Heterogeneous Catalysis in Liquid-Phase Oxidation of Olefin. II. Dependence of the Structure of Vanadium-Chromium Binary Oxide Catalyst for Oxidation of Cyclohexene on the Method of Preparation

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The influence of preparative conditions on the structure and catalytic activity of V–Cr oxide catalyst for the liquid-phase oxidation of cyclohexene has been investigated. Three series of binary oxide, V-Cr-D, V-Cr-E, and V-Cr-F, were prepared from acidic, neutral, and alkaline media, respectively. The specific activity of the catalyst was found to be in the order: V-Cr-D>V-Cr-E>V-Cr-F, the catalyst prepared from acidic medium showing the highest activity. The results of structure analysis showed the formation of several chromium isopolyvanadates, *i.e.*, chromium pyrovanadate, chromium metavanadate, and unknown phase (probably chromium polyvanadates), together with V_2O_5, Cr_2O_3, and solid solution of Cr^{6+} in V_2O_5 lattice. The formation of chromium isopolyvanadate having a higher degree of condensation of the vanadate anion was promoted by use of a more acidic medium in the catalyst preparation. The higher activity for autoxidation was obtained with the catalyst containing the more condensed isopolyvanadate. Epoxidation seems to proceed by the hydroperoxide intermediate mechanism on the active site differing from that for autoxidation.

Properties of heterogeneous catalysts in liquid-phase oxidation of cyclohexene were studied using several binary oxides containing vanadium.[1] Vanadium-chromium system (V–Cr) was found to be relatively active for the oxidation, in which epoxidation of cyclohexene also proceeded. The insoluble catalyst system seems to contain two types of active site, one effective for autoxidation of cyclohexene, *i.e.*, for radical chain reaction, and the other for selective epoxidation of cyclohexene with 1-cyclohexenyl hydroperoxide (HPO) formed by autoxidation. The activity of the V–Cr catalyst for oxidation of acrylaldehyde is considerably affected by its preparative conditions.[2] It seems that the active species is a chromium isopolyvanadate and its formation is promoted by use of an acidic medium. We have studied the effects of the methods of preparation of the V–Cr catalyst on its property. Three series of vanadium-chromium oxide were prepared from acidic, neutral, and alkaline media, and their structures and catalytic activity for oxidation of cyclohexene have been investigated in detail.

Experimental

Catalysts. Three series of binary oxide catalyst were prepared in the following way. A combination of three raw materials such as V_2O_5 hydrate+$Cr(NO_3)_3 \cdot 9H_2O$, V_2O_5 hydrate+$Cr(OH)_3$ hydrate, or NH_4VO_3+$Cr(OH)_3$ hydrate was employed in the preparation of the catalysts from acidic, neutral, or alkaline media, respectively.

The raw materials were mixed and kneaded with a small amount of water 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 three series of binary oxide, each consisting of catalysts of different compositions, are denoted by V-Cr-D (from acidic), V-Cr-E (from neutral), V-Cr-F (from alkaline medium). V_2O_5 hydrate was prepared as previously reported,[1] and $Cr(OH)_3$ hydrate was obtained as precipitate by addition of dilute ammonia to an aqueous solution of $Cr(NO_3)_3 \cdot 9H_2O$. The catalyst was pulverised and used as powder of particle size smaller than 100 mesh. The composition (in terms of atomic % of Cr/(V+Cr)), symbol, and specific surface area (S_s) are given in Table 1.

Apparatus and Procedure of Catalytic Reaction. The oxidation reaction was carried out at 60 °C for 5 h under 1 atm of O_2 pressure using a batch system.[1] 20.0 ml of cyclohexene, 50.0 ml of benzene as solvent, and 50.0 mg of the binary oxide catalyst were used in each reaction.

Analyses of Reaction Products and Catalysts. The reaction products, HPO and cyclohexene oxide (OXIDE), were determined by the iodometric method and gas-chromatography.[1]

The structure of the catalyst was studied by means of X-ray diffraction and infrared absorption, the surface area being obtained by the BET method.[1] Differential thermal analysis and thermo gravimetric analysis of the samples before calcination were carried out with a Thermoflex YGHD type thermal analyser (Rigaku Denki Co.). Electron spin resonance absorption spectra were recorded with a JES-3BX type ESR spectrometer (X-band). For removal of V_2O_5, the catalyst was immersed in 6 M ammonia for two days, separated by filtration, washed with water, and dried at 150 °C for one day.

