Heterogeneous Catalysis in Liquid-Phase Oxidation of Olefin. I. Activity of Vanadium System Catalysts for Oxidation of Cyclohexene

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The catalytic activities of various binary oxides containing vanadium for the liquid-phase oxidation of cyclohexene have been studied, in comparison with those of one component oxides and soluble metal acetylacetonates. The reaction was carried out at 60 °C in benzene solvent. The distribution of reaction products suggests the occurrence of autoxidation and epoxidation when vanadium system catalysts are used. Among the binary catalysts, V–Cr and V–Mo systems showed relatively high specific activities, especially high activity being obtained by the former systems calcined at a low temperature. It seems that cyclohexene oxide is formed mainly by two successive catalytic processes, *i.e.*, the formation of cyclohexenyl hydroperoxide by autoxidation and the selective oxidation of cyclohexene with the hydroperoxide. The machanism of epoxidation was confirmed by the reaction of cyclohexene with *t*-butyl hydroperoxide in the presence of V–Cr catalyst.

Studies have been carried out in the field of liquid-phase oxidation of olefins with insoluble catalysts containing transition metals. Cyclohexene was often used as a model reactant.[1,2] Meyer *et al.*[1] showed the heterogeneous-homogeneous character of the reaction with MnO_2 and CoO as catalysts. Gould and Rads[2] studied the distribution of reaction products and suggested that the atomic number and oxidation state of transition metal in the catalyst are important in determining the course of the reaction. However, these studies are almost restricted to the activity of one component metal oxide, scarcely any attempts to test the catalytic activity of binary oxide system being made.

V_2O_5 was found to be comparatively active for the liquid-phase oxidation of acrylaldehyde.[3] It has been frequently used as a catalyst for vapor-phase oxidation of some hydrocarbons, many investigations being published about the high activity obtained by combining V_2O_5 and another oxide. The high activity is thought to be caused by the formation of different structures from those of original oxides.[4] A similar phenomenon is expected also in a liquid-phase oxidation. Vanadium-chromium binary oxide shows higher activity than the individual one component oxide in the liquid-phase oxidation of acrylaldehyde.[5] The catalytic activity of the binary oxide was discussed in connection with its structure, and the active species in this catalyst was thought to be phase Y which is a chromium isopolyvanadate.

On the other hand, soluble metal complexes of vanadium, as well as those of molybdenum or tungsten, catalyze the selective epoxidation of olefin with organic hydroperoxide.[6] The oxidation of cyclohexene with binary oxide catalyst containing vanadium seems to be of interest in view of the epoxidation. For the purpose of studying the effects of addition of second component to vanadium pentoxide, various binary oxides containing vanadium were prepared, and their catalytic activities for the oxidation of cyclohexene have been examined in comparison with those of one component oxides and soluble metal acetylacetonates. These results are reported in this paper.

Experimental

Catalysts. Metal acetylacetonates [$Me(acac)_n$], *i.e.*, $VO(acac)_2$, $Cr(acac)_3$, $Mn(acac)_2$, $Mn(acac)_3$, $Fe(acac)_3$, $Co(acac)_2$, $Co(acac)_3$, $Ni(acac)_2$, $Cu(acac)_2$, $Zn(acac)_2$, and $MoO_2(acac)_2$ (Tokyo Chemical Industry Co.) were used.

One component metal oxides were prepared as follows. Cr_2O_3, Mn_2O_3, Fe_2O_3, CoO, NiO, CuO, ZnO, and Bi_2O_3 were prepared by calcination of the corresponding metal hydroxides at 450 °C for 6 h in air. The hydroxide was precipitated by addition of dilute aqueous ammonia to an aqueous solution of the corresponding metal nitrate, followed by separation from the solution by filtration, sufficient washing with water, and drying at 100 °C for one day. V_2O_5 was prepared by calcining V_2O_5 hydrate precipitated by addition of concentrated nitric acid to a warm aqueous solution of NH_4VO_3 and the subsequent washing, and drying mentioned above. MoO_3 and WO_3 were similarly prepared by calcining $H_2MoO_4 \cdot H_2O$ and H_2WO_4, respectively.

