



Title	INVESTIGATION OF ZnO-Cr ₂ O ₃ MIXED CATALYST BY ELECTRON MICROSCOPE AND SELECTED-AREA ELECTRON DIFFRACTION
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Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 4(2), 109-131
Issue Date	1956-08
Doc URL	http://hdl.handle.net/2115/24640
Type	bulletin (article)
File Information	4(2)_P109-131.pdf



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INVESTIGATION OF $\text{ZnO-Cr}_2\text{O}_3$ MIXED CATALYST BY ELECTRON MICROSCOPE AND SELECTED-AREA ELECTRON DIFFRACTION

By

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(Received March 1, 1956)

The structure of $\text{ZnO-Cr}_2\text{O}_3$ mixed catalyst prepared by the thermal decomposition of basic ZnCrO_4 was investigated with the aids of an electron microscope and selected-area electron diffraction, and several informations on its structure and the decomposition process were obtained. A useful technique was devised in order to distinguish ZnCr_2O_4 crystallites dispersed in the ZnO phase of the mixed catalyst in a view-field of an electron microscope.

I. Introduction

$\text{ZnO-Cr}_2\text{O}_3$ mixed catalysts are of special importance in industrial chemistry, e.g. methanol synthesis, so the structural studies on these catalysts were carried out by several authors. As well known, from the X-ray study and activity test on a mechanical mixture of ZnO and Cr_2O_3 , HÜTTIG¹⁾ found that there took place a solid state reaction at 600°C with spinel formation and the maximum activity of this catalyst in the case of methanol decomposition was realized at the transition state to spinel. Recently, using X-ray and an electron microscope, NATTA and his coworkers²⁾ studied on the crystallite size of the mixed catalysts prepared by various methods, and concluded that any $\text{ZnO-Cr}_2\text{O}_3$ mixed catalyst is composed of two phases, i.e. ZnO and ZnCr_2O_4 , and presents higher resistance to the "aging" of catalyst than non-promoted ZnO catalyst, and that the promoting action is mainly due to the hindering action of the promoter, Cr_2O_3 upon the recrystallization of ZnO .

Although electron microscopy and X-ray diffraction, as in the above instances, yield valuable informations concerning the identification of phases constituting the mixed catalyst and their crystallite sizes, those

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1) G. E. HÜTTIG, Z. Elektrochem. 38, 442 (1932); 41, 527 (1935).

2) G. NATTA, "Catalysis", Vol. 3, 349 (1955).

concerning the crystallographic relationship between these phases, the crystallite forms, and the state of dispersion of ZnCr_2O_4 crystallites can not always be obtained by these methods, because the mixed catalysts are usually in agglomerate state and these phases are indistinguishable from each other in a view-field of an electron microscope.

From this point of view, the present author has developed a new preparative technique (carbon specimen-supporting film technique) for the electron microscopy of the mixed catalyst, by the use of which ZnCr_2O_4 crystallites dispersed in the ZnO phase of the catalyst could be distinctly distinguished in a view-field of an electron microscope. It has also been found that by using this technique and the selected-area electron diffraction method in close conjunction one can overcome the above-mentioned difficulties and obtain further informations on the structure of the catalyst.

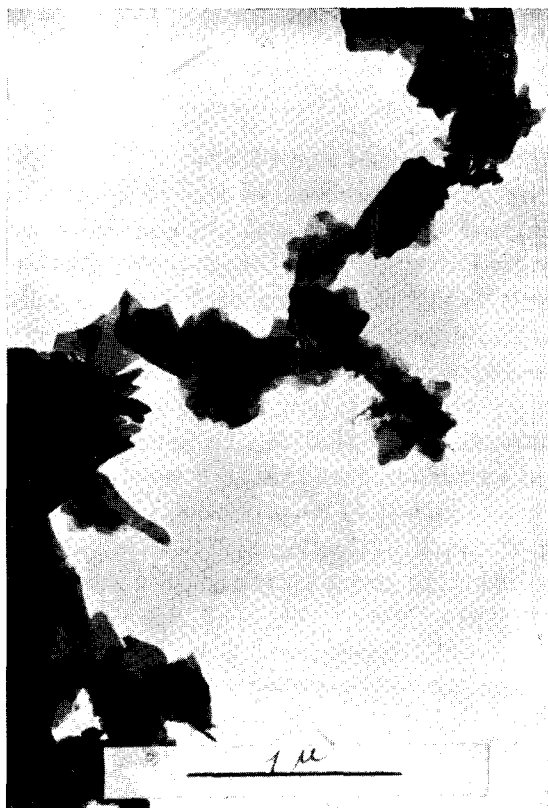


Fig. 1 a Basic ZnCrO_4 on a collodion film.

In Section II of this paper will be described this technique as well as the two-step carbon replica technique for the direct observation of the solid form of the ZnCr₂O₄ crystallite, and in Section III will be given the results obtained of the thermal decomposition process of basic ZnCrO₄ and the structure of the mixed catalyst formed by the decomposition.

II. Experimental Procedure

A. Sample.

The mixed catalyst was prepared by thermal decomposition of basic ZnCrO₄ at 500°C for 10 hours in air. The basic ZnCrO₄* used in this experiment was flossy and yellowish powder consisting of indeterminate flake-like crystallites of 3000~4000 Å in diameter as shown in Fig. 1a. Its selected-area electron diffraction pattern (Fig. 1b) indicated that the crystal lattice was hexagonal with $a_0=8.5$ Å, the (001)-axis of



Fig. 1b Selected-area electron diffraction pattern of a single crystal of basic ZnCrO₄. $S_0 \parallel (001)$ -axis of basic ZnCrO₄.