Results

Surface Area of Catalyst. The surface area of catalyst varies a great deal with the preparative conditions and composition of catalyst (Table 1), the value being in the order: V-Cr-F>V-Cr-E>V-Cr-D. The catalyst prepared from the more alkaline medium shows a higher value.

X-Ray Diffraction of Catalyst. Typical diffraction patterns of the binary system catalysts are shown in Fig. 1. The formation of two phases, X and Y, besides V_2O_5 and Cr_2O_3 in the V–Cr catalyst used for acrylaldehyde oxidation has been recognized by X-ray diffraction analysis.[2] In the present work, these four phases were also observed. The diffraction lines are

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* Formation of several chromium isopolyvanadates is expected in this binary system.[2] 450 °C was shosen as temperature of calcination so that these isopolyvanadates, *i.e.*, $Cr(VO_3)_3$,[3] $(Cr_2O)(VO_3)_4$,[4] and $Cr_4(V_2O_7)_3$,[5] might be obtained in stable form.

TABLE 1. COMPOSITION, SYMBOL, AND SPECIFIC SURFACE AREA OF CATALYST

Composition Cr/(V+Cr) (atomic %)	D-Series		E-Series		F-Series	
	Symbol	S_s (m^2/g)	Symbol	S_s (m^2/g)	Symbol	S_s (m^2/g)
0	D-0	4.1	E-0	5.2	F-0	7.1
10	D-1	11.3	E-1	9.1	F-1	10.1
20	D-2	10.1	E-2	13.6	F-2	23.6
30	D-3	7.9	E-3	12.4	F-3	37.7
40	D-4	8.7	E-4	15.7	F-4	57.1
50	D-5	8.3	E-5	13.9	F-5	73.3
60	D-6	8.2	E-6	18.6	F-6	73.6
70	D-7	7.7	E-7	17.0	F-7	82.5
80	D-8	8.0	E-8	10.7	F-8	65.8
90	D-9	7.3	E-9	10.7	F-9	43.4
100	D-10	8.7	E-10	36.3	F-10	47.2

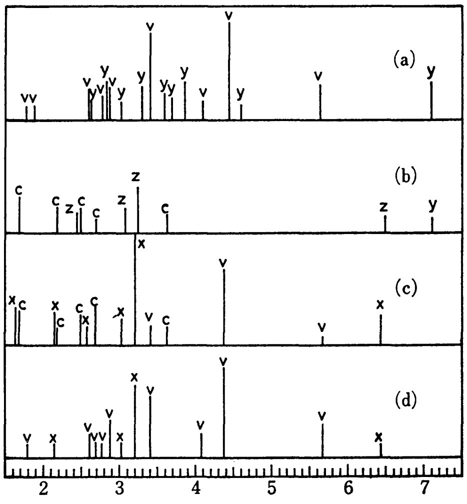

Fig. 1. X-Ray diffraction patterns of V-Cr catalysts.
v: V_2O_5, y: phase Y, x: phase X, z: phase Z, c: Cr_2O_3.
(a) D-3, (b) D-7, (c) E-5, (d) F-3.

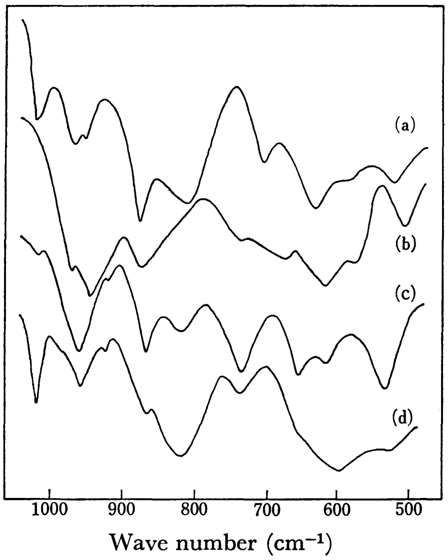

Fig. 2. Infrared spectra of V-Cr catalysts.
(a) D-3, (b) D-7, (c) E-5, (d) F-3.

