oxide catalyst oxidized more propylene than the other mixed catalysts over the entire range of partial pressures of propylene. The three mixed catalysts containing 10, 18 and 30 mol% MoO_3 seem to act in a similar way, while in those containing more than 50 mol% MoO_3 a dilution effect of MoO_3 is observed.

The concentrations of some products in the exit gas when the R. P. O. is 4 : 1 are shown in Fig. 5. Those of carbon monoxide and carbon dioxide became smaller upon the addition of MoO_3, while that of acrolein was almost constant for the three catalysts containing 10 , 18 and 30 mol% MoO_3. In the mixed catalysts containing more than 50 mol% MoO_3, the concentrations of the four reaction products decreased linearly upon the addition of MoO_3. Figure 6 shows the selectivity to acrolein of the vanadium oxide catalyst and of the mixtures containing up to 30 mol% MoO_3.

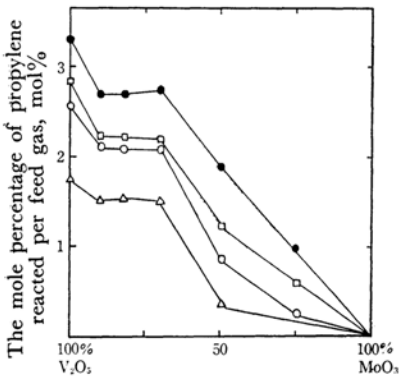

Fig. 4. The over-all conversion of propylene as a function of the composition of vanadium molybdenum oxide catalysts.
470°C, amount of catalyst: 300 mg
(diluted with quartz chips of 12-mesh)
● $P_{C_3H_6}$=0.8 atm ○ $P_{C_3H_6}$=0.2 atm
□ $P_{C_3H_6}$=0.4 atm △ $P_{C_3H_6}$=0.1 atm

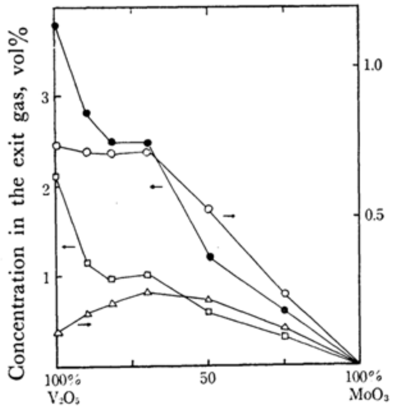

Fig. 5. The concentration of reaction products as a function of the composition of vanadium-molybdenum oxide catalysts.
470°C, $P_{C_3H_6}$=0.4 atm, amount of catalyst: 300 mg (diluted with quartz chips of 12-mesh)
● CO ○ CH_2=CHCHO
□ CO_2 △ CH_3CHO

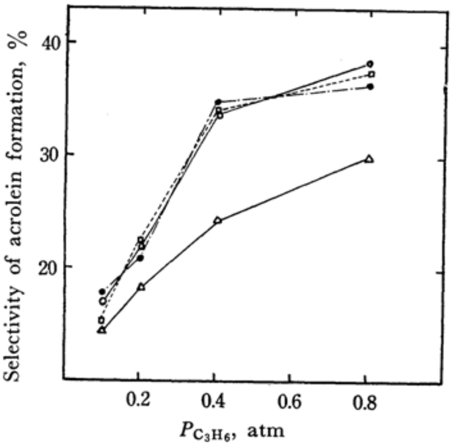

Fig. 6. The effect of the propylene partial pressure on the selectivity of acrolein formation. 470°C, amount of catalyst: 300 mg (diluted with quartz chips of 12-mesh)

○ $V_2O_5 : MoO_3 = 7 : 3$ ● $V_2O_5 : MoO_3 = 9 : 1$
□ $V_2O_5 : MoO_3 = 9 : 2$ △ $V_2O_5 : MoO_3 = 10 : 0$

The mixed catalysts raised the selectivity to some extent; they showed little difference from one another in the reaction activity of the conversion and selectivity.

The addition of MoO_3 did not lead to any improvement in the conversion of propylene or in the yield of acrolein in the oxidation with a large amount of propylene, while the addition resulted in increases in the conversion of benzene and in the yield of maleic anhydride with respect to the benzene oxidation in the oxidizing atmosphere.[7] These findings that the mixed catalysts containing up to 30 mol% MoO_3 act in a similar way in the catalytic action with respect to conversion and selectivity correspond with the fact that the addition of up to about 25 mol% MoO_3 to V_2O_5 results in the formation of a solid solution.[10,11] Therefore, it may be considered that the formation of a solid solution has some effect on the catalytic activity in a reducing atmosphere as well as in an oxidizing one.

It is possible that a molybdenum oxide and solid solution system comes into existence when the molybdenum oxide content exceeds the maximum solubility in vanadium oxide. The results of Fig. 4 show that the pure molybdenum oxide catalyst oxidizes little propylene. Consequently, it may be presumed that molybdenum oxide other than that dissolved in vanadium oxide acts as a diluent in the mixtures containing more than 50 mol% MoO_3.

The authors wish to express their thanks to Professor Shingo Ando for his continued advice and encouragement in this work.

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10) A. Magneli and B. M. Oughton, *Acta Chem. Scand.*, **5**, 585 (1951).

11) K. Tarama, S. Teranishi and Y. Yasui, *Kogyo Kagaku Zassi (J. Chem. Soc. Japan, Ind. Chem. Sect)*, **60**, 1222 (1957).