* Obtained from Kanto Kagaku Co.; its chemical formula was found to be ZnCrO₄·2.5Zn(OH)₂.

the crystal being perpendicular to the flake. As will be described in Section III, it was found as results of the differential thermal analysis and X-ray diffraction that this basic ZnCrO_4 was decomposed endothermically into ZnO and some intermediate product at 320°C and further into ZnCr_2O_4 and ZnO at 513°C (cf. Fig. 2).

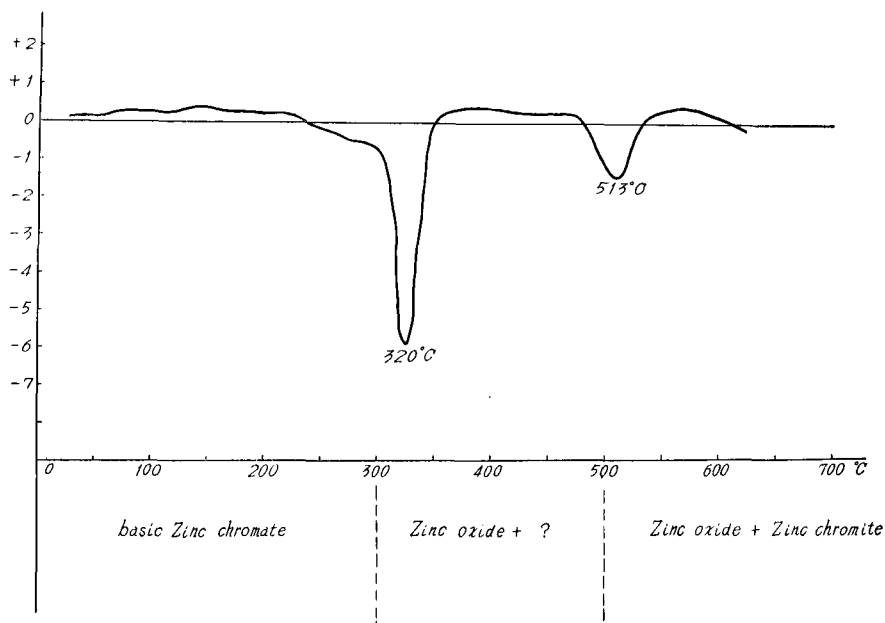


Fig. 2 The differential thermal analysis curve of basic ZnCrO_4 .

B. Carbon Specimen-Supporting Film Technique.

This preparative technique is illustrated in Fig. 3, A. An optical slide glass was coated with a thin collodion film by dipping it in 0.2~0.5% solution of collodion in amylacetate. After the film had been dried the specimen was spread over it, and then a carbon evaporation film³⁾ was deposited on this specimen in vacuum. After being scored to give 1 mm^2 , the carbon film was separated from the slide glass by dissolving the collodion in alcohol-ether, the specimen spread over the collodion film being transferred onto the carbon film. This carbon film with the specimen was immersed into hot 24% hydrochloric acid in order to dissolve the ZnO phase of the specimen, and then the film was washed in several changes in distilled water. A special care had to

3) D. E. BRADLEY, British J. Applied Physics 5, 65 (1954).

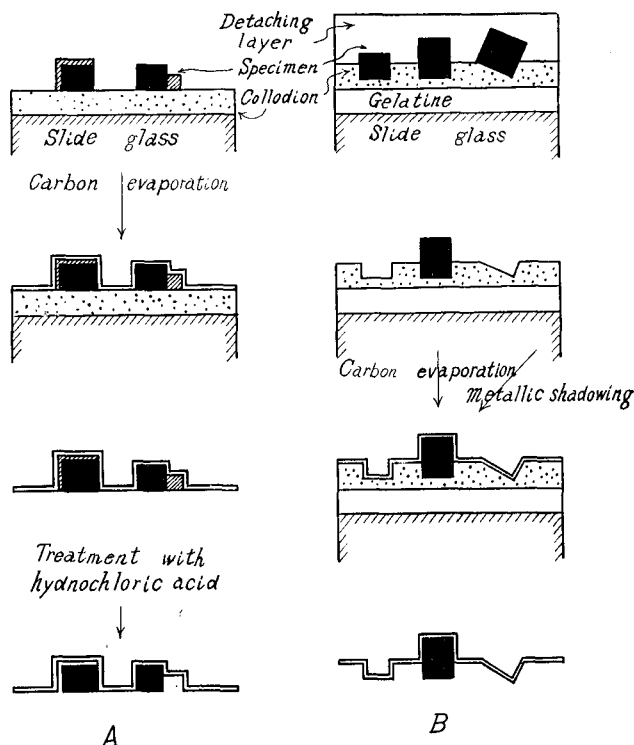


Fig. 3 Procedures of the carbon specimen-supporting film technique (A) and the two-step carbon replica technique (B).

be taken to protect the film from breakage during this procedure. In the present work this difficulty could be avoided by dipping the film in 90%, 50% and 20% alcohols in turn, before the carbon film being immersed into hydrochloric acid.

Although metallic shadowing was not employed in this case, shaded electron images of the specimen could be observed as will be illustrated in Section III. This is very advantageous in the case of the selected-area electron diffraction study, because the metallic shadowing gives a complex diffraction pattern while the amorphous carbon film does not.

C. Two-Step Carbon Replica of ZnCr_2O_4 Crystallites.

The mixed catalyst in this research contained rather large particles of ZnCr_2O_4 , the form of which could be observed very distinctly by the use of the "two-step carbon replica" (cf. Section III, B and Fig. 21). Fig. 3, B illustrates this carbon replica technique. An optical slide

glass coated with gelatine film was covered with collodion by dipping it in 0.2–0.5% solution of collodion in alcohol-ether, and just before the film was dried the specimen was blown onto the film from an injector without a needle. A detaching layer of ethylcellulose was deposited on the collodion film holding the specimen from 10% solution of ethylcellulose in trichlorethylene. By stripping this layer off the collodion film, the greater part of the specimen was removed from the collodion film to the detaching layer, and thereby the first-step collodion replica was obtained. The second-step replica was prepared by evaporating carbon onto the first-step replica and by dissolving the collodion in alcohol-ether.