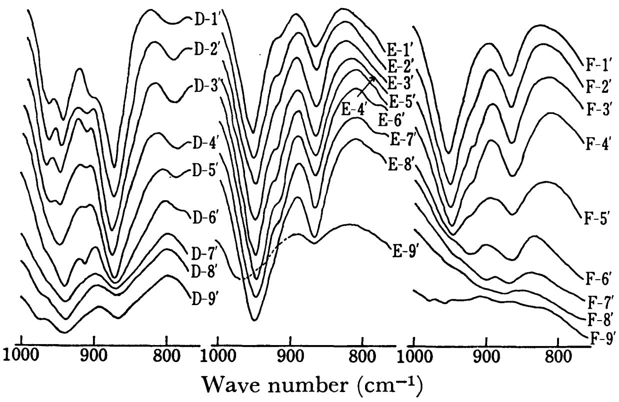

Fig. 3. Infrared spectra of V-Cr catalysts treated with NH_3.

classified into four groups; v, c, x, and y (belong to V_2O_5, Cr_2O_3, X, and Y, respectively). Several unknown lines (z) appeared in V-Cr-D catalysts of higher Cr content. The lines y were found only in V-Cr-D catalysts, while the lines *x* were observed in the other binary system, V-Cr-E and V-Cr-F. Furthermore, the *d*-spacing value of the strongest line of V_2O_5: d=4.38 Å (001 plane) increased in proportion to the Cr content, reaching 4.47 Å in D-4, only in the patterns of V-Cr-D catalysts.

Infrared Spectra. Infrared spectra of the catalysts before and after treatment with ammonia are shown in Figs. 2 and 3, respectively. Mark (′) shows the catalyst treated with ammonia. The spectrum changes considerably with composition and the preparing conditions. An absorption band at about 1020 cm^{-1} (Fig. 2) is assigned to the stretching vibration of V=O bond in V_2O_5.[6] The band in D-1 and D-2 broadens toward frequency slightly lower than 1020 cm^{-1}. D-1′-D-4′ show the spectra which coincide fairly well with those of chromium metavanadate ($Cr(VO_3)_3$).[7] The spectra of E-1′—E-8′ and F-1′—F-5′ might be due to chromium pyrovanadate ($Cr_4(V_2O_7)_3$).[7] The band observed at about 800 cm^{-1} in D-1′—D-5′ is also recognized, though weak, in E-6′—E-8′.

DTA and TGA of Catalyst. In order to clarify the solid-phase reaction during the preparation of the catalysts, thermoanalyses of the samples after being dried at 100 °C (before calcination) were carried out in the range 100—750 °C. The results are shown in Fig. 4. The sharp endothermic peak at 680 °C is due to the melting of V_2O_5, and the sharp exothermic one observed with the decrease of weight at 410 °C might be due to the dehydration of $Cr(OH)_3$.[8] Several endo- and exothermic peaks observed between 100 and 200 °C with the samples of D-series are mainly due to the decomposition of chromium nitrate. An exothermic peak observed with D-0 at 320 °C seems to be due to dehydration of V_2O_5 hydrate. The peak shifted toward high temperature by addition of $Cr(NO_3)_3$. An exothermic peak at *ca.* 410 °C in D-series of high Cr content (Fig. 4, D-5) recognized with weight loss proportional to the Cr content, might be due to the dehydration of

