# *Thermionic Emission from Catalyst for Ammonia Synthesis. I. Electron Microscopic Images of the Catalysts*

By Hiroshi UCHIDA and Naoyuki TODO

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## Introduction

Potash is an important promoter used in iron catalysts for ammonia synthesis and Fischer-Tropsch synthesis. On heating the catalyst, potash or potassium becomes liable to emit electrons or potassium ions from the surface. In this connection, C.H. Kunsman[1] measured thermionic emission from iron catalysts for ammonia synthesis already in 1926 and recently Y. Osumi[2] observed the electronic emission image of the catalyst in the oxidic as well as the reduced state and attained to notably interesting results in comparison with the optical. It can be readily understood that the measurements of the thermoelectronic emission provide detailed knowledge on the state of potash in the catalyst. The authors studied accordingly the thermoionic emission by means of the electronic image observation as well as the quantitative thermionic measurement on the catalysts whose catalytic activity for ammonia synthesis, microscopic structure and surface structure, such as area and average pore size, had already been investigated. Results

1) C. H. Kunsman, *J. Phys. Chem.*, **30**, 535 (1926).
2) Y. Osumi, This Bulletin, **26**, 515 (1953).

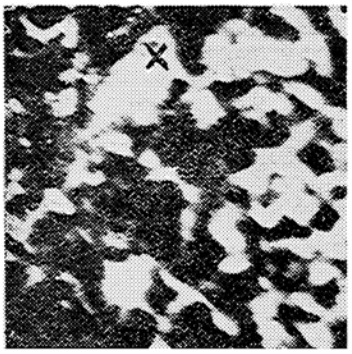

Fig. 1a. Cat. No. 1
Electronic image (830°C)
(Oxide) ×40

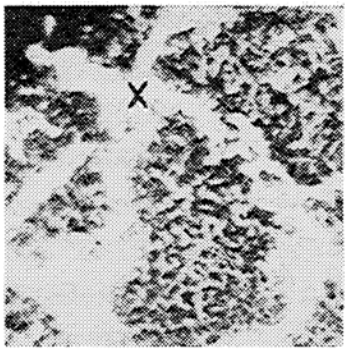

Fig. 1b. Cat. No. 1
Electronic image (450°C)
(Reduced for 5 min.)

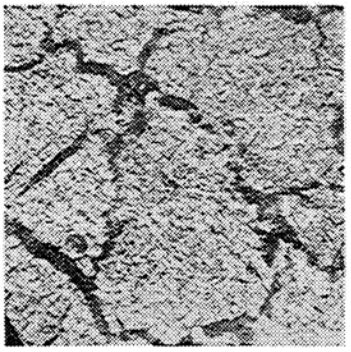

Fig. 1c. Cat. No. 1
Optical image
(After electr. emis.)

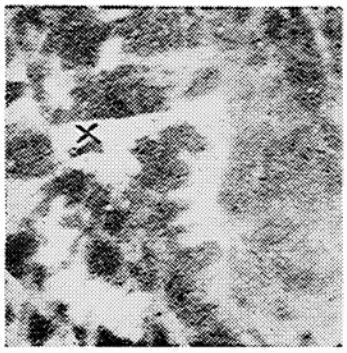

Fig. 2a. Cat. No. 2
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(Oxide)

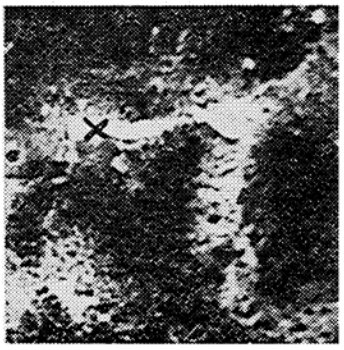

Fig. 2b. Cat. No. 2
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(Reduced for 20 min.)