III. Experimental Results

A. Decomposition Process.

Preliminary informations concerning the thermal decomposition of basic ZnCrO_4 were obtained by the differential thermal analysis (D. T. A.) and the X-ray examination of the decomposition products at several stages of D. T. A. Fig. 2 shows the D. T. A. curve of basic ZnCrO_4 , where one observes two endothermic reactions at 320°C and 513°C . The X-ray diffraction patterns, Fig. 4 indicate that whereas the diffraction lines referred to ZnO appeared simultaneously with the decomposition of basic ZnCrO_4 at about 300°C , the lines of ZnCr_2O_4 began to appear at about 500°C . Besides a few lines referred to some intermediate of the decomposition were observed in the region between 300°C and 500°C , although the intermediate has not been identified yet. The first sinking of the D. T. A. curve is therefore ascribed to the decomposition of basic ZnCrO_4 into a mixture of ZnO and the intermediate, and the second sinking to the formation of ZnCr_2O_4 by decomposition of the intermediate.

On the other hand, several morphological and crystallographical informations about the decomposition products have been obtained by means of electron microscopy and selected-area electron diffraction, as described in the following.

In this research it was observed that basic ZnCrO_4 in an electron-microscope was easily decomposed under an intense electron beam⁴⁾ into

4) Similar observations in the cases of halides, oxides, hydroxides, etc. were reported by several authors: e. g., V. E. COSSELETT, *J. Applied Physics* **18**, 844 (1947); F. A. HAMM and E. von NORMAN, *J. Applied Physics* **19**, 1097 (1948); R. B. FISCHER, *J. Applied Physics* **25**, 894 (1954).

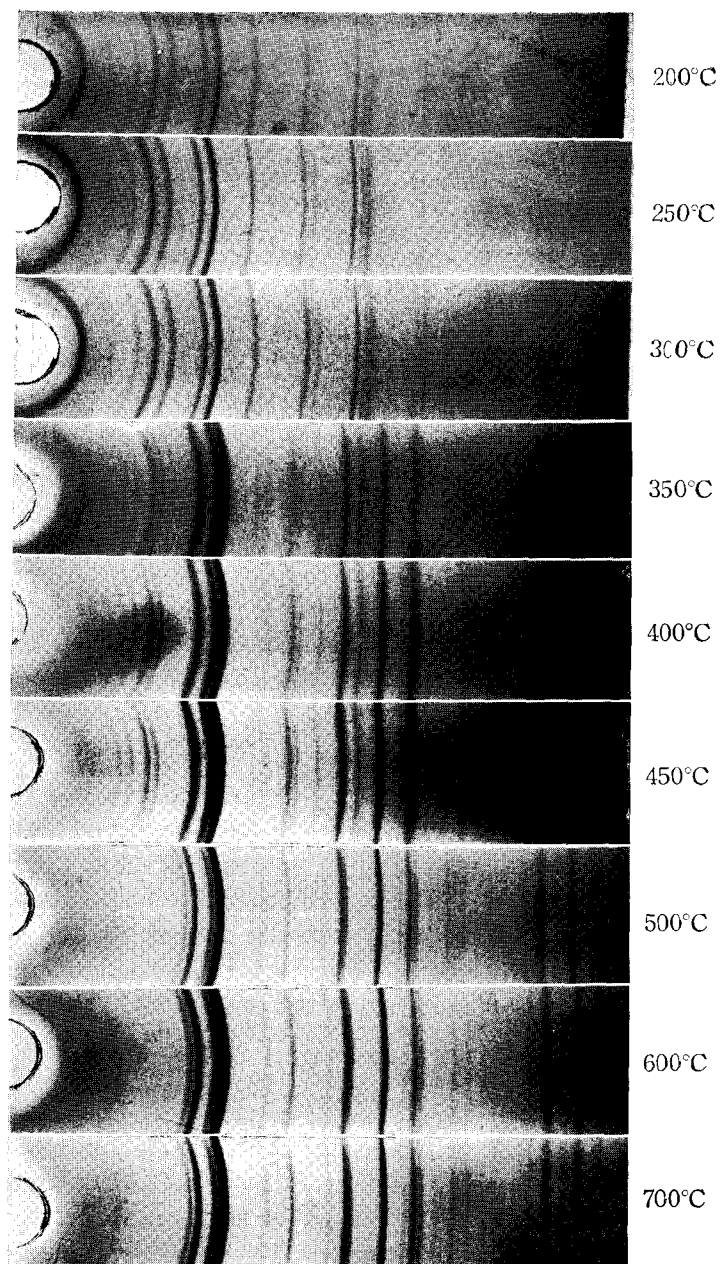


Fig. 4 X-ray (Cu-K α radiation) powder diffraction patterns obtained at several stages of the decomposition of basic ZnCrO₄.

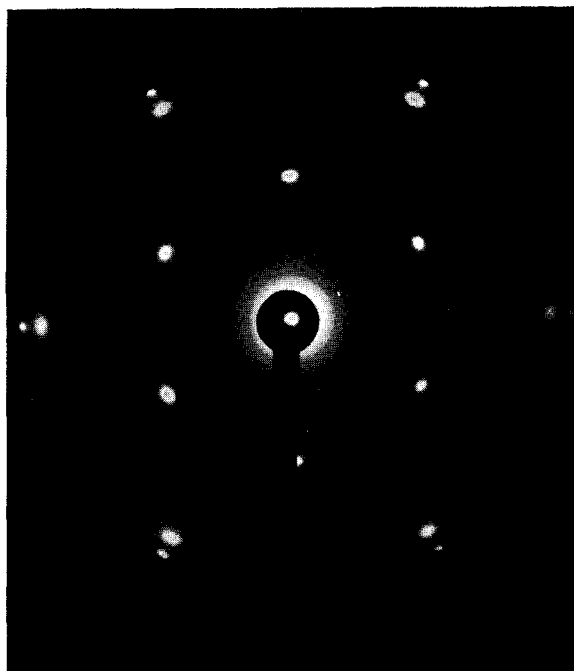


Fig. 5 The selected-area electron diffraction pattern of basic ZnCrO_4 decomposed under an intense electron beam. Distinct spots are ascribed to basic ZnCrO_4 and diffuse spots to ZnO .