In order to study the effects of addition of second component (C_{II}) to V_2O_5, 20 kinds of binary system oxides, *i.e.*, V–Li (1/1),* V–Na (1/1), V–K (1/1), V–Mg (1/1), V–Ca (1/1), V–Sr (1/1), V–Ba (1/1), V–Cr (1/0.4), V–Mn (1/0.4), V–Fe (1/0.4), V–Co (1/0.4), V–Ni (1/0.4), V–Cu (1/0.4) V–Zn (1/0.4), V–Mo (1/0.2), V–W (1/0.2), V–B (1/0.4), V–P (1/0.4), V–Sb (1/0.4), and V–Bi (1/0.4), were prepared in the following way. A mixture of V_2O_5 hydrate and raw material of second component; hydroxide of alkali or alkaline earth metal, nitrate of Cr, Mn, Fe, Co, Ni, Cu, Zn, or Bi, $H_2MoO_4 \cdot H_2O$, H_2WO_4, H_3BO_3, H_3PO_4, or Sb_2O_5, was kneaded with a small amount of water at 80 °C for 6 h.** The resulting paste was dried at 100 °C for one day, and calcined at 400 °C for 3 h in the air. Since V–Cr and V–Mo systems showed high specific activities, both systems were calcined at 600 and 800 °C in order to study the effects of calcination temperature. For the purpose of indicating the calcination temperature, catalysts are denoted by $V\text{–}C_{II(400)}$, $V\text{–}C_{II(600)}$, and $V\text{–}C_{II(800)}$, respectively.

In all cases, a particle size of metal oxide used as catalyst was smaller than 100 mesh.

Apparatus and Procedure of Reaction. The oxidation reaction was carried out at 60 °C and under 1 atm of oxygen using a gas-sealed system with an oxygen recycling unit (Fig. 1). Catalyst and benzene as a solvent were put into the reactor. Cyclohexene (20.0 ml, prepurified by passing over activated alumina to eliminate hydroperoxide) was then added, and the stirring of the reaction mixture and bubbling of oxygen (flow

* The fractional number in parentheses is the atomic ratio of V/C_{II}.

** A three component system, V–S–K (1/1/2), was also made from a mixture of V_2O_5 hydrate and K_2SO_4.

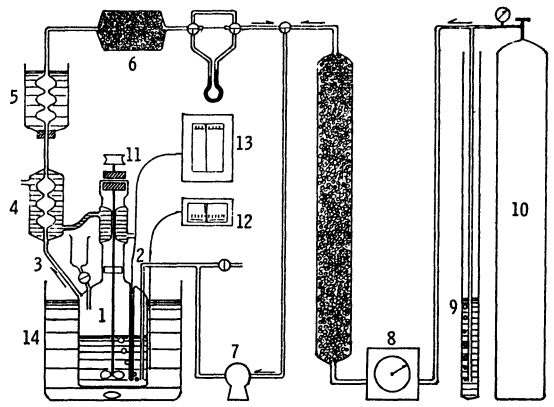


Fig. 1. Reaction apparatus.
1: Reactor, 2: gas inlet, 3: gas outlet, 4: water-cooled condenser, 5: ice–water-cooled condenser, 6: carbon dioxide-elimination tube, 7: gas-recycling pump, 8: gas meter, 9: pressure controller, 10: O_2 tank, 11: magnetic stirrer, 12: reaction temperature controller, 13: reaction temperature recorder, 14: glycerol bath.

rate; 200 ml/min) into it were started. The effluent gas mixture flowing out from the reactor was passed through the condensers and the carbon dioxide-elimination tube, and was recycled by the pump into the reactor. In order to keep the inside pressure at one atm, oxygen was supplied through a gas meter.

In order to clarify the mechanism of epoxidation the reaction of cyclohexene with *t*-butyl hydroperoxide was carried out in benzene under 1 atm of dry nitrogen using a 20 ml of glass flask. The reactor was placed on a shaker so that the catalyst was uniformly suspended.

Analyses of Reaction Products and Catalysts. The oxidation products were assayed as follows. Cyclohexenyl hydroperoxide was determined by the iodometric method described by Wagner *et al.*[7] The remaining components were determined by gas chromatography using a column of PEG 6000 after treating the sample with a sufficient amount of triphenylphosphine so as to reduce quantitatively the hydroperoxide into alcohol.[2] Solvent of benzene was used as an internal standard. Cyclohexene (unconverted), cyclohexene oxide, cyclohexenone, and cyclohexenol were determined. In the case of the reaction with *t*-butyl hydroperoxide, the unreacted hydroperoxide and cyclohexene oxide formed were determined by the iodometric method and gas chromatography, respectively.

The catalysts were analyzed by the following methods. The surface area was determined by the BET method using nitrogen. Powder-type X-ray diffraction pattern was obtained with a diffractometer of Geigerflex D-3F type (Rigaku Denki Co.) with Cu*K*α radiation. Infrared spectrum was recorded with a JASCO-DS 403 G grating spectrophotometer with samples prepared in the form of KBr pressed discs.

