Heterogeneous Catalysis in the Liquid-phase Oxidation of Olefins. III. Activity of Supported Vanadium–Chromium Binary Oxide Catalyst for the Oxidation of Cyclohexene

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The liquid-phase oxidation of cyclohexene has been conducted in benzene using a vanadium–chromium binary oxide supported on γ-Al_2O_3 or SiO_2 as the catalyst. Three series of catalysts have been prepared by a kneading method using the following combinations of raw materials; $NH_4VO_3+Cr(NO_3)_3\cdot 9H_2O+$alumina hydrate (Catalyst G), $NH_4VO_3+(NH_4)_2CrO_4+$alumina hydrate (H), and $NH_4VO_3+Cr(NO_3)_3\cdot 9H_2O+$silica sol (I). It has been found that the activity of the supported binary system is due to the interactions between the metal oxides and the carrier. The contributions of compounds such as the chromium isopolyvanadates appear to add to the above activity. The order of catalytic activity has been established as : I>H>G. The V_2O_5–SiO_2 system in the I series showed the highest activity, but rapidly became depleted in the course of reaction. The second highest activity was given by Cr_2O_3–SiO_2 system, on which Cr^{5+} species was observed. In both cases, the vanadium and chromium metal ions may be coordinated tetrahedrally on SiO_2. The Cr_2O_3–Al_2O_3 in the H series contained Cr^{5+} ions and exhibited high activity which may be attributed to the tetrahedral configuration. It is thought that the tetrahedral complexes catalyze the autoxidation of cyclohexene by decomposing 1-cyclohexenyl hydroperoxide.

Vanadium–chromium binary oxides (V–Cr) have shown activities in the liquid-phase oxidations of acrylaldehyde[1)] and cyclohexene.[2,3)] The activities were found to be largely influenced by the method of catalyst preparation, *i.e.*, the use of a more acidic medium promoted the formation of chromium isopolyvanadate which contained a more condensed vanadate anion, resulting in the increase in catalytic activity.[3)]

With practical catalysts, the active components are generally supported on carriers such as silica and alumina which possess a high surface area; that the carriers have a profound effect on the activity of catalyst has been demonstrated. A one component system, *i.e.*, supported V_2O_5 or Cr_2O_3, has been extensively used as a catalyst for example in gas-phase oxidation of hydrocarbons and in the polymerization of ethylene, respectively. The dependency of the activity of γ-Al_2O_3- or SiO_2-supported one component systems on the surface structure has been investigated in detail.[4—10)] In the present work, the liquid-phase oxidation of cyclohexene has been conducted using γ-Al_2O_3- or SiO_2-supported V–Cr system as the catalyst. The effects of the carriers and the methods of preparation on the activity have been discussed.

Experimental

Catalysts. The supported binary system catalysts were prepared by the kneading method as follows; aqueous solutions of the raw materials of vanadium and chromium oxide components were poured into alumina hydrate (Shokubai Kasei Co., Ltd.) or silica sol (Snowtex, Kokusan Kagaku Co., Ltd.), and the mixture kneaded at 80 °C for 6 h, dried at 100 °C for one day, and calcined at 450 °C for 5 h in air. The resulting catalyst was pulverized and used (30—40 mesh particle size powder). NH_4VO_3, $Cr(NO_3)_3\cdot 9H_2O$, and $(NH_4)_2CrO_4$ were used as the raw materials for the metal oxide components. The symbol, concentration (calculated as $V_2O_5+Cr_2O_3$ (wt %)) and composition of supported metal oxides (in terms of atomic % of Cr/(V+Cr)), and specific surface area (S_s) are given in Tables 1 and 2.

Apparatus and Procedure. The oxidation was conducted at 60 °C for 4 h under 1 atm of O_2 using the batch system.[2)] Cyclohexene (20.0 ml, purified by passing it over activated alumina to eliminate the hydroperoxide), benzene as solvent (50.0 ml), *t*-butyl hydroperoxide (BHPO) (0.1 ml), and the catalyst (50.0 mg) were used in each reaction. BHPO purified by distillation (40.0 °C/25 mmHg) was added such that reproducible results of oxidation were obtained.

Analyses of Reaction Products and Catalysts. The reaction products; 1-cyclohexenyl hydroperoxide (HPO), 2-cyclohexen-1-one (ONE), 2-cyclohexen-1-ol (OL), and cyclohexene oxide (OXIDE) were determined by the iodometric method and gas chromatography.[2)]

The surface area of the catalyst was measured by the BET method, the structure being studied by means of X-ray diffraction and infrared absorption.[2)] X-Ray photoelectron spectroscopy (XPS) measurements were carried out on a Du Pont ESCA 650 B using monochromatic Al $K\alpha$ radiation in order to clarify the surface properties of the catalyst. The power of X-ray radiation was 300 W (7.5 kV, 40 mA) in all measurements. All binding energy values were referred to the contamination C 1s line (285.0 eV).

Results and Discussion

Surface Area of Catalyst. Both γ-Al_2O_3 and SiO_2 prepared in the present work gave similar values of S_s. This value increased by supporting metal oxides on γ-Al_2O_3, and decreased on SiO_2 (Table 1). On the γ-Al_2O_3 carrier, the use of $(NH_4)_2CrO_4$ caused a small increase in S_s, compared with that of $Cr(NO_3)_3\cdot 9H_2O$ (Table 2).