ZnO as verified by its selected-area electron diffraction pattern, Fig. 5. This pattern indicates that the ZnO crystallites are so highly orientated that the pattern is almost that of a single crystal, and that the ZnO crystallites have an orientation relationship with the basic ZnCrO_4 crystal, the (001)- and (100)-axes of the former being nearly parallel to the (001)- and (210)-axes of the latter, respectively. On the other hand, ZnCr_2O_4 phase was never observed in any pattern obtained in similar cases.

By the use of the carbon specimen-supporting film technique the micrographs of the decomposition products at several stages of D. T. A. were taken (Figs. 6, 7, 8, 9 and 12). The basic ZnCrO_4 without heat-treatment gave an electron image of transparent exuviae-like replica (Fig. 6) with no remarkable feature on the surface of the crystallites. In Fig. 7 of the prepartate at about 300°C , one sees some crateriform markings on the surface, which are presumably ascribed to the dehydration of basic ZnCrO_4 . Some roughness appeared in place of these



Fig. 7 Replica of basic ZnCrO_4 at about 300°C .

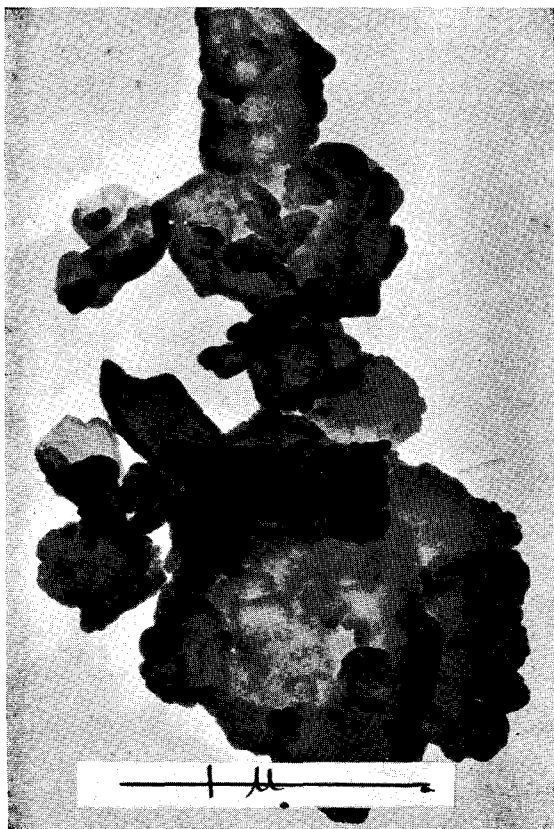


Fig. 6 Replica (= carbon specimen-supporting film) of basic ZnCrO_4 without heat-treatment.

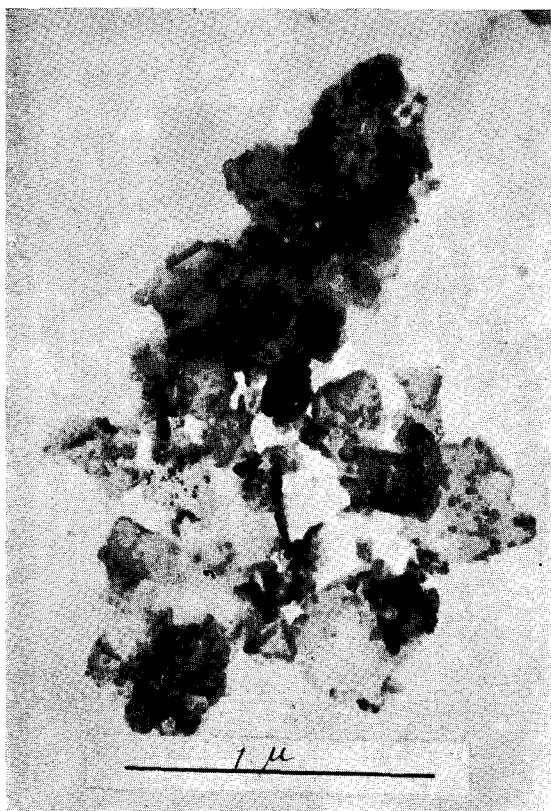


Fig. 8 Replica of basic ZnCrO_4 at about 400°C . Note the tiny particles retained in the exuviae.



Fig. 12 Replica of basic ZnCrO_4 at about 600°C .

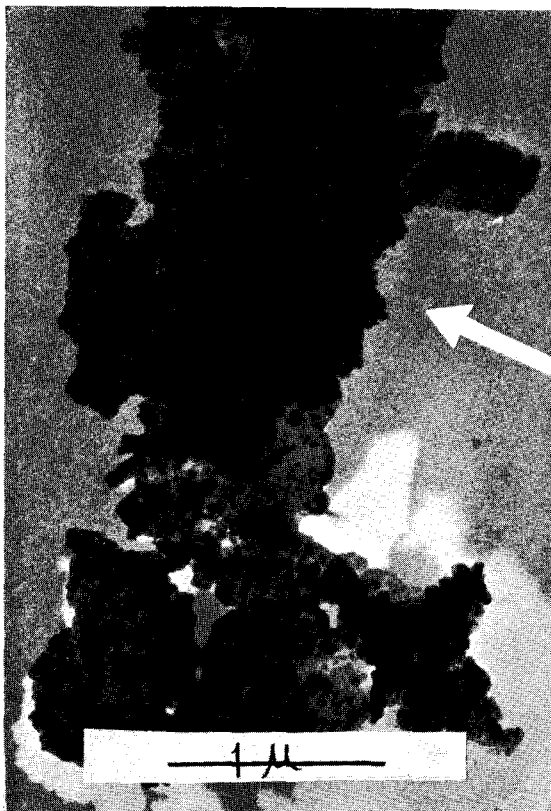


Fig. 9 Replica of basic ZnCrO_4 at about 500°C .