Results and Discussions

When an olefin is oxidized by radical chain mechanism, the peroxy radical formed has two reactivities, hydrogen abstraction from olefin and addition to olefin. It was experimentally found that both contributions change a great deal with the structure of olefin.[8,9] According to the result of cyclohexene oxidation by Mayo *et al.*,[8] the main part of the autoxidation products is cyclohexenyl hydroperoxide, and the amount of cyclohexene oxide is very small, indicating that hydrogen abstruction proceeds mainly. It might be concluded that cyclohexene oxide is scarcely formed in the radical chain reaction. Experiments with use of a radical initiator also gave similar results. As an example, by the 4 h reaction in benzene solvent with a thermal initiator of azobisisobutyronitrile (AIBN) (10^{-2} mol/l), 90.4% of cyclohexenyl hydroperoxide, 3.2% of cyclohexene oxide, 2.5% of cyclohexenone, and 3.9% of cyclohexenol were formed.***

However, it was reported that relatively large amount of cyclohexene oxide was formed in the case of using some transition metal catalysts. Gould and Rado[2] carried out the oxidation of neat cyclohexene using soluble acetylacetonates or insoluble oxides of various transition metals as a catalyst at 70 °C under the oxygen pressure of 6.5 atm. A relatively high yield of cyclohexene oxide was obtained with molybdenum or vanadium compound catalyst, such as $Mo_2(acac)_2$, VO-

Table 1. Reaction results with $Me(acac)_n$ catalyst[a]

Cat.	Conv. (%)	Yield (%)		Select. (%)		Rate ($\times 10^6$mol/l s)		Ind. Per. (min)	React. time (min)
		Oxide	HPO	Oxide	HPO	R_{max}	R_{end}[b]		
$VO(acac)_2$	—	—	—	—	—	—	—	—	240
$Cr(acac)_3$	—	—	—	—	—	—	—	—	240
$Mn(acac)_2$	5.40	0.23	3.88	4.3	71.9	43.8	8.6	145	265
$Mn(acac)_3$	6.10	0.21	3.33	3.4	54.6	80.5	15.6	5	114
$Fe(acac)_3$	0.78	0.07	0.64	9.0	81.9	6.3	6.3	222	300
$Co(acac)_2$	7.10	0.22	4.52	3.1	63.7	79.0	11.7	32	100
$Co(acac)_3$	2.60	0.13	1.97	5.0	75.8	8.6	6.3	74	240
$Ni(acac)_2$	2.30	0.08	1.96	3.5	85.2	6.3	6.3	53	240
$Cu(acac)_2$	2.30	0.08	1.77	3.5	77.0	13.3	10.2	94	180
$Zn(acac)_2$	—	—	—	—	—	—	—	—	240
$MoO_2(acac)_2$	—	—	—	—	—	—	—	—	240

a) 20 ml of cyclohexene, 50 ml of benzene and 7×10 ml of metal acetylacetonate were used. The reaction temperature was 60 °C. The O_2 pressure was 1 atm. b) The rate of oxygen absorption just before the cessation of the reaction.

*** Each of these values was calculated based on converted cyclohexene, showing selectivity.

TABLE 2. REACTION RESULTS WITH ONE COMPONENT METAL OXIDE CATALYST[a)]

Cat.	Conv. (%)	Yield (%)		Select. (%)		Rate ($\times 10^6$mol/l s)		Ind. Per. (min)	React. time (min)
		Oxide	HPO	Oxide	HPO	R_{max}	R_{end}		
V_2O_5	1.56	0.36	0.61	23.1	39.1	3.1	2.4	120	300
Cr_2O_3	2.00	0.10	1.58	5.0	79.0	5.5	4.7	150	240
Mn_2O_3	4.95	0.18	3.96	3.6	80.0	13.3	7.8	19	240
Fe_2O_3	0.74	0.03	0.63	4.1	85.3	1.6	1.6	212	240
CoO	2.60	0.08	1.94	3.1	74.6	4.7	3.9	93	240
NiO	—	—	—	—	—	—	—	—	240
CuO	—	—	trace	—	—	—	—	—	240
ZnO	—	—	—	—	—	—	—	—	240
MoO_3	—	trace	trace	—	—	—	—	—	240
WO_3	—	—	—	—	—	—	—	—	240
Bi_2O_3	—	—	—	—	—	—	—	—	240

a) 20 ml of cyclohexene, 50 ml of benzene and 50 mg of metal oxide were used. The reaction temperature was 60 °C. The O_2 pressure was 1 atm.

$(acac)_2$, MoO_3 or V_2O_5. Therefore, in the present work, the activity of one component metal catalyst was first of all studied. The following results were obtained by use of acetylacetonates and oxides of several metals as catalysts.