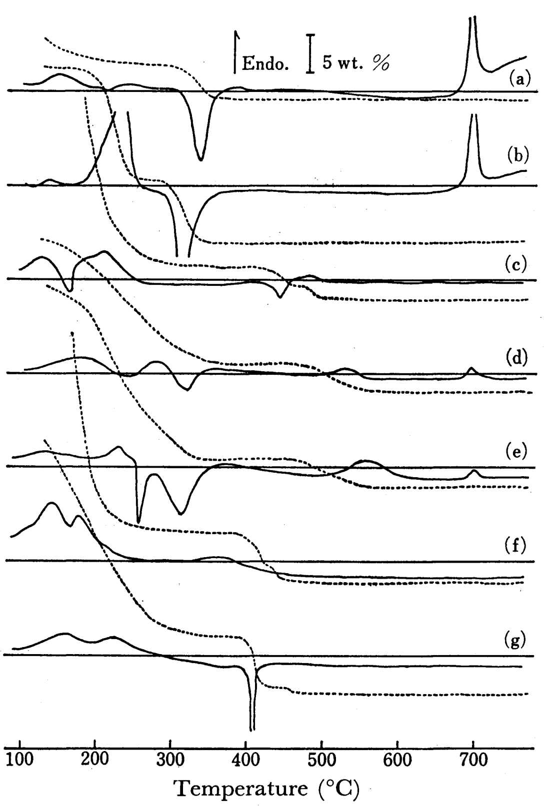

Fig. 4. DTA and TGA curbes of V–Cr binary oxides. (a) D-0, (b) F-0, (c) D-5, (d) E-5, (e) F-5, (f) D-10, (g) E-10.
—— DTA, ------ TGA.

$Cr(OH)_3$ formed by the partial hydrolysis of $Cr(NO_3)_3$ during the course of mixing of the raw materials. The samples of E-series show several obscure peaks with weight loss below 300 °C, and an exothermic peak in the vicinity of 500 °C (Fig. 4, E-5). The weight loss at about 320 °C decreases with increase in Cr content, that at about 500 °C being roughly proportional to the Cr content. The temperature of the latter peak was lowered with increase in Cr content. Series-F show an exothermic peak at about 210°C, two exothermic peaks at about 220 and 300 °C, and a weak endothermic peak near 500 °C (Fig. 4, F-5). The peaks at 210 and 300 °C are due to the decomposition of ammonium metavanadate. The weak endothermic peak at 500 °C is accompanied by weight loss proportional to the Cr content as in the case of V–Cr-E.

ESR Spectra of Catalyst. The form of spectra varies remarkably, depending on the preparing conditions of catalyst. Typical spectra are shown in Fig. 5. D-1—D-3 show spectra consisting of a strong narrow signal superposed on a broad one (Fig. 5, a and b), the narrow signal having a peak-to-peak line width (ΔH_{msl}) of 60—110 G and g value of 1.96. The intensity of the narrow signal is higher in the catalysts having lower Cr content, the strongest one being observed with D-1. The catalyst of low Cr content in E and F-series also show similar types of spectrum, but the intensity of the narrow signal is very weak. Furthermore, ΔH_{msl} of the broad signal varies a great deal; 300—500 G in V–Cr-D, and 400—1200 G, being very broad, in both V–Cr-E and V–Cr-F. Thus, the broad signals in V–Cr-D series are clearly distinguishable from those of V–Cr-E and V–Cr-F series. In the case of D-4 and D-5, the narrow signal is probably hindered by the broad signal which is observed strongly. D-6—D-9 show spectra having additional maximum in weak fields (Fig. 5, d).

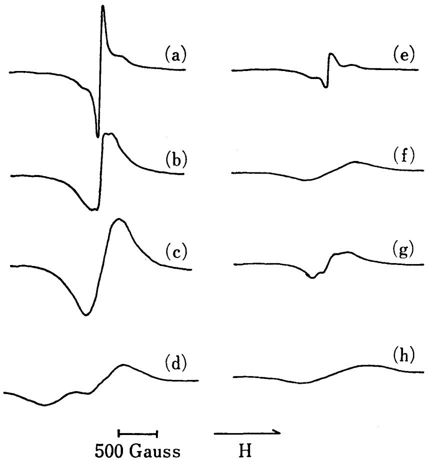

Fig. 5. ESR spectra of V–Cr catalysts.
(a) D-1, (b) D-2, (c) D-5, (d) D-7, (e) E-1, (f) E-7, (g) F-1, (h) F-7.

Results obtained for the single component catalysts are as follows. D-0, E-0, and F-0 show a very weak signal having ΔH_{msl} of about 80 G and g value of 1.96, while the spectra of Cr_2O_3 vary depending on the preparing conditions. D-10 shows a spectrum similar to D-7, however, the spectra of both E-10 and F-10 consist of a single broad signal.