Fig. 10 The selected-area electron diffraction pattern of the colloidal particles (see the arrow in Fig. 9).

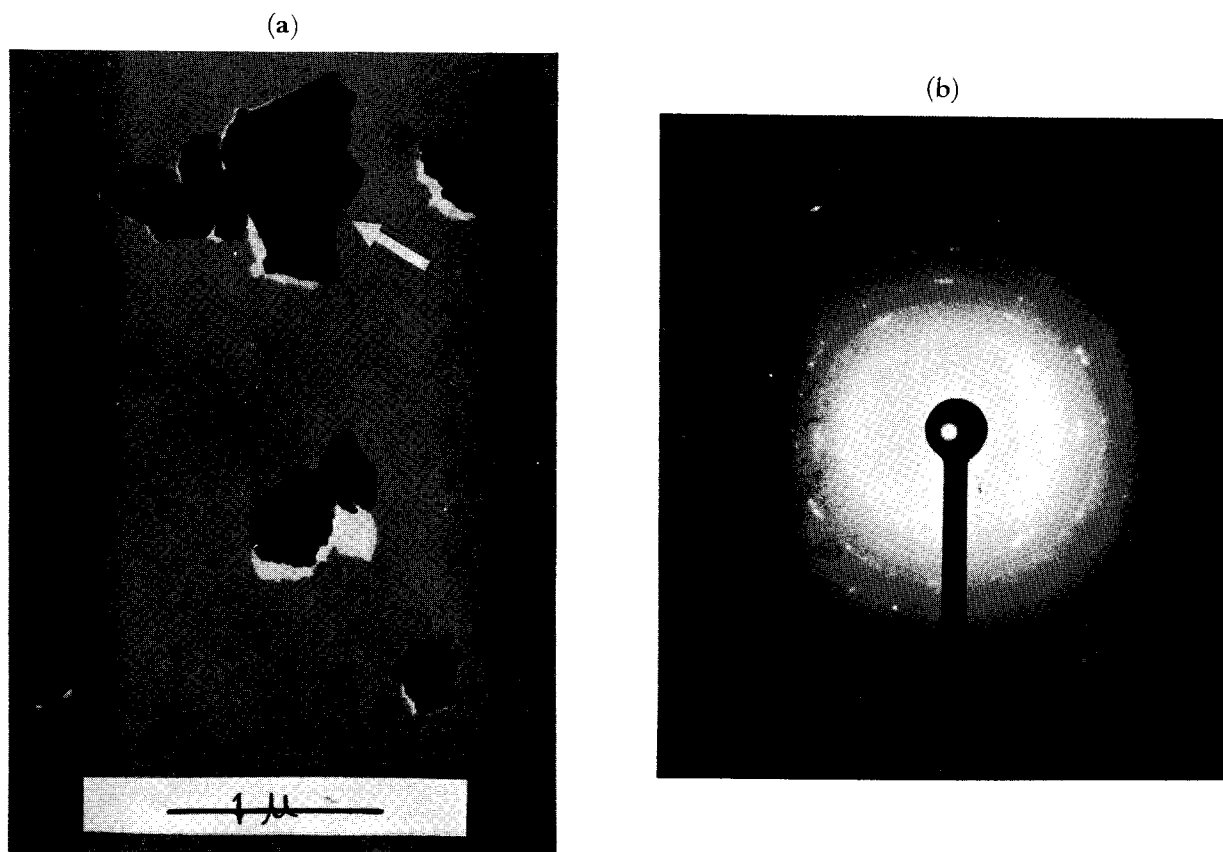


Fig. 11 Replica of a single particle of basic ZnCrO_4 at about 500 C
(a) and its selected-area electron diffraction pattern (b).

markings at about 350°C, which indicated that ZnO crystallites were created by the decomposition of basic ZnCrO₄. As the decomposition proceeded at about 400°C, this roughness grew into 200~300 Å in diameter as shown in Fig. 8. Another characteristic feature of this figure is the appearance of tiny particles less than 100 Å retained in the exuviae. At about 500°C the particles grew into colloidal particles of 300~500 Å in diameter as shown in Fig. 9. These particles which survived the hydrochloric acid treatment were identified with ZnCr₂O₄ by their selected-area electron diffraction pattern (Fig. 10) indicating randomly disposed ZnCr₂O₄ crystallites. Further the pattern (Fig. 11. b) obtained from the preparate of a single basic ZnCrO₄ flake (notice the arrow in Fig. 11 a) consisted of the (220)- and (440)-arcs in hexagonal symmetry accompanied by a few additional rings. This indicates the preferred orientation of ZnCr₂O₄ crystallites, i. e. each of these crystallites has not only the (111)-zone axis as the preferred direction, but is disposed with a preferred orientation round this axis. The additional rings, the (311)- and (400)- rings, may be ascribed to the bending of these crystallites or the basic ZnCrO₄ flake. Combining this observation with the orientation-relationship between the ZnO and basic ZnCrO₄ crystal observed in the basic ZnCrO₄ decomposed under an intense electron beam (*vide supra*), we see that the (111)-axes (the preferred direction) of the ZnCr₂O₄ crystallites precipitated in the ZnO phase are parallel to the (001)-axis of the ZnO crystal. In the cases of the products at about 600°C or above, the ZnCr₂O₄ crystallites are sintered into considerable massive particles (Fig. 12).