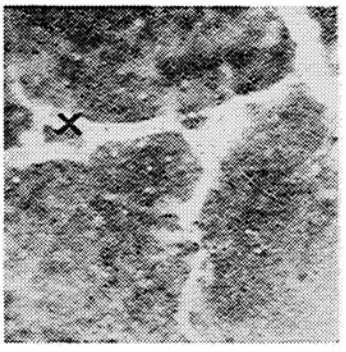

Fig. 2c. Cat. No. 2
Electronic image (760°C)
(After 30 min. observ. of
Fig. 2b)

Fig. 2d. Cat. No. 2
Optical image
(After electr. emis.)

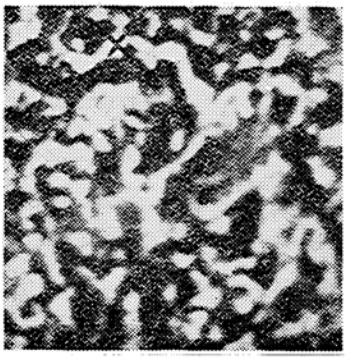

Fig. 3a. Cat. No. 3
Electronic image (800°C)
(Oxide)

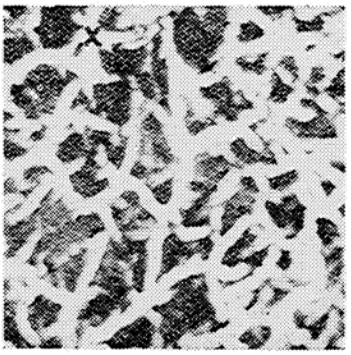

Fig. 3b. Cat. No. 3
Electronic image (780°C)
(Reduced for 5 min.)

obtained on the electronic image observation have lead to a qualitative understanding of potash in the synthetic ammonia catalyst. The results on this thesis will be described in this paper, while the quantitative measurement will be described in the next.

## Experimental

**Procedures.**—The surface electron microscope was of similar type to that used by N. Sasaki[3] and Y. Osumi[2]. Specimens for the electron microscope examination were prepared by polishing with emery paper, finishing with grade 0.5 and finally on cloth to get rid of emery dust from voids. They were of 4 mm. in diam. and 1–1.2 mm. in thickness. The temperature could be raised by heating tungsten filament inserted into the specimen holder and was measured by means of a thermocouple spot-welded as close as possible to the specimen. After the electronic images had been observed on oxidic state, the oxide was reduced at 450°C by passing hydrogen through the microscope at normal pressure. The reduction was stopped at intervals to observe successive alternation of the electronic image. Immediately after the electronic observations, the specimens were removed from the electron microscope to an optical microscope under which they were observed by oblique illumination so that a fair estimate of cracks and hollows on the section was facilitated. The specimens were fused synthetic ammonia catalysts prepared according to a procedure by G. Shima and one of the authors[4] and of the following respective different compositions of the promoters, No. 1: 1% $K_2O$, No. 2: 5% $Al_2O_3$, 1% $K_2O$, No. 3: 4% $Al_2O_3$, 1% CaO, 1% $K_2O$, No. 4: 3% $Al_2O_3$, 2% $SiO_2$, 1% $K_2O$, No. 5: 3% $Al_2O_3$, 2% $SiO_2$, 1% CaO, 1% MgO, 2.5% $K_2O$. Their actual potash content was determined by the use of hexyl calcium and found somewhat less than what was expected from the composition of raw material, as shown below respectively, No. 1: 0.86%, No. 2: 0.81%, No. 3: 0.89%, No. 4: 0.71%, No. 5: 1.91%.

## Experimental Results

The electronic images are shown from Figs. 1 through 5, in each of which the magnification factor is 40 with an exception of Fig. 4 (×60), together with respective optical micrographs after the electronic observations.*

**Catalyst No. 1.**—At an earlier stage of 3 minutes, observations showed a bright net work of the emission which gradually decreased in brightness to Fig. 1a which remained almost the same for additional 10 minutes. On reducing the oxide for five minutes, a bright and quite different net work of the emission appeared at such a low temperature as that of 450°C (Fig. 1b). Besides this image, there was not found any homogeneous emission which used to appear on the catalysts containing alumina. On raising the temperature to 750°C, the emission rapidly disappeared. The subsequent optical image is shown in Fig. 1c. In comparison with Figs.1a, b and c, the cracks in the optical image coincide accurately with the net works of Fig.1b, whereas they do not with Fig. 1a.