Addition of BHPO. The results of using the G-5 catalyst are shown in Table 3 (Run Nos. 6 and 7). In the absence of BHPO, the induction period of oxygen uptake showed no fixed value, resulting in no reproducibility for the conversion. By adding a small amount of BHPO, reproducible results were obtained (Run No. 7). No oxygen absorption was observed for 5 h in the absence of catalyst and BHPO; the addition of 1 ml of BHPO caused a small amount of oxygen

TABLE 1. CONCENTRATION OF SUPPORTED METAL OXIDES, SYMBOL, AND SPECIFIC SURFACE AREA OF CATALYST

Concentration $V_2O_5+Cr_2O_3$ (wt %)	γ-Al_2O_3-series[a)]		SiO_2-series[b)]	
	Symbol	S_s, (m^2/g)	Symbol	S_s, (m^2/g)
0	γ-Al_2O_3	220	SiO_2	210
1	V-Cr-γ-Al_2O_3-(1)	246	V-Cr-SiO_2-(1)	202
5	V-Cr-γ-Al_2O_3-(5)	277	V-Cr-SiO_2-(5)	181
10	V-Cr-γ-Al_2O_3-(10)	293	V-Cr-SiO_2-(10)	160
20	V-Cr-γ-Al_2O_3-(20)	270	V-Cr-SiO_2-(20)	142

a) Cr/(V+Cr): 50 atom %. b) Cr/(V+Cr): 70 atom %. Both series were prepared from NH_4VO_3 and $Cr(NO_3)_3 \cdot 9H_2O$.

TABLE 2. COMPOSITION OF SUPPORTED METAL OXIDES, SYMBOL, AND SPECIFIC SURFACE AREA OF CATALYST

Composition Cr/(V+Cr) (atom %)	G-Series[a)]		H-Series[b)]		I-Series[c)]	
	Symbol	S_s, (m^2/g)	Symbol	S_s, (m^2/g)	Symbol	S_s, (m^2/g)
0	G-0	261	H-0	255	I-0	109
20	G-2	274			I-2	105
30			H-3	268		
40	G-4	282			I-4	124
50	G-5	265	H-5	249		
60	G-6	260			I-6	132
70			H-7	232	I-7	138
80	G-8	252			I-8	131
100	G-10	244	H-10	212	I-10	136

a) Prepared from NH_4VO_3, $Cr(NO_3)_3 \cdot 9H_2O$, and alumina hydrate. b) Prepared from NH_4VO_3, $(NH_4)_2CrO_4$, and alumina hydrate. c) Prepared from NH_4VO_3, $Cr(NO_3)_3 \cdot 9H_2O$, and silica sol. Concentration of metal oxides (calculated as $V_2O_5+Cr_2O_3$) was 20 wt % in each series.

TABLE 3. OXIDATION OF CYCLOHEXENE[a)]

Run No.	Catalyst	Amount of BHPO added (ml)	Induction period (min)	R_{max} (mol/l·s)	Conversion of cyclohexene (%)	Selectivity			
						HPO (%)	ONE (%)	OL (%)	OXIDE (%)
1	—	1	110	3.13×10^{-6}	3.7	—	—	—	—
2	γ-Al_2O_3	1	240	—	—	—	—	—	—
3	SiO_2	1	179	3.36×10^{-6}	3.8	—	—	—	—
4	V-Cr-D-5[b)]	—	110—120	3.24×10^{-5}	10.1	40.3	10.5	25.2	20.3
5	V-Cr-D-5[b)]	0.1	10	3.31×10^{-5}	25.0	38.5	9.7	24.5	21.0
6	G-5	—	150—300	1.03×10^{-4}	c)	16.9[c)]	30.5[c)]	35.3[c)]	15.1[c)]
7	G-5	0.1	4	1.06×10^{-4}	30.1	15.2	31.3	36.0	12.6

a) Cyclohexene (20.0 ml), benzene (50.0 ml), and catalyst (50.0 mg) were used. The reaction temperature was 60 °C, the reaction time 4 h, and the oxygen pressure 1 atm. b) V-Cr-D-5 is the unsupported catalyst reported in a previous paper.[3)] Cr/(V+Cr); 50 atom %, and S_s; 8.3 m^2/g. c) The value of conversion was not precisely obtained, as the induction period was not constant. The values of selectivity are average values.

absorption (Run No. 1). Both γ-Al_2O_3 and SiO_2 showed no activity. V–Cr–D-5 is the unsupported binary oxide catalyst which showed high activity in a previous report[3)] (Run Nos. 4 and 5, S_s 8.3 m^2/g). The activity of the V–Cr system of G-5 showing a S_s of 265 m^2/g may be attributed to the large surface area.

The effect of the addition of BHPO is shown in Fig. 1. The induction period was greatly reduced by the addition of a small amount of BHPO, producing an almost constant induction period when the amount of BHPO exceed 0.1 ml. There is the possibility that the BHPO affects the reaction reults, *e.g.*, the product distribution may be changed by a stoichiometric epoxidation of cyclohexene with BHPO, *etc.* In order to avoid such possibilities, the amount of BHPO was fixed at 0.1 ml (9.2×10^{-4} mol) which is extremely small compared with the amount of cyclohexene (20 ml; 1.97×10^{-1} mol). The values of selectivity were not affected as shown in the two pairs of reaction (Run Nos. 4 and 5 and Run Nos. 6 and 7). BHPO appears to work mainly as an initiator by way of its decomposition on the catalyst. In all subsequent reactions, 0.1 ml of BHPO was added to obtain reproducible results.