Activities of One Component Metal Catalysts. The results with metal acetylacetonate catalysts are given in Table 1. Cobalt and manganese also show high activity. The activity depends on the oxidation states or coordination numbers. In the reaction with $Co(acac)_2$ catalyst, a rapid absorption of oxygen was observed after the color of reaction solution turned from pink to green, suggesting the formation of cobaltic ion. The induction period was shortened by the addition of *t*-butyl hydroperoxide, the oxygen absorption being also accompanied by a similar change of color. Hydroperoxide seemes to be decomposed by way of its coordination to cobalt. Then, the chain reaction starts. In contrast, $Co(acac)_3$ shows relatively low activity which may be ascribed to the larger stability of the six-coordinated octahedral structure.[10)] A long induction period and a low activity observed with $Mn(acac)_2$ indicate that manganous ion inhibited, as reported by Gould and Rado[2)] the autoxidation of cyclohexene by reacting with cyclohexenyl peroxy radical. $Cr(acac)_3$ was reported to have activity in the oxidation of neat cyclohexene.[2)] However, it showed no oxygen absorption in the present work. The deactivation observed especially with $Co(acac)_2$ and $Mn(acac)_3$ seems to result from the formation of the metal oxides or basic chelate. This is supported by the fact that precipitates formed during the course of reaction.

The results of the reactions with several matal oxides catalysts are given in Table 2. Mn_2O_3 shows the highest activity. In spite of the inactivity of chromium and vanadium in the chelate form, their oxides showed activity. Meyer *et al.*[1)] reported that chromium(III) oxides seem to initiate the reaction only by the decomposition of hydroperoxide, while cyclohexene itself may be the initiating agent in the reaction activated by cobalt and manganese oxides. In the present study, the long induction period observed in the reaction with chromium(III) oxide may be due to the accumulation of the hydroperoxide. Manganese oxide exhibiting a considerably short induction period is thought to initiate the reaction without decomposing the hydroperoxide.

Concerning the reaction products, the following results were obtained. The main product with the active catalysts was cyclohexenyl hydroperoxide, the amount of cyclohexene oxide being very small. The selectivity of the hydroperoxide was lower with manganese and cobalt catalysts than with the other catalysts except V_2O_5. This is thought to be caused by the formation of cyclohexenol and cyclohexenone accompanied by the radical decomposition of hydroperoxide. Contrary to the results obtained by Gould and Rado,[2)] MoO_3, $MoO_2(acac)_2$, and $VO(acac)_2$ gave no epoxide. Fairly high selectivity of the epoxide was attained only with V_2O_5. The other catalysts showed low values of selectivity which are near those obtained by using the thermal initiator AIBN.

Details of the Reaction with V_2O_5. In order to clarify the oxidation with V_2O_5 and compare the results with that with other catalysts, several reactions were carried out. The distributions of products in the reactions are given in Table 3. V_2O_5 showed a higher selectivity of cyclohexene oxide than the other catalysts. The high selectivity does not seem to be explained by the radical chain mechanism. The epoxidation with V_2O_5 seems to proceed either by the oxygen activation

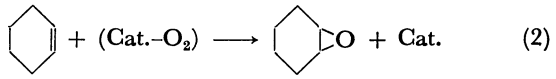
TABLE 3. DISTRIBUTION OF OXIDATION PRODUCTS[a)]

Cat.	Conv. (%)	Select. (%)				React. time (min)
		HPO	ONE	OL	Oxide	
$Co(acac)_2$	12.31	61.7	15.7	18.8	2.7	240
$Mn(acac)_3$	10.72	61.6	12.3	15.5	2.5	240
Mn_2O_3	6.69	69.5	8.5	10.9	2.4	240
Cr_2O_3	4.17	77.3	6.7	8.3	2.4	240
V_2O_5	1.81	34.1	4.1	24.5	20.7	240
$V\text{–}Cr_{(400)}$	5.73	40.3	10.6	27.3	23.4	300
V–Mn	2.58	33.8	9.8	29.8	20.1	300

a) 50 ml of cyclohexene and 50 ml of benzene were used with metal acetylacetonate of 10^{-1} mol or metal oxide of 100 mg. The reaction temperature was 60 °C. The O_2 pressure was 1 atm.

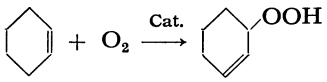
mechanism or the hydroperoxide intermediate mechanism. The former can be shown by

$$\text{Cat.} + O_2 \longrightarrow (\text{Cat.}\text{-}O_2) \quad (1)$$



(2)

and the latter by



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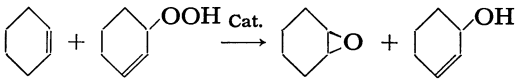

(4)

Reaction 3 proceeds by a radical chain mechanism.