**Catalyst No. 2.**—Bright emission patterns were observed together with weaker emission over the whole surface of the oxide (Fig. 2a). On reduction, twenty minutes were required until an abrupt and a very marked change of the image took place as is shown in Fig. 2b. A part of the emissions from the oxide disappeared and new assemblages of fine bright specks appeared. On continuing the reduction for thirty minutes, the specks disappeared and the emission became rather homogeneous over the whole surface across which a few emission bands still shone.** Cracks and a few particular grains surrounded with cracks on the optical image (Fig. 2d) corresponded exactly to the places where the brighter emissions took place on Fig. 2b.

**Catalyst No. 3.**—As is shown in Fig. 3a, emission images with marked contrast developing appeared on the oxide. A few minutes after the beginning of reduction, the image changed abruptly to a new net work almost independent of the image in the oxide (Fig. 3b). On the continued observations, the emissions decreased in number and brightness till to Fig. 3c which could be closely related to the optical image (Fig. 3d).***

**Catalyst No. 4.**—The emission was so weak that the image could hardly be observed at the temperatures below 880°C (Fig. 4a). As it had been reported[5], the catalyst, added with silica, contained glassy inclusions on the polished section of the oxide (Fig. 4b). When the emission images were compared with the optical on the oxide, it could readily be detected that the bright emissions occurred from the glassy inclusions. The major part of the emission images remained after the reduction.

**Catalyst No. 5.**—The emissions became suf-

3) N. Sasaki, R. Ueda. T. Kuroda and H. Okamoto, *J. Soc. Metal, Japan*, **16**, 165 (1950).

4) G. Shima and H. Uchida, *Rep. Chem. Ind. Res. Instit. Tokyo*, **45**, 369 (1950).

* A paper provided with more of photographs will be published in the *Rep. Chem. Ind. Res. Instit., Tokyo.*

** On the electronic images from the oxide, there were observed black specks which began to shine after the oxide was reduced for 20 minutes; specks of this sort were observed only on catalyst No. 2 and the nature has not been accounted for in this paper.

*** When magnesia was used instead of lime, there were not found any emissios on the oxide except for those from the places corresponding to the cracks.

ficient to be observed at 780°C. Among the emission images, some took crystalline appearances (Fig. 5a), corresponding to the crystalline inclusions* which used to appear on the polished sections with increasing amounts of potash, as reported previously[5]. On reduction, the images of crystalline outline remained, whereas those of narrower bands and specks disappeared, and a rather homogeneous emission over the whole surface associated with a number of new narrow bands appeared (Fig. 5b). The emission image obtained after the reduction relates to the optical (Fig. 5c) similar to the findings with catalyst No. 2.

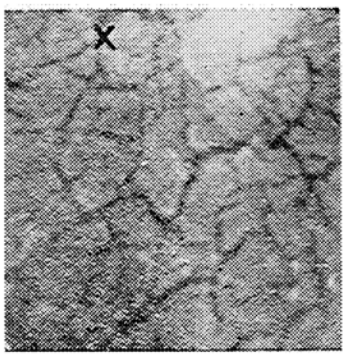

Fig. 3c. Cat. No. 3
Electronic image (850°C)
(After 5 min. observ. of Fig. 3b)

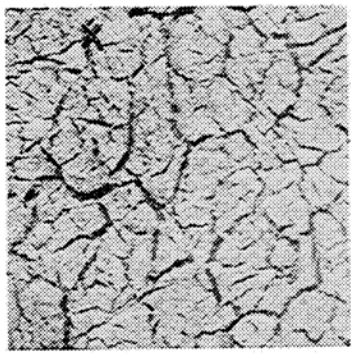

Fig. 3d. Cat. No. 3
Optical image
(After electr. emis.)