Oxygen Uptake. The curves of oxygen uptake

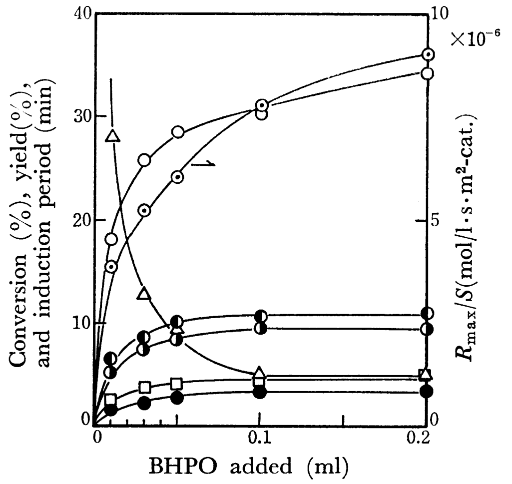


Fig. 1. Effect of the addition of BHPO. 20.0 ml of cyclohexene, 50.0 ml of benzene, and 50.0 mg of G-5 catalyst were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
⊙ R_{max}/S, ○ conversion of cyclohexene, □ yield of HPO, ◑ yield of ONE, ◐ yield of OL, ● yield of OXIDE, △ induction period.

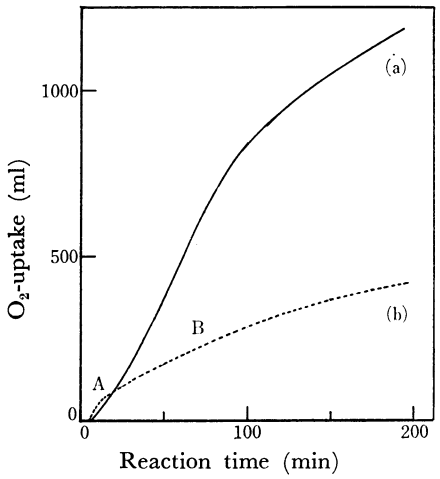
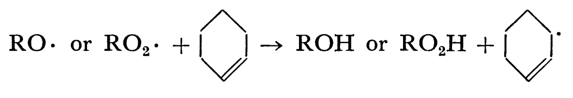


Fig. 2. Oxygen absorption.
(a) Catalyst: G-5, (b) catalyst: I-0. 20.0 ml of cyclohexene, 50.0 ml of benzene, and 50.0 mg of the catalyst were used. The reaction temperature was 60 °C, and the O_2-pressure was 1 atm.

are shown in Fig. 2. Most of the catalysts used gave a typical S-shaped oxygen absorption curve (a); I-0, I-2, and I-4 show different types of absorption (b). In the latter type, rapid absorption was observed immediately after the induction period (A), followed by a linear decrease in the rate of oxygen uptake (B). As the V_2O_5–SiO_2 system illustrates the high activity for the decomposition of BHPO into radicals[11] (Eq. 1), the rapid reaction at A may be due to a chain reaction (Eqs. 2, 3, and 4) induced by the radicals formed from BHPO.

$$\text{BHPO} \xrightarrow{M^{n+}/M^{(n+1)+}} \text{RO}\cdot \text{ and } \text{RO}_2\cdot \qquad (1)^{12)}$$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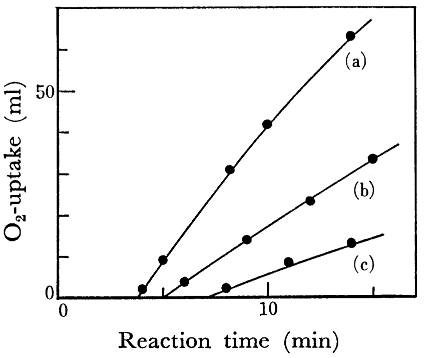
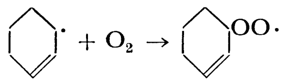


Fig. 3. Effect of the amount of BHPO added on the oxygen absorption.
BHPO added; (a) 0.1 ml (b) 0.05 ml (c) 0.03 ml 20.0 ml of cyclohexene, 50.0 ml of benzene, and 50.0 mg of I-0 catalyst were used. The reaction temperature was 60 °C, and the O_2-pressure was 1 atm.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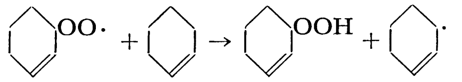
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M indicates the metal on the catalyst. Evidence for such an induction period was conducted with several oxidations with a I-0 catalyst and a changing amount of BHPO, the results of which are given in Fig. 3 (A is magnified). As can be seen, the maximum rate of O_2-uptake at A (R_{max}-A) showed a first order dependency on the amount of BHPO added, supporting the above mechanism. The rate at B, which suggests a steady state in the oxidation, was independent of the amount of BHPO added. As BHPO was decomposed rapidly on V_2O_5–SiO_2,[11] the O_2-uptake at B may be uniquely due to the radical chain of cyclohexene oxidation, the rate of which is shown by R_{max}-B. The specific activity, *i.e.*, the maximum rate per unit surface area of the catalyst, and the induction period of O_2-uptake are shown in Figs. 4 and 5.

Effect of Amount of Metal Oxides Supported. Figure 4 illustrates the effect of the amount of metal oxides supported on γ-Al_2O_3 or SiO_2. It is of interest that the activity on SiO_2 increased rapidly when a small amount (about 1 wt %) of metal oxides was supported, and remained almost constant with further additions. On γ-Al_2O_3, however, high acitivity was obtained only when a sufficient amount of metal oxides was supported. The product distributions are shown in Figs. 6 and 7. The formations of the two types of active site, *i.e.*, one effective for the autoxidation and another for the selective epoxidation of cyclohexene with HPO, on V–Cr system catalyst have been reported.[2,3] For the present catalysts, two types of active site appear to form, because the OXIDE formation was accompanied with that of OL, suggesting selective epoxidation. The autoxidation which produces HPO and ONE appears to be well catalyzed on the catalyst including a small amount of metal oxides.