Oxidation Reaction. The reaction results obtained for the three series of V–Cr catalysts are shown in Figs. 6 and 7. The order of specific activity shown in terms of the maximum rate of oxygen absorption per unit

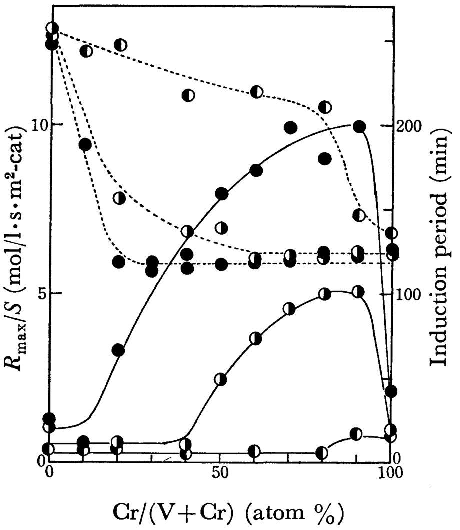

Fig. 6. Specific activities of V–Cr catalysts and induction periods of oxygen uptakes.
● V–Cr-D, ◑ V–Cr-E, ◐ V–Cr-F,
—— specific activity, ------ induction period.

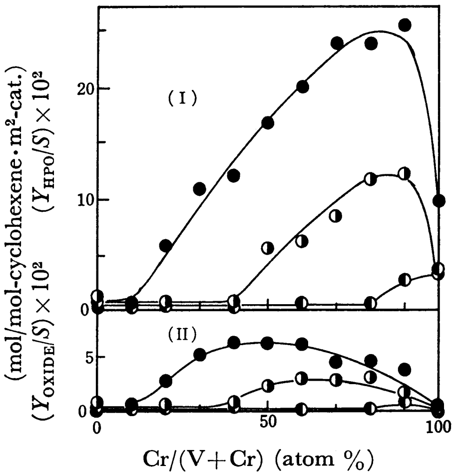

Fig. 7. Formations of HPO (I) and OXIDE (II) in the oxidations with V–Cr catalysts.
● V–Cr–D, ◑ V–Cr–E, ◐ V–Cr–F.

surface area of the catalyst (R_{max}/S) is: V–Cr–D>V–Cr–E>V–Cr–F (Fig. 6). The activity of each binary system is high when Cr content is high, the highest value being obtained at 90 atom % of Cr in all the three series. An induction period for oxygen uptake was 120—130 min with the relatively active catalysts, *i.e.*, D-2—D-9 and E-5—E-9, and the higher content of Cr caused decrease in its value (Fig. 6). Fig. 7 shows the yield of HPO or OXIDE per unit surface area of each catalyst (Y_{HPO}/S or Y_{OXIDE}/S). The values of Y_{HPO}/S show a very similar tendency to the oxygen uptake in Fig. 6. OXIDE was obtained only with the catalyst active for HPO formation. However, dependency of epoxidation on the catalyst composition differs clearly from that of HPO formation, the maximum value of Y_{OXIDE}/S being obtained with the catalyst with much less Cr content.

Discussion

Structure of Catalyst. Solid solution is formed in the binary oxide containing V, such as V–Mo and V–W.[6] For V–Cr system, Kurina *et al.*[9] reported that the solid solution is formed in the binary oxide prepared from NH_4VO_3 and $Cr(NO_3)_3 \cdot 9H_2O$.