Various studies have been carried out on the formation and reactivity of adsorbed oxygen species on the surface of metal oxides in the field of vapor-phase oxidation. Yoshida *et al.*[11] considered that O_2^-, an adsorbed oxygen species on partially reduced V_2O_5–SiO_2 catalyst, oxidizes propylene at room temperature by a mechanism involving the intermediate of epoxide structure. In the present study, the reduced vanadium species existed also in V_2O_5 catalyst,† and the oxygen activation mechanism is therefore possible. However, in spite of this argument in favor of the oxygen activation process, the fairly large amount of hydroperoxide in the products suggests the availability of another mechanism involving the radical chain reaction 3. The hydroperoxide intermediate mechanism is also supported by the presence of a large amount of cyclohexenol.

In the reactions with cobalt and manganese catalysts, the main products were cyclohexenyl hydroperoxide, cyclohexenol, and cyclohexenone, and the formation of cyclohexene oxide was very small. Such distribution of products may be explained by an acceleration of the radical chain reaction due to the Haber-Weiss mechanism. The distribution of oxidation products with Cr_2O_3 was similar to that with cobalt and manganese catalysts. Cr_2O_3 seems to accelerate the radical chain reaction by decomposing the hydroperoxide.

Reaction Results with Binary Oxide Catalysts. V_2O_5 catalyzes the epoxidation of cyclohexene. The activity of V_2O_5 catalyst increases in acrylaldehyde oxidation when it is modified with another metal oxide, Cr_2O_3, resulting in change of catalyst structure.[5] Similar phenomena concerning the catalyst for vapor-phase oxidation have been reported.[4] The catalytic activities of various binary oxides containing vanadium were tested also in the liquid-phase oxidation of cyclohexene.

Oxygen absorption was observed for several binary oxides. The results are given in Table 4. Concerning the maximum rate of oxygen absorption (R_{max}), the activity of the catalysts can be put in the order $\text{V–Cr}_{(400)} \gg \text{V–Cr}_{(600)} \gg \text{V–Mn} > \text{V–P} > \text{V–Fe} \simeq \text{V–Bi} \simeq \text{V–Mo}_{(800)}$, the other systems showing extremely low activity. The V–Cr system in particular showed high activity. This binary system showed higher activity when calcined at lower temperature, which coincides with results observed in the study of acrylaldehyde oxidation.[5] The activity of the V–Mo system, in contrast, appeared only when calcined at 800 °C. With respect to the formation of cyclohexene oxide, most of these binary systems showed comparatively higher ability than the one component metal oxides (Table 2) or metal acetylacetonates (Table 1).

Structure and Activity of V–Cr and V–Mo Systems. In the liquid-phase oxidation with insoluble metal oxide catalysts, the reaction proceeds by a heterogeneous initiation mechanism on the surface of catalysts.[1] The specific surface area (S_s) of the catalyst having relatively high activity was measured and is given in Table 5, together with the specific activity (R_{max}/S), *i.e.*, the maximum rate of oxygen absorption per unit surface area of the catalyst. The V–Cr system calcined at a low temperature also showed higher values in specific activity.

According to the results of X-ray diffraction analysis (Fig. 2), $\text{V–Cr}_{(400)}$ and $\text{V–Cr}_{(600)}$ showed diffraction

Table 4. Reaction results with binary oxide catalyst[a]

Cat.	Conv. (%)	Yield (%)		Select. (%)		Rate ($\times 10^6$mol/l s)		Ind. Per. (min)	React. time (min)
		Oxide	HPO	Oxide	HPO	R_{max}	R_{end}		
$\text{V–Cr}_{(400)}$	8.52	1.90	3.44	22.3	40.4	25.8	20.6	91	300
$\text{V–Cr}_{(600)}$	3.92	0.98	1.38	25.0	35.2	14.9	14.9	165	330
$\text{V–Cr}_{(800)}$	1.29	0.27	0.34	20.9	26.4	2.3	2.3	200	270
V–Mn	4.39	0.86	1.99	19.6	45.3	4.7	4.7	103	270
V–Fe	3.33	0.56	1.27	16.8	38.2	3.1	3.1	133	270
V–Ni	1.88	0.33	0.74	17.6	39.1	1.6	1.6	194	270
$\text{V–Mo}_{(800)}$	1.76	0.57	0.12	32.4	6.8	3.1	1.6	108	270
V–W	0.53	0.11	0.29	20.8	54.7	0.8	0.8	247	270
V–P	1.39	0.59	0.31	42.4	22.3	3.9	3.9	110	270
V–Sb	1.44	0.65	0.21	45.2	14.6	2.4	2.4	198	270
V–Bi	3.23	0.62	0.39	19.2	12.1	3.1	2.4	100	270