Effect of Composition of Metal Oxides. Figure 5 shows the influence of the composition of metal

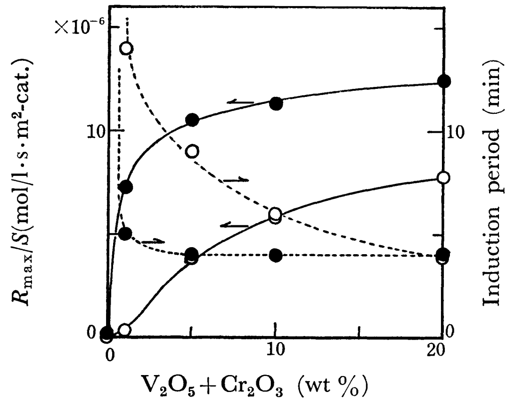


Fig. 4. Effect of the concentration of metal oxides supported.
20.0 ml of cyclohexene, 50.0 ml of benzene, and 50.0 mg of the catalyst were used. The reaction temperature was 60 °C, and the O_2-pressure was 1 atm. Catalyst; ● V–Cr–SiO_2 (Cr/(V+Cr)=70 atom%), ○ V–Cr–γ-Al_2O_3 (Cr/(V+Cr)=50 atom%).

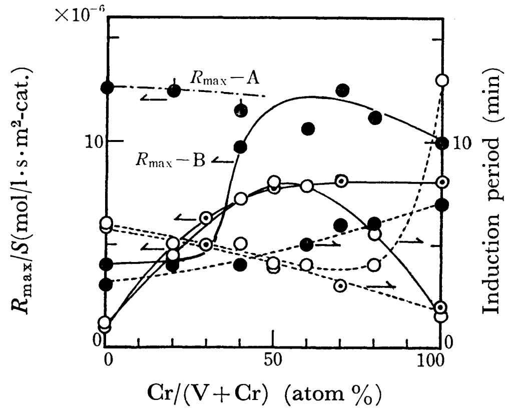


Fig. 5. Effect of the composition of metal oxides supported.
20.0 ml of cyclohexene, 50.0 ml of benzene, and 50.0 mg of the catalyst were used. The reaction temperature was 60 °C, and the O_2-pressure was 1 atm. Catalyst; ● I-series, ⊙ H-series, ○ G-series. Concentration of metal oxides supported, $V_2O_5+Cr_2O_3$: 20 wt %.

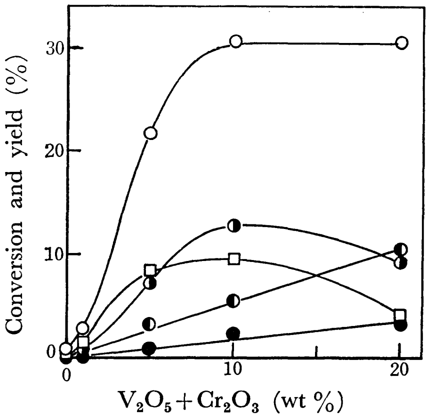


Fig. 6. Effect of the concentration of supported metal oxides on γ-Al_2O_3.
20.0 ml of cyclohexene, 50.0 ml of benzene, 50.0 mg of the catalyst, and 0.1 ml of BHPO were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
○ Conversion of cyclohexene, □ yield of HPO, ◑ yield of ONE, ◐ yield of OL, ● yield of OXIDE.

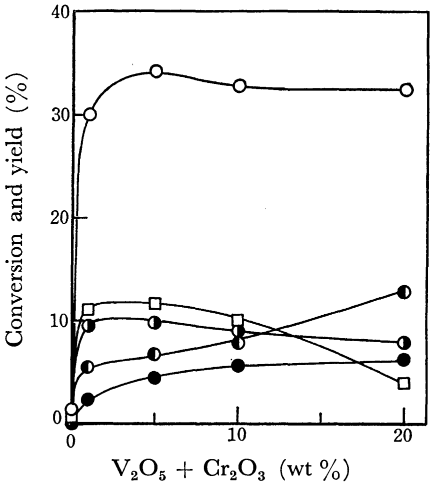
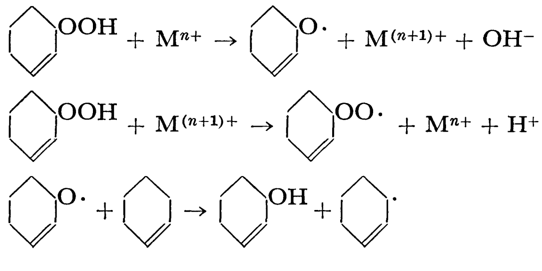


Fig. 7. Effect of the concentration of supported metal oxides on SiO_2
20.0 ml of cyclohexene, 50.0 ml of benzene, 50.0 mg of the catalyst, and 0.1 ml of BHPO were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
○ Conversion of cyclohexene, □ yield of HPO, ◑ yield of ONE, ◐ yield of OL, ● yield of OXIDE.

oxides supported. In the case of the I-series catalyst, the two types of reaction rate, *i.e.*, R_{max}-A and R_{max}-B, are shown together. The activity of the binary system on SiO_2 was higher than that on γ-Al_2O_3, when adopting the value of R_{max}-A/S. According to the oxygen uptake in B, the activities (R_{max}-B/S) of only two catalysts I-0 and I-2 showed similar values to those of the γ-Al_2O_3-supported system, *i.e.*, the two catalysts exhibited high activities at the start of oxygen uptake, being largely deactivated during the oxidation. It is noteworthy that V_2O_5–SiO_2 (I-0) showed a high activity (R_{max}-A/S) in comparison with V_2O_5–Al_2O_3. In the activity of the γ-Al_2O_3-supported systems, clear difference between the G- and H-series catalysts including the large amount of Cr was observed, H-series prepared from $(NH_4)_2CrO_4$ being more active than the G-series from $Cr(NO_3)_3\cdot 9H_2O$. The difference was observed in both the R_{max}/S and the induction period.