By means of X-ray analysis, a diffraction pattern of V_2O_5, and an increase in *d*-spacing of 001 plane proportional to the Cr content, following Vegard's law were observed in D-1—D-4 catalysts. An interfacial solid solution seems to be formed in the catalysts. These catalysts show a narrow signal in their ESR spectra, the values of g and ΔH_{msl} being very similar to the values of the weak signal of the V_2O_5 spectra. The weak signal of V_2O_5 is thought to be due to quadrivalent vanadium ions, V^{4+}, resulting from lattice defects.[6] The narrow signal might be due to V^{4+} ions. The reduction of vanadium species is considered to occur as a result of the charge compensation of the chromium atoms (probably, Cr^{6+}) introduced into the lattice of V_2O_5 by the formation of the solid solution. This is supported by the fact, in D-1 and D-2, the infrared absorption band at 1020 cm^{-1} broadens toward lower frequency. The broadening may be due to the formation of V^{4+}=O bond, resulting from solid solution. In both series of V–Cr–E and V–Cr–F, the catalysts containing a small amount of Cr show a very weak narrow signal in their ESR spectra, its highest intensity being observed with E-1 and F-1.** However, no clear change in the *d*-spacing was observed. This suggests that the amount of solid solution is considerably smaller in both V–Cr–E and V–Cr–F than in V–Cr–D. The intensity of the narrow signal can be put in the order: V–Cr–D>V–Cr–E>V–Cr–F. It is suggested that more acidic preparative conditions are favorable for the formation of solid solution.

By means of X-ray diffraction, three phases, X, Y, and Z were observed in the catalysts. The patterns of X and Y coincide with those of $Cr_4(V_2O_7)_3$[5] and $Cr(VO_3)_3$,[3] respectively. Phases X and Y might be chromium pyrovanadate and chromium metavanadate, respectively. The *d*-spacing values of lines classified into z in V–Cr–D (Fig. 1, b) vary somewhat depending on the composition of catalyst, the lines z being hardly attributed to single component. Phase Z might be a mixture of several compounds. In order to clarify the influence of preparing conditions on the formation of these phases, the intensities of two characteristic peaks selected for two phases, $Cr_4(V_2O_7)_3$ (d=3.19 Å) and $Cr(VO_3)_3$ (d=3.87 Å), in Fig. 1, are plotted as a function of the composition of each catalyst series, together with that of both phases of V_2O_5 (d=4.37 Å) and Cr_2O_3

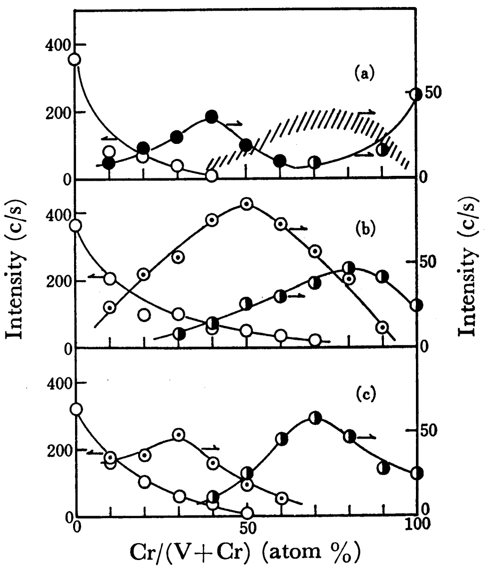

Fig. 8. Intensities of X-ray diffraction lines.
(a) V–Cr–D (b) V–Cr–E (c) V–Cr–F
○ d=4.38 Å (V_2O_5), ⊙ d=3.19 Å ($Cr_4(V_2O_7)_3$), ● d=3.87 Å ($Cr(VO_3)_3$), /// $d \simeq 3.2$ Å (phase z), ◑ d=2.67 Å (Cr_2O_3).

** No narrow signal was observed in the catalyst prepared from NH_4VO_3 and $Cr(NO_3)_3 \cdot 9H_2O$.[2] However, Kurina *et al.*[9] reported that the binary oxide similarly prepared shows the narrow signal of V^{4+} in the solid solution, its intensity reaching maximum at 5 mol% of Cr. Disappearance of the narrrow signal seems to be due to the fact that the signal was hindered by the strong broad one, since the catalysts contain more than 17% of Cr.

(d=2.67 Å) (Fig. 8). In order to show the existence of phase Z, the line near d=3.2 Å was selected for the sake of convenience. Its intensity is indicated by shading. The intensity of the peak of $Cr(VO_3)_3$, recognized only in D-1—D-6 catalysts, was observed to reach a maximum at 40 atom % of Cr. The values of Cr content at the maximum intensity of the $Cr_4(V_2O_7)_3$ peak are *ca.* 50 and 30 atom % in V–Cr-E and V–Cr-F, respectively.