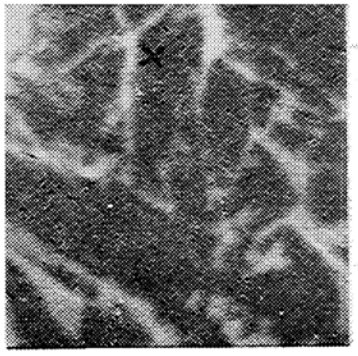

Fig. 4a. Cat. No. 4
Electronic image (900°C)
(Oxide) (×60)

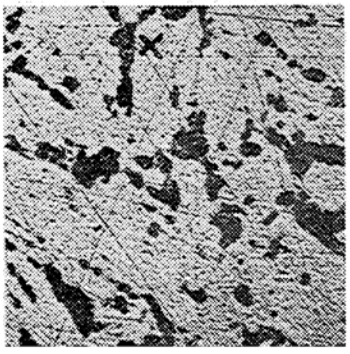

Fig. 4b. Cat. No. 4
Optical image of oxide
by vertical illuminat.
(×60)

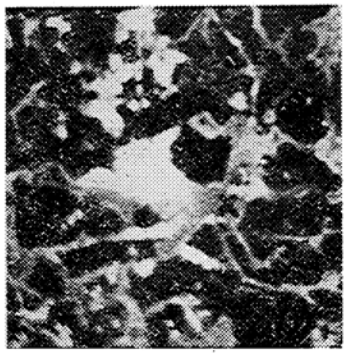

Fig. 5a. Cat. No. 5
Electronic image (850°C)
(Oxide) ×40

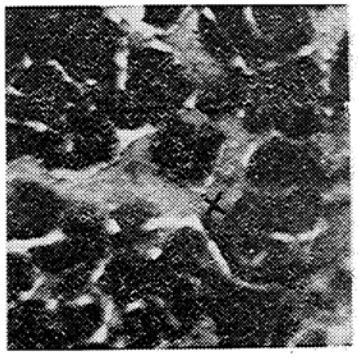

Fig. 5b. Cat. No. 5
Electronic image (780°C)
(Reduced for 5 min.)

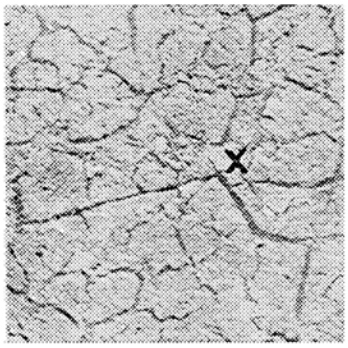

Fig. 5c. Cat. No. 5
Optical image
(After electr. emis.)

**Grain Boundary.**—On polishing on emery paper and then with red iron oxide on a rotating pad, well marked grain boundaries by ordinary vertical illumination were developed by etching with hydrochloric acid as shown in Fig. 7 at a magnification of X 100. Broader grain boundaries enclose large grains (parent grain) which are divided into a number of fine fragments by unifrom orientation of etch marks on the grains. The catalyst consists of a mosaic like structure of such fine

* On catalyst No. 5, the inclusions could be observed only on the section thoroughly polished with red iron oxide on a rotating pad, in use of which the electronic emission observations were difficult to investigate.

5) H. Uchida, N. Todo and K. Ogawa, *Rep. Chem Ind. Res. Instit., Tokyo*, **46**, 11 (1951).

grains***. Though the specimens polished to such an extent that they were used for the electron emission revealed also patterns shown in Fig. 6, they could be by no means related to the grain boundaries in Fig. 7. It has thus proved that a prediction of grain boundaries from optical patterns on the specimen prepared for the electronic emission is a matter of considerable difficulty. On the other hand, when the section of Fig. 7 was reduced, every crack developed along the etch marks, i. e. the grain boundaries Fig. 9. This could be also confirmed on the other catalysts.