Reaction Scheme. The product distributions obtained with the three series of catalysts are shown in Figs. 8, 9, and 10. The results can be interpreted by the following reaction scheme which has been proposed in the literatures.[2,13–18)]



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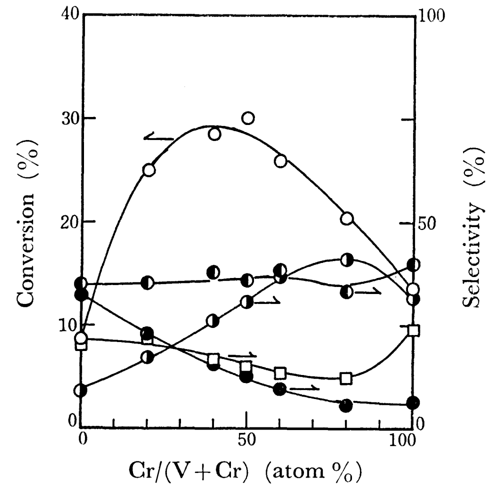


Fig. 8. Product distributions in the oxidation with G-series catalysts.
20.0 ml of cyclohexene, 50.0 ml of benzene, 50.0 mg of the catalyst, and 0.1 ml of BHPO were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
○ Conversion of cyclohexene, □ selectivity of HPO, ◑ selectivity of ONE, ◐ selectivity of OL, ● selectivity of OXIDE.

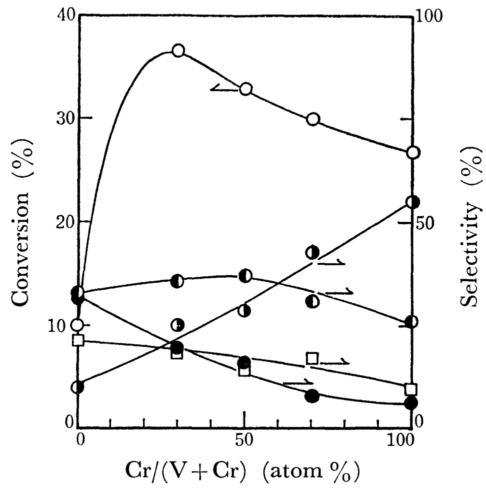
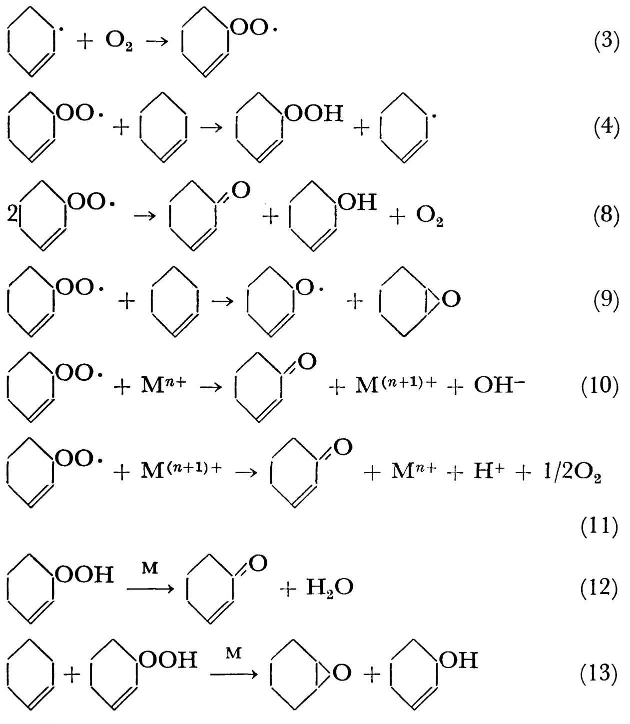


Fig. 9. Product distributions in the oxidation with H-series catalysts.
20.0 ml of cyclohexene, 50.0 ml of benzene, 50.0 mg of the catalyst, and 0.1 ml of BHPO were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
○ Conversion of cyclohexene, □ selectivity of HPO, ◑ selectivity of ONE, ◐ selectivity of OL, ● selectivity of OXIDE.



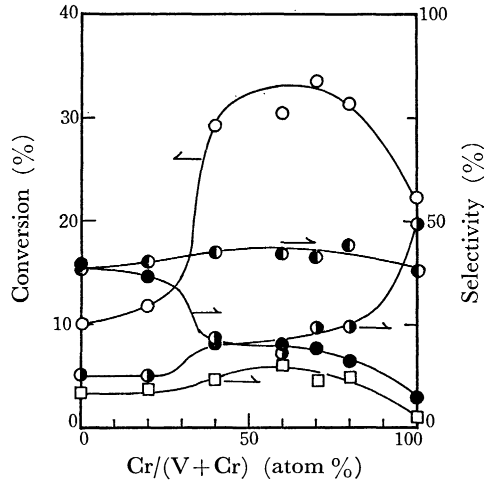


Fig. 10. Product distributions in the oxidation with I-series catalysts.
20.0 ml of cyclohexene, 50.0 ml of benzene, 50.0 mg of the catalyst, and 0.1 ml of BHPO were used. The reaction temperature was 60 °C, the reaction time was 4 h, and the O_2-pressure was 1 atm.
○ Conversion of cyclohexene, □ selectivity of HPO, ◑ selectivity of ONE, ◐ selectivity of OL, ● selectivity of OXIDE.