The infrared spectra suggest the formation of $Cr(VO_3)_3$ in the catalysts of D-1—D-4 and $Cr_4(V_2O_7)_3$ in E-1—E-8 and F-1—F-5. The compositions of these catalysts coincide with those classified by X-ray analysis, with respect to the formation of $Cr(VO_3)_3$ and $Cr_4(V_2O_7)_3$. However, a very weak absorption band was observed at about 800 cm^{-1} in E-6′—E-8′, in spite of the absence of $Cr(VO_3)_3$ The results suggest the formation of amorphous $Cr(VO_3)_3$. According to the report given by Olivier,7) the absorption bands between 750 and 1050 cm^{-1} are assigned to the stretching vibrations of V–O bonds, varying markedly with the type of isopolyvanadate anion. $Cr(VO_3)_3$ has a chain structure of VO_6 octahedra connected with each other by sharing an edge,10) the bands in its spectrum being assigned as: 970 and 945 cm^{-1} to ν_sVO_2 and 915 and 800 cm^{-1}*** to VO_6. On the other hand, $Cr_4(V_2O_7)_3$ contains V_2O_7 group which consists of two VO_3 pyramids linked by a V–O–V bridge.11) The following assignments might be made: 950 cm^{-1} to ν_sVO_3 and 870 cm^{-1} to $\nu_{as}VO_3$. Catalysts D-6—D-9 containing phase Z as classified by X-ray analysis show very broad bands centered at *ca.* 940 and 870 cm^{-1} in the range of V–O stretching vibrations. No such spectra seem to have been reported. They suggest some chromium polyvanadates containing anions of higher degrees of condensation. The nature of the anionic vanadate species in alkaline, neutral, and acidic solutions has been the subject of numerous investigations. A typical example of the types of vanadate anions is as follows.12)

pH 6.7 9.6 12.6
anion poly→←meta→←pyro→←ortho

It is reasonably considered that chromium polyvanadates are formed in D-6—D-9 whose preparing conditions are more acidic than those of D-1—D-5. The fact that D-6—D-9 show some randomness in the d-spacing values and the frequencies of infrared absorption might be due to the diversity of the type of polyvanadate.

Samples of the binary system show thermal changes not observed in each of the one component systems (Fig. 4). In each of the three series, the endothermic peak due to the melting of V_2O_5 was rapidly weakened with the increase in Cr content, not being observed in the sample containing less amount of V than 40 atom %. This suggests that some solid-phase reactions took place during the course of calcination. It is considered that the weight loss observed at *ca.* 500 °C especially in E and F-series is mainly due to the dehydration of $Cr_4(V_2O_7)_3\cdot nH_2O$.5) The dehydration is more difficult than that of $Cr(VO_3)_3\cdot mH_2O$, requiring a long period or a higher temperature. There is a possibility that undesirable water remains in the binary catalysts. However, the infrared spectra of the catalysts show no absorption band of H–O–H bending vibration at *ca.* 1600 cm^{-1}, indicating that the dehydration is nearly completed by at 450 °C for 5 h.

The electron spin resonance spectra show broad signals whose value of ΔH_{msl} vary considerably. ΔH_{msl} of these signals were relatively small in V–Cr-D, but fairly large in both V–Cr-E and V–Cr-F. The peak-to-peak height was especially great in V–Cr-D. It is difficult to assign these broad signals. However, the relatively strong signal observed in D-2—D-6 might be assigned to a paramagnetic species included in $Cr(VO_3)_3$, since its intensity correlates fairly well with the amount of $Cr(VO_3)_3$ estimated from the results of X-ray diffraction and infrared analysis. In a similar manner, the very broad signals observed with some V–Cr-E and V–Cr-F catalysts may be assigned to a paramagnetic species in $Cr_3(V_2O_7)_4$. The broadening of these signals might be due to the dislocalization of the unpaired electron owing to the ordering of the structure containing the paramagnetic species. In the infrared spectra of E-6—E-8, a weak absorption band was observed which may be assigned to the stretching vibration of VO_6 in $Cr(VO_3)_3$. However, the electron spin resonance spectra of these catalysts show no broad signal of $Cr(VO_3)_3$, contrary to our expectation. Spectra having an additional maximum in weak fields were observed in D-7–D-10, the intensity increasing with the amount of Cr_2O_3 estimated by X-ray diffraction. This type of signal seems to be due to Cr_2O_3. However, E-10 and F-10 show only a broad signal, suggesting a difference between Cr_2O_3 prepared from $Cr(NO_3)_3$ and that from $Cr(OH)_3$.