a) 20 ml of cyclohexene, 50 ml of benzene, and 50 mg of binary oxide were used. The reaction temperature was 60 °C. The O_2 pressure was 1 atm. No oxidation occurred for a period of 300 min with the binary oxides (not contained in this Table), *i.e.*, V–alkali metal, V–alkaline earth metal, V–Co, C–Cu, V–Zn, $\text{V–Mo}_{(400)}$, and $\text{V–Mo}_{(600)}$ catalysts.

† The existence of the V^{4+} ions was suggested by ESR measurement.

Table 5. Surface area and specific activity of binary oxide catalyst

Cat.	S_s (m^2/g)	R_{max}/S ($\times 10^6$mol/l s m^2-cat.)
$V-Cr_{(400)}$	7.3	62.5
$V-Cr_{(600)}$	8.0	36.0
$V-Cr_{(800)}$	2.5	16.4
V–Mn	11.5	9.4
V–Fe	23.4	3.1
$V-Mo_{(400)}$	1.1	—
$V-Mo_{(600)}$	1.4	—
$V-Mo_{(800)}$	1.3	53.2
V–P	4.0	20.3
V–Bi	3.5	18.8
V_2O_5	5.2	10.9

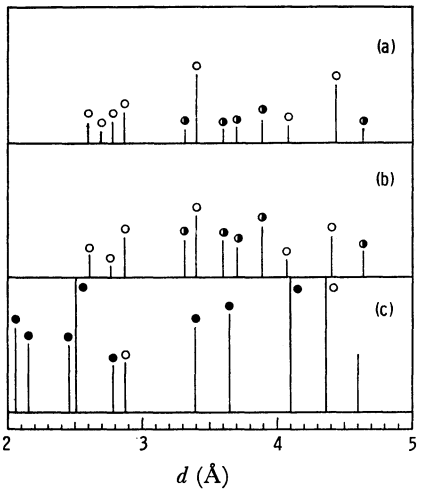

Fig. 2. X-Ray diffraction patterns of V–Cr system catalysts.
(a) $V-Cr_{(400)}$, (b) $V-Cr_{(600)}$, (c) $V-Cr_{(800)}$,
○: V_2O_5, ◑: phase Y, ●: $CrVO_4$.

lines of V_2O_5 and phase Y which was reported to be a chromium isopolyvanadate.[5] However, $V-Cr_{(800)}$ showed no lines of phase Y but gave the lines of V_2O_5 and chromium orthovanadate ($CrVO_4$). While $V-Cr_{(800)}$ showed the line of d=4.38 Å which is thought to be of the plane (001) in pure V_2O_5, the lines observed with $V-Cr_{(400)}$ and $V-Cr_{(600)}$ gave the values 4.43 and 4.41 Å, respectively. This indicates that the c-axis of V_2O_5 crystal was elongated in $V-Cr_{(400)}$ and $V-Cr_{(600)}$, suggesting the formation of interfacial solid solution.†† The diffraction peaks of phase Y were slightly stronger in the pattern of $V-Cr_{(600)}$ than in that of $V-Cr_{(400)}$, while the line width of the peaks was broader in the latter. Thus, it seems that the crystallinity of phase Y is lower in the catalyst calcined at lower temperature. In the IR spectra, the absorption bands of phase Y[5] were observed in both $V-Cr_{(400)}$ and $V-Cr_{(600)}$, especially sharply in the latter catalyst. However, $V-Cr_{(800)}$ showed no such absorption bands. Thus, phase Y and the solid solution were observed in the active V–Cr binary catalysts. Phase Y is mainly formed in the catalysts prepared from NH_4VO_3 and $Cr(NO_3)_3 \cdot 9H_2O$.[5] On the other hand, the catalysts in the present work were prepared from V_2O_5 hydrate and $Cr(NO_3)_3 \cdot 9H_2O$. In spite of the difference in the preparative method, the formation of phase Y was observed in both cases.