For the purpose of studying the action of the catalysts on hydroperoxide, the decomposition of BHPO was conducted at 60 °C in a N_2 atmosphere. All the catalysts used except I-0—I-6** gave *t*-butyl alcohol (85%), di-*t*-butyl poerxide (10%), and acetone (5%), showing that the decomposition of BHPO proceeds *via* a homolytic mechanism.[12] The homolytic decomposition of HPO (Eqs. 5 and 6) must also be considered. Reactions 3 and 4 are chain propagating and Reaction 8 is a biradical termination, by which equimolar amounts of ONE and OL are formed. Reaction 9 is the addition of the peroxyl radical to cyclohexene, although the contribution is very small.[13] Reactions 10 and 11 are an adaptation of the mechanism recently proposed by Mizukami *et al.* in the oxidation of tetralin.[18] The dehydration of HPO on the catalyst

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** When using these catalysts, isobutylene and di-*t*-butyl ether were formed together with three products mentioned above. The details of the decomposition of BHPO will be reported in a later paper.

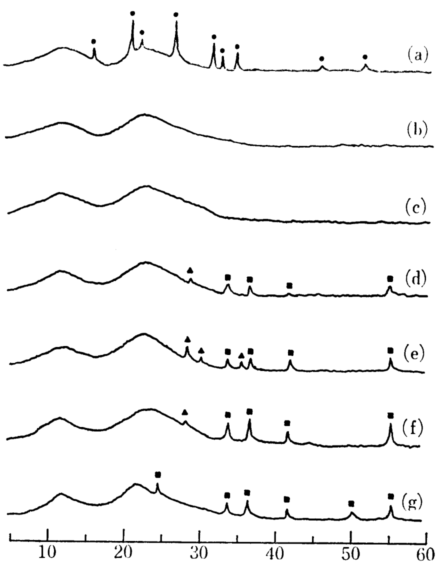

Fig. 11. X-Ray diffraction diagrams of I-series catalysts (Cu *K*α).
a : I-0, b : I-2, c : I-4, d : I-6, e : I-7, f : I-8, g : I-10.
● : V_2O_5, ▲ : $Cr_4(V_2O_7)_3$, ■ : Cr_2O_3.

(Eq. 12) must also be considered as reported by Neuburg *et al.*17) and Reaction 13 is the selective epoxidation already reported.2) It may be easily understood that the selective epoxidation proceeded well on the catalyst containing large amount of vanadium. On γ-Al_2O_3, a higher value of conversion was obtained with the H-series , the G- and H-series showing a similar pattern of product distribution up to a Cr content of about 70 atom %. Beyond this value, ONE increased in the H-series and the formation of HPO and OL took precedence over the G-series. Thus, a higher ratio of ONE/OL and simultaneously higher activity (Fig. 5) given by the H-series at higher Cr content, suggests that Reactions 10, 11, and 12 may be useful together with the biradical termination (Eq. 8) as the mechanism for ONE formation. On the other hand, OL is considered to form mainly by Reactions 7 and 8 and the selective epoxidation when using catalysts containing a lot of vanadium. The stabilities of ONE and OL under reaction conditions were examined: separate solutions with 10 ml of ONE and OL in benzene (50 ml containing BHPO (0.1 ml)) were prepared and oxidized at 60 °C with G-5 catalyst (50 mg). ONE did not show any conversion to further oxidized products after 4 h of reaction, whilst an extremely small amount (about 0.8 mol %) of OL was converted into the ketone after 4 h.

I-0 and I-2 showing the high activities at the beginning were deactivated quickly as described above, resulting in low conversion. This suggests the instability of the active species on I-0 and I-2.

Structure of Catalysts. It has already been reported1–3) that several chemical compounds, *e.g.*, chromium divanadate ($Cr_4(V_2O_7)_3$), chromium metavanadate ($Cr(VO_3)_3$), and chromium polyvanadates, together with V_2O_5 and Cr_2O_3 form in the catalysts of the V–Cr system. These species largely influence catalytic activity. In the present binary system supported on γ-Al_2O_3 or SiO_2, the contributions of the species formed by the interaction between metal oxides and carrier may be reasonably expected together with those of the above chemical compounds. The former contributions have been extensively studied by many researchers.4–10) When each of V_2O_5 andCr_2O_3 was supported on γ-Al_2O_3 or SiO_2 by impregnation, various problems were encountered, among which one can quote the stabilization and the role of different valency states of metals. The system under study appears to show further complexity due to the binary oxide being supported on γ-Al_2O_3 or SiO_2 by the kneading method.

X-Ray diffraction diagrams of the I-series catalysts are shown in Fig. 11. Several weak diffraction lines of V_2O_5, $Cr_4(V_2O_7)_3$, and Cr_2O_3 were observed together with two broad lines of fine SiO_2 crystals. The γ-Al_2O_3 supported systems (G- and H-series) did not exhibit any lines other than the broad lines of γ-Al_2O_3. The indication is that the crystal of the metal oxides developed better on SiO_2 than on γ-Al_2O_3, the interspacing of the lattice planes of each metal oxide being the same as that of each pure oxide. Yoshida *et al.*5) reported that γ-Al_2O_3 interacts with V_2O_5 more strongly than SiO_2 as a carrier of the impregnated catalyst. In the system here, prepared by the kneading method, further interaction may be expected as observed in the case of the coprecipitated Cr_2O_3–Al_2O_3 (Cr_2O_3; 19.6 mol %) system, in which the only structure detected by X-ray diffraction measurement was γ-Al_2O_3.9) Infrared absorption spectra of the γ-Al_2O_3-supported system showed a strong broad band of γ-Al_2O_3 below 1000 cm^{-1} which covered the characteristic absorption bands of V_2O_5, Cr_2O_3, and chromium isopolyvanadates.3) The binary systems supported on SiO_2; I-0—I-7, exhibited weak absorption bands centered at about 950 and 870 cm^{-1}, together with the strong absorption bands at 1100 and 800 cm^{-1} of SiO_2. The weak bands may be assigned to the vibrations of VO_3 in $Cr_4(V_2O_7)_3$,3) the formation of $Cr_4(V_2O_7)_3$ together with V_2O_5 and Cr_2O_3 being thus clarified in the binary system of I-series. Such formation need not be excluded from the γ-Al_2O_3-supported system, though it may not be detected.