In the above observations with the carbon specimen-supporting film technique, the intermediate as found in the X-ray examination could not be detected, which means that the intermediate was soluble in hydrochloric acid.

B. The Mixed Catalyst.

The mixed catalyst changed its colour from brown to light green or reversely according as it was in contact with a reducing or oxidizing atmosphere, respectively. Figs. 13 and 14 are the micrographs of these "oxidized" (brown) and "reduced" (green) catalysts supported on collodion films by the usual method. From these we see that the "reduced" catalyst is almost identical with the "oxidized" catalyst except that the former is surrounded by fringes ascribable to some contamination in the electron microscope during photographing. Both



Fig. 13 The "oxidized" catalyst on a collodion film.



Fig. 14 The "reduced" catalyst on a collodion film.
Note fringes surrounding the particles.

the catalysts were composed of slightly transparent and opaque areas for electrons, and moreover the former area consisted of "random" aggregates of crystallites of several hundred angstroms (notice the arrow 1 in Fig. 13) and a few of "flake-like" aggregates (2000~3000 Å in diameter) of crystallites (the arrow 2 in Fig. 13).

This transparent area was further examined by selected-area electron diffraction, from which it was found to be ZnO phase. It is noteworthy that in the diffraction pattern (Fig. 15) of the spot 1 in Fig. 13, only (hk0)-rings, i. e. the (100)-, (110)- and (200)-rings, are anomalously strong in intensity, while the pattern (Fig. 16) of the spot 2 bears a resemblance to the diffraction pattern of Fig. 5. These features are of interest in regard to the form of ZnO crystallites. Namely, when a certain zone axis of every crystallite is nearly parallel to the incident beam, there will appear only those rings which correspond to planes through the zone axis. Then, if each crystallite is disposed randomly round the zone axis the rings will be of uniform intensity round the circumferences and if each is disposed with a preferred orientation round the axis, the rings will split into arcs forming almost a cross grating pattern. From such a consideration, the above anomaly in intensity was found to be ascribed to the fact that the ZnO crystallites in the "random" aggregate were disposed randomly round the (001)-axes, while the "flake-like" aggregate with the normal parallel to the (001)-axis of ZnO was nearly a single crystal. Such a preferred orientation of ZnO crystallites may be attributed to the flake-like crystallite form, since the normal to the flake is the most probable preferred direction of orientation. The opaque area, on the other hand, gave no distinct selected-area electron diffraction pattern because of poor penetration of electrons.

With the application of the carbon specimen-supporting² film technique to the catalyst, the two phase, one being soluble and the other insoluble in hydrochloric acid, could be distinguished distinctly from each other as shown in Figs. 17a and 17b. The most significant structure exhibited there is transparent exuviae of the ZnO phase in which are retained both opaque polygonal and colloidal particles of ZnCr₂O₄ surviving the treatment with hydrochloric acid. This interpretation of Fig. 17 was also confirmed by the selected-area electron diffraction patterns of the opaque and transparent areas, Figs. 18 and 19. The former indicates randomly disposed ZnCr₂O₄ crystallites, while the latter amorphous pattern is ascribable to the carbon evaporation film.

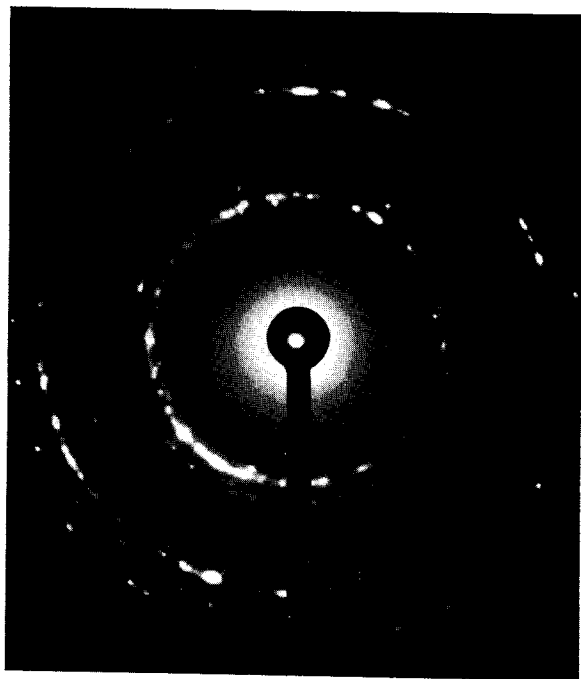


Fig. 15 The selected-area electron diffraction pattern of randomly disposed ZnO crystallites (see the arrow 1 in Fig. 13). Note the absence of the (200)-ring.

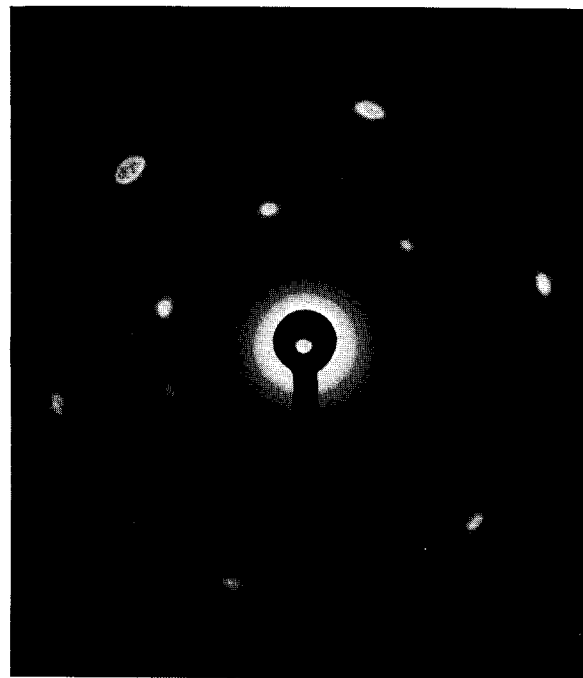


Fig. 16 The selected-area electron diffraction pattern of highly orientated ZnO crystallites (see the arrow 2 in Fig. 13).