The specific activity of $V-Mo_{(800)}$ came next to that of $V-Cr_{(400)}$. However, $V-Mo_{(400)}$ and $V-Mo_{(600)}$ were inactive. Concerning the catalytic activity of the V–Mo system, studies have been carried out in the field of vapor-phase oxidation, and the relationship between the activity and the structure of this system was studied in detail. The activity of this system was explained either by the formation of solid solution of MoO_3 in V_2O_5,[4] or by the formation of chemical compounds.[13] Two types of compound, *i.e.*, $Mo_6V_9O_{40}$ and $Mo_4V_6O_{25}$, were formed in the catalyst used for the oxidation of benzene to maleic anhydride. The X-ray diffraction patterns of $V-Mo_{(400)}$ and $V-Mo_{(800)}$ are shown in Fig. 3. $V-Mo_{(400)}$ gave only the diffraction lines of V_2O_5 and MoO_3. However, in the IR spectra of $V-Mo_{(400)}$ and $V-Mo_{(600)}$, two weak absorption bands were observed at 955 and 1035 cm^{-1} together with the bands of V_2O_5 and MoO_3, suggesting the formation of some amorphous structure. On the other hand, $V-Mo_{(800)}$ showed several new lines together with the lines of V_2O_5, and the d-spacings of the new peaks were in fair agreement with the values of $Mo_6V_9O_{40}$. The diffraction data also indicate formation of solid solution. The d-spacing value of the strongest line of V_2O_5, *i.e.*, d=4.38 Å (001) in pure V_2O_5 and observed in $V-Mo_{(400)}$, was found at d=4.30 Å in $V-Mo_{(800)}$. Consequently, the lattice dimension of c-axis is shortened. According to the results of IR analysis of $V-Mo_{(800)}$, the absorption band assigned to the stretching vibration of V=O double bond was slightly displaced toward lower frequency from 1020 cm^{-1} of pure V_2O_5, broadening considerably. The results agree fairly well with those obtained by Yoshida.[4] Thus, a solid solution of MoO_3 in V_2O_5, belonging to a substitutional type, is formed in $V-Mo_{(800)}$. $V-Mo_{(400)}$ or $V-Mo_{(600)}$ is

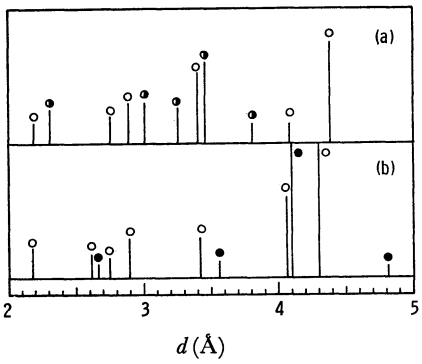

Fig. 3. X-Ray diffraction patterns of V–Mo system catalysts.*
(a): $V-Mo_{(400)}$, (b): $V-Mo_{(800)}$.
○: V_2O_5, ◑: MoO_3, ●: $Mo_6V_9O_{40}$.
* The pattern of $V-Mo_{(600)}$ was similar to of $V-Mo_{(400)}$.

†† It was confirmed that the interfacial solid solution is formed in the binary system. It was observed by Kurina *et al.*[12] that the solid solution is also formed in the binary oxide prepared from NH_4VO_3 and $Cr(NO_3)_3 \cdot 9H_2O$. However, the existence of phase Y was not reported.

considered to be a simple mixture of V_2O_5, MoO_3 and the amorphous structure, and V–$Mo_{(800)}$ to consist of the solid solution and $Mo_6V_9O_{40}$. $Mo_6V_9O_{40}$ contains a reduced vanadium species, V^{4+}, the amount of which is one-ninth of the total vanadium.[13] The reduced vanadium species is also included in the solid solution.[4] V–$Mo_{(400)}$ and V–$Mo_{(600)}$ are inactive††† in spite of the existence of V_2O_5. Since MoO_3 initiates no oxidation, the activity of V–$Mo_{(800)}$ may be due to the reduced species. This V^{4+} ion was also considered to be contained in both Y and the solid solution observed in the V–Cr system. However, this system also contains a chromium species which is considered to be active for the decomposition of hydroperoxide in the form of Cr_2O_3. Thus, though the increase of activity caused by the addition of both chromium and molybdenum oxides seems to be correlated with change of catalyst structure, detailed discussions on this problem are necessary.

Details of the Activity of V–Cr System. The V–Cr system was found to be fairly active for cyclohexene oxidation, especially for the oxidation. In order to elucidate the mechanism of the reaction, the distribution of products in the reaction with V–$Cr_{(400)}$ was studied. The results are shown in Table 3 together with those of the V–Mn catalyst.