Relationship between Structure and Catalytic Activity. The correlation of the catalyst composition to R_{max}/S differs clearly from that to Y_{OXIDE}/S, in each series of binary system (Figs. 6 and 7). The oxygen uptake is rationally assumed to be mainly due to the radical chain reaction. It is considered that the active species for autoxidation differs from that for epoxidation. Since epoxidation was observed only with the catalysts which gave HPO (Fig. 7), epoxidation is thought to proceed selectively with HPO. Thus, the results we obtained support the suggestion that epoxidation proceeds by a hydroperoxide intermediate mechanism catalyzed by the vanadium–chromium oxide having two types of active site, one effective for the autoxidation and the other for the selective epoxidation.1)

The activity for autoxidation shown by R_{max}/S might be explained as follows. Chromium polyvanadates and $Cr(VO_3)_3$ were observed in the catalysts of D-series; $Cr(VO_3)_3$ (suggested only by the infrared absorption) and $Cr_4(V_2O_7)_3$ in those of E-series; and $Cr_4(V_2O_7)_3$ in those of F-series. From a comparison of the distribution of these isopolyvanadates in the three series with specific activities (Fig. 6), it seems that the activity for autoxidation is largely affected by the type of chromium isopolyvanadate in the catalyst, its activity being in the order: chromium polyvanadates $>Cr(VO_3)_3>Cr_4(V_2O_7)_3$.

*** The band at about 800 cm^{-1} was assigned to the stretching of V–O–V bond.2) However, the assignment to VO_6 octahedron may be more reasonable because of the absence of the band in the spectrum of $Cr_4(V_2O_7)_3$.

Chromium isopolyvanadate with a higher degree of condensation shows a higher activity. The long induction periods observed in all the reactions may be due to the accumulation of HPO. Thus, autoxidation is considered to be initiated by the radical decomposition of HPO with the binary catalyst. According to the results of Meyer *et al*,;[13] chromium oxide decomposes hydroperoxide, it is thought that the active species for autoxidation contains chromium.**** The correlation of catalyst composition to Y_{HPO}/S is similar to that to $R_{\max}/S$. This is explained by the fact that HPO is the main product of the autoxidation of cyclohexene by radical chain mechanism.

Concerning epoxidation, exact discussions are difficult since it may have first-order dependence on HPO concentration. All we can say is that the active species for the epoxidation differs from that for the autoxidation. It might consist of vanadium.

Studies on the vapor-phase oxidation with V system catalysts[6] show that the formation of solid solution causes the increase of catalytic activity. However, no such phenomenon has been observed. This might result from the difference in the catalytic mechanism between liquid-phase and vapor-phase oxidation.

Higher activity of the V–Cr catalyst was obtained by use of the more acidic medium. This might result from the variety of vanadate anions formed on mixing of the raw materials. It is suggested that various isopolyvanadate anions form depending on the acidity of medium.[12] Their existence may largely influence the structure and activity of the binary oxide catalyst.

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**** In order to study the surface state of the catalysts, X-ray photoelectron spectroscopy was carried out. No shift was observed in the V $2p_{3/2}$ line between $V_2O_5(V^{5+})$ and V_2O_4 (V^{4+}),[14] but some shift was recognized in the Cr $2p_{3/2}$ line between $Cr_2O_3(Cr^{3+})$ and $K_2Cr_2O_7(Cr^{6+})$.[15] The binding energies of Cr in the binary catalysts remain approximately constant, 587 eV (Cr $2p_{1/2}$) and 557 eV (Cr $2p_{3/2}$), suggesting that chromium species on the surface of the catalysts have the same charge (probably of Cr^{3+}).