Fig. 17 a Micrograph of the mixed catalyst obtained by the carbon specimen-supporting film technique (in the case of a thicker carbon film).

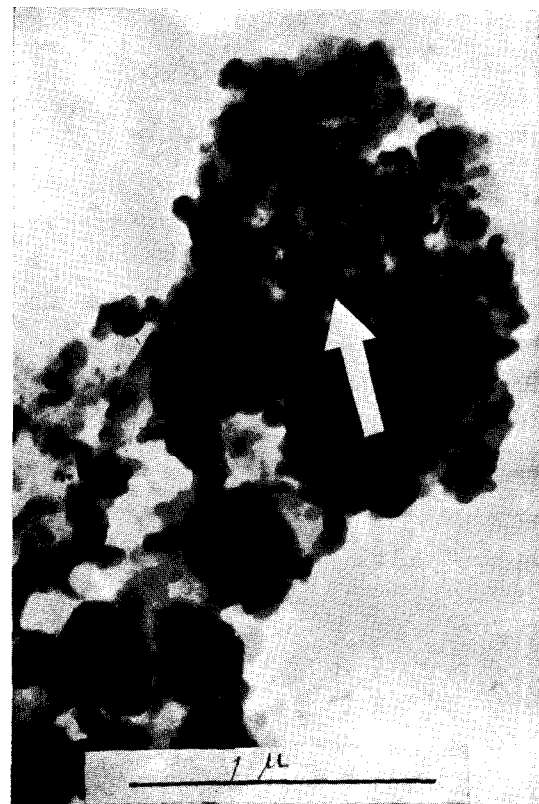


Fig. 17 b Ditto (in the case of a thin carbon film).



Fig. 18 The selected-area electron diffraction pattern of the opaque colloidal particles in Fig. 17b. This indicates a small amount of randomly disposed ZnCr_2O_4 crystallites (see the arrow in Fig. 17b).



Fig. 19 The selected-area electron diffraction pattern of the transparent area in Fig. 17a. This pattern is ascribable to the amorphous carbon film (see the arrow in Fig. 17a).

Further investigations on the polygonal and colloidal particles of ZnCr₂O₄ were carried out with a view to elucidate their crystallite forms. Fig. 20 illustrates the polygonal particles freed from the colloidal particles by centrifuge after removal of the ZnO phase by hydrochloric acid. In this micrograph we see that the polygonal particles have a definite form, but it is rather difficult to determine whether the polygons are cube, octahedron or other. Therefore, the two-step carbon replica technique (Section II C) was applied to these polygonal particles for the direct observation of their solid forms. Fig. 21 shows the replica in which octahedral crystallites, as expected from the crystal habit of spinel, are distinctly observed.

On the other hand, Fig. 22 shows that the colloidal particles are flake-like and 100–500 Å in diameter, and the normal to every flake is parallel to the incident beam. The interference markings which indicate the bending of crystallites were observed in another photograph (not given here). The selected-area electron diffraction pattern of such an area, Fig. 23 exhibits an anomaly in the relative intensities of the rings as compared with the X-ray pattern of the polygonal particles of ZnCr₂O₄; i. e. the (220)-, (422)- and possibly (440)-rings are increased in their relative intensities (cf. Table 1). According to the foregoing discussion on the preferred orientation, the selected-area electron diffraction pattern of this area, Fig. 23 would be expected

TABLE 1. Relative Intensities of the Diffraction Rings

(hkl)	X-ray*	Selected-area electron diffraction**
111	(1)	unobservable***
200	—	unobservable***
220	(5)	(10)
311	(10)	(8)
222	(1)	(0.5)
400	(2)	(2)
331	(0.2)	(0.5)
420	—	—
422	(1.3)	(4)
333	(3.5)	(4)
440	(4)	(8)

* Obtained from the counter diffractometer curve.

** Obtained by the visual method.

*** Owing to the central halation.



Fig. 20 The polygonal ZnCr_2O_4 particles on a collodion film (Cr-shadowing).

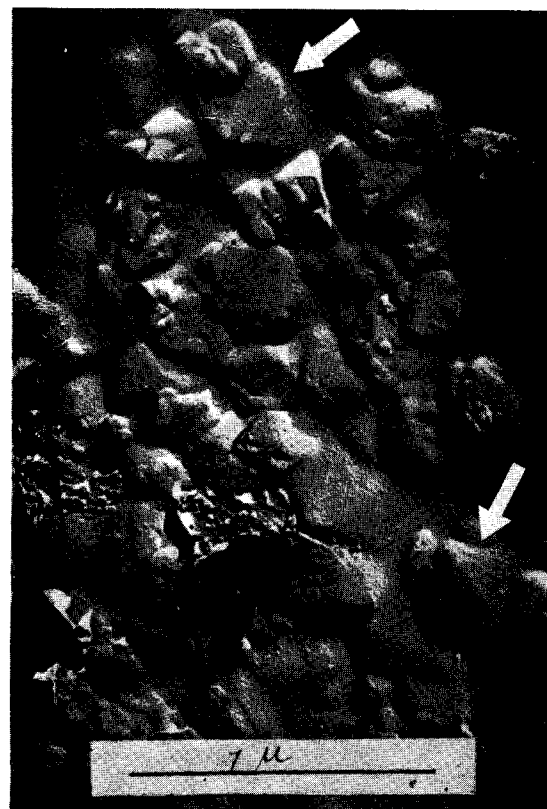


Fig. 21 Two-step carbon replica of the polygonal ZnCr_2O_4 particles. Arrows indicate the octahedrons.