Both V–$Cr_{(400)}$ and V–Mn gave a product distribution similar to that with V_2O_5, fairly high selectivity of cyclohexene oxide being obtained. The epoxidation, therefore, is thought to proceed mainly by the hydroperoxide intermediate mechanism in the same way as in the reaction with V_2O_5. On the other hand, the hydroperoxide may be formed by radical chain reaction. The binary system catalysts might have two types of active site, one effective for the radical chain reaction and the other for the epoxidation with the hydroperoxide. Arzoumanian *et al.*[14] reported that the high selectivity of epoxide is obtained in the cyclohexene oxidation with soluble metallic catalyst system, and that this catalyst system is made up of two types of active component; a complex of Rh or Ir effective for the autoxidation, and that of Mo or V for the selective epoxidation. In the present study, it can be presumed that the two types of active site coexist on the surface of catalyst active for epoxidation.

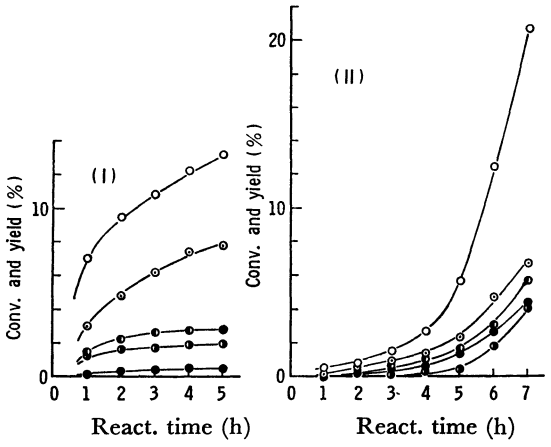

Fig. 4. Product distribution of the cyclohexene oxidation with $Co(acac)_2$ (I) and V–$Cr_{(400)}$ (II).
Reaction temperature: 60 °C, concentration of catalyst: 10^{-3} mol/l ($Co(acac)_2$), 1 g/l (V–$Cr_{(400)}$).
P_{O_2}: 1 atm
○: Conversion of cyclohexene,
⊙: yield of cyclohexenyl hydroperoxide,
◑: yield of cyclohexenone,
◐: yield of cyclohexenol,
●: yield of cyclohexene oxide.

††† This inactivity may be due to the amorphous structure.

Table 6. Epoxidation of cyclohexene with *t*-butyl hydroperoxide[a]

Cat.	Conv. of hydroperoxide (%)	Yield of epoxide (%)
$MoO_2(acac)_2$[c]	64.3	72.6
$VO(acac)_2$[c]	33.5	38.4
$Co(acac)_2$[c]	53.1	5.6
V–$Cr_{(400)}$[d]	26.3	35.6

a) Concentrations of cyclohexene and *t*-butyl hydroperoxide were 0.45 and 0.41 mol/l, respectively. Solvent was benzene, and the reaction temperature was 60 °C. b) Based on reacted hydroperoxide. c) Concentration of catalyst was 10^{-3} mol/l, and reaction time was 2 h. d) Concentration of catalyst was 5 g/l, and reaction time was 3 h.

Co(acac)$_2$ shows high activity at the beginning of the reaction, its activity being lowered with reaction time (Fig. 4). This seems to be due to the change of chelate into the insoluble state. Concerning the distribution of products, cyclohexeneyl hydroperoxide continued to be the main component throughout the reaction time, the amount of cyclohexene oxide remaining very small. Cyclohexene oxide is considered to be formed by the addition mechanism in radical chain reactions as recognized with AIBN. Thus, a typical autoxidation proceeds in the reaction with $Co(acac)_2$ catalyst. In contrast, the activity of V–$Cr_{(400)}$ was low at the biginning of the reaction but increased rapidly with reaction time. That is, the lowering of activity was not observed with this binary oxide. The selectivity of cyclohexenyl hydroperoxide was not so high as in the reaction with $Co(acac)_2$. The amount of both cyclohexene oxide and cyclohexenol was larger than that of cyclohexenone resulting from the decomposition of cyclohexenyl hydroperoxide. In order to clarify the mechanism of epoxidation, several reactions of cyclohexene with *t*-butyl hydroperoxide were carried out in the presence of catalyst (Table 6). $MoO_2(acac)_2$ shows high activity for epoxidation with hydroperoxide.[6] A small amount of epoxide observed in the case with $Co(acac)_2$ seems to be found by the reaction of cyclohexene with *t*-butyl peroxyradical. The yield of epoxide obtained with V–$Cr_{(400)}$ is similar to that with $VO(acac)_2$, suggesting that epoxidation by the hydroperoxide intermediate mechanism proceeds together with the radical decomposition of hydroperoxide. The successive catalytic processes concerning the formation of the epoxide (Eqs. 3 and 4) are supported; the first one consists of the hydroperoxide formation as in a typical autoxidation process, and the second, a selective olefin oxidation wherein the hydroperoxide acts as the oxidizing agent.

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