Recently, XPS studies have been conducted to elucidate the surface properties of γ-Al_2O_3-7) or SiO_2-6) supported chromia systems. The advantages of the XPS technique are its ability in simultaneously detemining the valencies of metal ions on the surface layer (—10 Å) of the catalyst and the interaction between the catalyst and the support. The first XPS spectra of Cr^{5+} were observed by Okamoto *et al.*7) who emphasized that the spin-orbit splitting of the Cr 2p level (ΔE) is useful together with the binding energy for discriminating the valence states of chromium. Moreover, it was pointed out that the chromium species on the catalyst surface can readily be photoreduced by X-ray radiation during XPS measurements.6,7) In order to avoid surface reduction, all spectra of the Cr 2p level were measured within 10 min exposure to X-ray flux, in which the photo-reduction

TABLE 4. BINDING ENERGY OF Cr 2p3/2 AND V 2p3/2, SPIN-ORBIT SPLITTING OF Cr 2p LEVEL, AND ASSIGNMENT OF VALENCY OF CHROMIUM

Catalyst or compound	Cr 2p3/2 (eV)	V 2p3/2 (eV)	ΔE (eV)	Assignment of Cr valency[a]
V_2O_5	—	515.9	—	—
VO(acac)$_2$	—	516.0	—	—
Cr_2O_3	576.7	—	9.8	3+
K_2CrO_4	579.6	—	9.1	6+
V-Cr-D-5	577.5	517.5	9.7	3+
G-0	—	517.4	—	—
G-4[b]	577.6	517.4	9.7	3+ (5+)
G-6	578.0	517.5	9.5	5+ (3+)
G-10	577.5	—	9.8	3+ (5+)
H-3[b]	577.5	517.4	9.7	3+ (5+)
H-5	577.8	517.4	9.5	5+ (3+)
H-7[c]	579.3	517.3	9.0	6 & 5+ (3+)
H-10[c]	579.7	—	9.1	6 & 5+
I-0	—	516.6	—	—
I-4	577.4	516.7	9.8	3+
I-6	577.6	516.5	9.1	5+ (3+)
I-10	577.9	—	9.1	5+ (3+)

a) Valence state in parentheses indicates minor one. b) This peak has a weak shoulder at higher binding energy. c) This peak shows a large broadening at lower binding energy.

TABLE 5. COMPARISON OF THE ACTIVITIES OF SEVERAL CHROMIUM SYSTEM CATALYSTS[a]

Catalyst[b]	Induction period (min)	R_{max} (mol/l·s)	Conversion of cyclohexene (%)	Selectivity			
				HPO (%)	ONE (%)	OL (%)	OXIDE (%)
V-Cr-γ-Al_2O_3	5	8.6×10^{-5}	29.0	20.1	22.2	35.0	18.5
Mo-Cr-γ-Al_2O_3	11	7.8×10^{-5}	28.8	11.5	20.5	37.1	30.3
W-Cr-γ-Al_2O_3	8	5.2×10^{-5}	20.2	17.6	45.0	28.3	7.3
Co-Cr-γ-Al_2O_3	8	6.5×10^{-5}	23.2	17.4	51.4	23.6	5.6
Mn-Cr-γ-Al_2O_3	5	5.8×10^{-5}	26.7	19.6	41.5	32.3	3.5

a) Cyclohexene (20.0 ml), benzene (50.0 ml), the catalyst (50.0 mg), and BHPO (0.1 ml) were used. The reaction temperature was 60 °C, the reaction time 4 h, and the O_2-pressure 1 atm. b) The catalysts (Me-Cr-γ-Al_2O_3) were prepared from the following raw materials; NH_4VO_3, $(NH_4)_6Mo_7O_{24}\cdot4H_2O$, $5(NH_4)_2O\cdot12WO_3\cdot5H_2O$, $Co(NO_3)_3\cdot6H_2O$, $Mn(NO_3)_3\cdot xH_2O$, $Cr(NO_3)_3\cdot9H_2O$, and alumina hydrate by the kneading method. The concentration of metal oxides supported on each catalyst was 20 wt % when calculated as V_2O_5, MoO_3, WO_3, Co_2O_3, Mn_2O_3, and Cr_2O_3. The composition of the binary system (Cr/(Me+Cr)) was 30 atom %.

was found to be negligible. The results of XPS measurements are shown in Table 4, the assignment of the valence states of chromium being done according to the results by Okamoto *et al.*[7] In the valence state of vanadium, Larrson *et al.*[19] observed a shift of the V 2p3/2 binding energy between V_2O_5 (516.6 eV) and VO(acac)$_2$ (515.1 eV), but it was not observed here (Table 4). Valdelievre *et al.*[20] obtained the V 2p3/2 values of 515.5 eV for V_2O_5 and 516.0 eV for V_2O_4 when studying the V_2O_5 catalyst in the oxidation of propylene. Therefore, it may be difficult to determine the valence state of vanadium, importance being given to the fact that the V 2p3/2 binding energy is lower on SiO_2 than on γ-Al_2O_3.