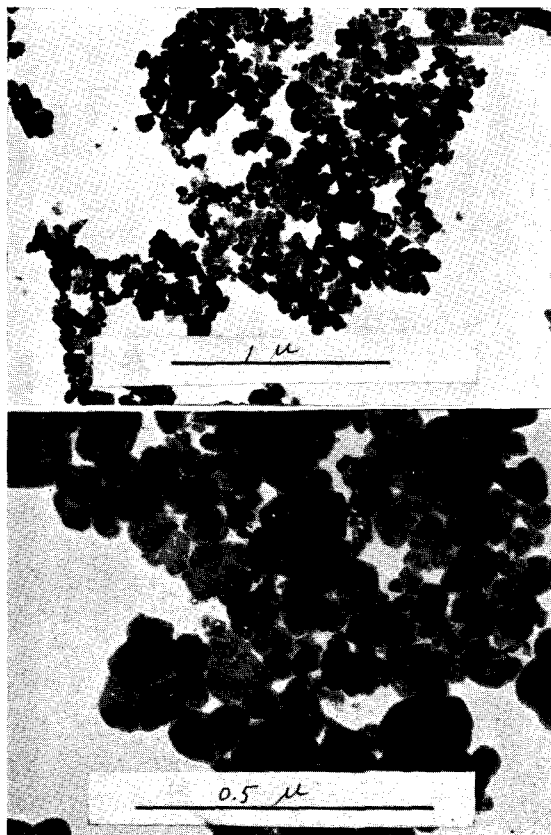


Fig. 22 The colloidal ZnCr_2O_4 particles on a collodion film.

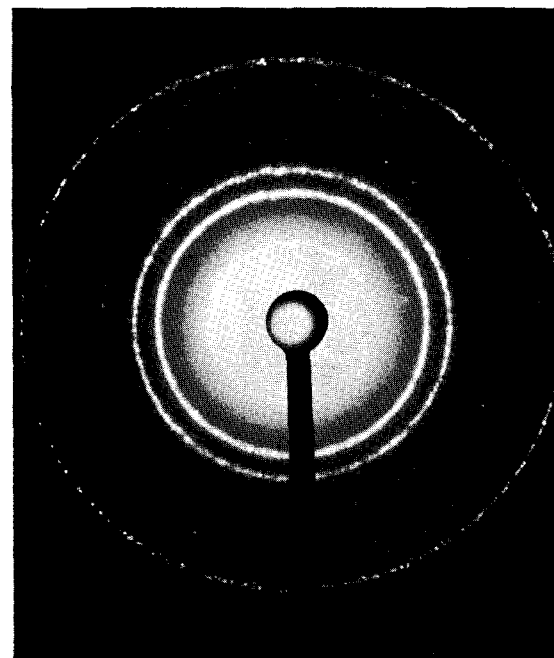


Fig. 23 The selected-area electron diffraction pattern of the colloidal particles in Fig. 22.

to consist of the rings corresponding to the net planes through the zone axis perpendicular to the flake, and additional rings ascribable to the bending of crystallite. Therefore, the above anomaly can be attributed to such preferred orientation that the colloidal particles are disposed randomly round the (111)-zone axis. Thus it is concluded that the flake surface is identified with the (111)-plane of ZnCr_2O_4 .

IV. Summary of Experimental Results

This paper describes a useful technique for the electron microscopy on the $\text{ZnO-Cr}_2\text{O}_3$ mixed catalyst prepared by thermal decomposition of basic ZnCrO_4 . By this technique the state of dispersion of ZnCr_2O_4 crystallites precipitated in the ZnO phase was revealed, and the tiny particles of ZnCr_2O_4 which have heretofore been observed only as "very amorphous" by X-ray could be observed.

In addition to them, valuable informations concerning the crystallite forms of ZnO and ZnCr_2O_4 have been obtained with the aid of selected-area electron diffraction as well as electron microscopy. These results will be summarized in the following.

A. On the ZnCr_2O_4 phase.

At the initial stage of the decomposition of basic ZnCrO_4 , a small amount of tiny ZnCr_2O_4 particles less than 100 \AA in diameter were observed in the ZnO phase. As the decomposition proceeded, they grew into colloidal particles less than about 500 \AA in diameter. Besides, there was a tendency for the (111)-axes of ZnCr_2O_4 crystallites to be disposed parallel to the (001)-axis of ZnO. At the final stage of decomposition, the ZnCr_2O_4 phase was found to be composed of colloidal and polygonal particles; the former was a flake-like ZnCr_2O_4 crystallite with poor growth in direction of the (111)-axis, and the latter was well crystallized mainly in octahedron in accordance with the crystal habits of spinel.

B. On the ZnO phase.

The ZnO crystallites at the initial stage of decomposition had so remarkable preferred orientation closely related with the crystal structure of the basic ZnCrO_4 substrate that they constituted an almost single crystal, in which the (001)- and (100)-axes of ZnO crystallites were parallel to the (001)- and (210)- axes of the basic ZnCrO_4 respectively. As the decomposition proceeded, they were recrystallized with lowering

in the degree of orientation. At the final stage of decomposition, ZnO phase was found to be composed mainly of aggregates of randomly disposed crystallites of 500~600 Å in diameter, and from their selected-area electron diffraction pattern it was concluded that the ZnO crystallite was of flake-like form having the (001)-plane as the flake surfaces.

Acknowledgments

The author wishes to express his sincere thanks to Professor J. HORIUTI, the director of this Institute, for his encouragement, and to Mr. T. SATO for his valuable discussions throughout this work.