Active Sites. The active sites on the supported V–Cr binary oxide catalyst may be classified into two types; autoxidation and selective epoxidation.[2] The latter site may consist mainly of vanadium species, although the details have not been clarified. The activities of several Me–Cr systems, when Me is V, Mo, W, Co, and Mn, have been compared (Table 5), exhibiting the following order of activity for selective epoxidation; Mo–Cr–γ-Al_2O_3>V–Cr–γ-Al_2O_3>W–Cr–γ-Al_2O_3. The order of metals, *i.e.*, Mo>V>W, agrees well with that observed in the selective epoxidation of olefins with organic hydroperoxide using soluble metal complexes.[21] Co, Mn, and Cr species did not contribute to the epoxidation but accelerated the autoxidation. Thus, the Mo–Cr or V–Cr binary system showed a high yield of OXIDE whose formation may have been aided by the dual functions of the systems, as observed in the homogeneous mixed catalyst system by Fusi *et al.*[22] and Arzoumanian *et al.*[23]

The former site appears more complex than the latter since the the value of $R_{\max}/S$ depends largely on the carrier (Figs. 4 and 5) and the composition of the binary system (Fig. 5). The activity of the G-series showed a maximum value at a composition of 50 atom % Cr, which may be due to the formation of chromium isopolyvanadates, as reported in the unsupported system.[3] Such an increase in the activity due to chemical compound formation may be also expected in the H-series and especially in the I-series, in which the formation of $Cr_4(V_2O_7)_3$ was clearly observed. A more important problem, however, appears to be the effect of the carrier on the activity. At high Cr content on γ-Al_2O_3, the H-series gives a higher rate and a simultaneously higher valence state of chromium (Table 4) than the G-series, suggesting the active species of highly charged chromium ions. The high valence state of chromium (Cr^{5+}) was also observed in the I-series supported on SiO_2 which showed high activity. One of the active species for autoxidation appears, therefore, to be the Cr^{5+} ions which form on the catalyst during preparation. The role of the Cr^{6+} species which still remains in the H-series (prepared from $(NH_4)_2CrO_4$) after calcination can not be ignored, but it is not so clear. The Cr^{5+} ions observed on G-4 and G-6 catalysts may mainly form in the interaction between the catalyst and carrier, since the unsupported system (V–Cr–D-5) does not show such evidence.

Van Reijen *et al.*[4] reported that Cr^{5+} is coordinated mainly tetrahedrally when supported on SiO_2 and square-pyramidally on γ-Al_2O_3, and that the tetrahedral complex (CrO_4) is more reactive than the squarepyramidal one (CrO_5). Such phenomena has also been confirmed in the literature.[8,10] Also the vanadium (V^{4+}) species is coordinated in (VO_4) on SiO_2 and in (VO_5) on γ-Al_2O_3,[4,5,24] and the (VO_4) on SiO_2 is highly reactive towards, *e.g.*, C_2H_4, being subsequently transformed into the stable (VO_5).[4] By contrast, the (VO_5) is more stable than the corresponding configuration of Cr^{5+}, *i.e.*, (CrO_5).[4] Moreover, when considering the coordination state in aqueous solution of the catalyst preparation, the tetrahedral $(CrO_4)^{3-}$ ion may be preferentially found in highly alkaline solution[25] whereas the coordination is square-pyramidal in acid solution, as well known for V^{4+} in many vanadyl complexes.[26] A part of the Cr^{5+} ions on H-10 and H-7 can be reasonably coordinated in the tetrahedral configuration, whereas those on G-8 in the square-pyramidal configuration. The order of reactivity of these configurations has been given by van Reijen *et al.*[4] as follows; $(VO_4)>(CrO_4)>(CrO_5)>(VO_5)$, in which only the ($VO_4$) is unstable. This order appears to explain the activity of the supported V–Cr binary system catalyst, when the configurations of vanadium and chromium complexes might be allowed on the carriers as described above. On SiO_2, the catalyst abundant in vanadium exhibited high activity (Fig. 5, $R_{\max}$-A/S) at the beginning of reaction, which decreased ($R_{\max}$-B/S) in the course of reaction. This may be due to the high reactivity and instability of the (VO_4) complex. The subsequently high activity of the chromium abundant catalyst on SiO_2 may be due to the (CrO_4) species which is reactive and simultaneously stable. When supported on γ-Al_2O_3, the catalysts of the H-series expected to contain the (CrO_4) complex in abundance exhibited higher activities than those of the G-series rich in chromium. It has been reported that the (CrO_4) complex was formed on SiO_2 even when small amounts of chromia was supported,[6] and therefore, the rapid increase in activity of the V–Cr–SiO_2 systems (Fig. 4) may be due to the (CrO_4) species formed. The tetrahedral complexes are thought to catalyze the autoxidation of cyclohexene through HPO decomposition (Reactions 5 and 6) which proceeds *via* coordination of HPO to a vacant site in the complex. The low activities of the G- and H-series of high vanadium content and also of the G-series of high chromium content may be attributed to the (VO_5) and (CrO_5) species, respectiviely, on γ-Al_2O_3 (Fig. 5). Thus, the activity of the supported V–Cr binary catalyst can be thought principally due to the formation of the two types of configuration; tetrahedral on SiO_2 and square-pyramidal on γ-Al_2O_3. It is supposed that the two modes of configuration are performed against the surroundings of the carrier, *i.e.*, the tetrahedral structure of SiO_2 and the spinel structure of γ-Al_2O_3.[10] The contribution of chemical compounds, such as chromium isopolyvanadates, appear to overlap the principal contribution of the two configurations, as observed in the G-series (Fig. 5).

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