## Discussion

It may be estimated with certainty that electrons may easily emit from the place rich in potash or potassium. If additives were always liable to accumulate in the grain boundaries of the oxide, the electronic emission would take place along the boundaries. In this respect, reference is made to a recent article by Y. Osumi[2] who has thought electrons emit mainly from the parts which existed at the grain boundaries as a result of his electronic and optical images comparison. He called this particular part B, distinguishing itself from another part A more abundant in the catalyst. However, in our observations, marked changes of the emission images took place frequently in course of reduction and the places on which the emission was observed in the oxidic state frequently did not correspond to those in the reduced state. Furthermore, the net works of the emission from the reduced, which are quite different from those from oxides, always coincide exactly with the grain boundaries. It, therefore, can not be said reasonably that the emission images from the oxides correspond always to the grain boundaries. Alternation of the emission images in course of the reduction occurred in different manners as described before. Among them, those which were observed on both the oxidic and the reduced were either of relatively wide bands (catalyst No. 2 and 3), or of crystalline outline (catalyst No. 5). Cracks were observed around them on the optical image. They may correspond to interfacial crystallites or grains rather than grain boundaries and the promotors such as potash may segregate in such particular grains. Y. Osumi has already observed that bright emission occurres along the cracks produced by reduction and the fact has been interpreted by himself as being due to migration of active substance such as potash or potassium from beneath to the surface by way of the cracks. The beautiful net work of the emission which coincides with the cracks may therefore give a measure for estimation of the cracks; however, it is not directly related to distribution of potash or potassium in the catalyst. Information concerning the distribution in the oxide may be afforded by another kind of the emission images, which is observed in the oxidic, but is scarcely ever observed at the same places in the reduced. The particular regions where the above kind of the image appears will be searched on the polished and etched section of catalyst No. 3 under an optical microscope. By ordinary vertical illumination (Fig. 7), there are found in the parent grain several shining areas which appear as voids when observed by oblique illumination (Fig. 8). The shining is due to the surface of the grains underlying these having dissolved out with hydrochloric acid. The voids could also be observed more or less marked on the other catalysts; for example, on catalyst No. 2, they were shallow and the areas shining by vertical

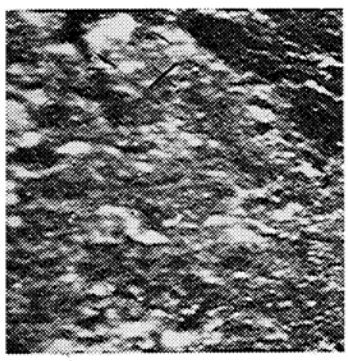

Fig. 6. Cat. No. 3
Oxide by oblique illumination
×100

Fig. 7. Cat. No. 3
Oxide by vertical illumination (Thoroughly polished and etched surface)

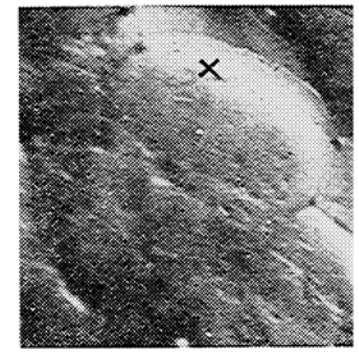

Fig. 8. Cat. No. 3
Fig. 7 by Oblique illumination

illumination were hardly observed. The parent grain may be thus estimated to be divided into those sub-grains which are readily etched with hydrochloric acid and those which are etched with difficulty more or less markedly according to the kind of the catalysts. The voids thus observed on catalyst No. 3 are mostly like the emission images from the oxide in shape and dimension. Since the subgrains readily etched are expected to be rich in potash and to be liable to emit electrons, the bright emission images on the oxide may well be related to the voids, that is to say, to the sub-grains which existed at the voids before they were dissolved out by hydrochloric acid.

Fig. 9. Cat. No. 3
Reduced surface of Fig. 8

On the catalysts No. 2, 3 and 4, the catalytic activities for ammonia synthesis were measured at a pressure of 100 kg./cm², and the surface areas*, the surface concentrations of potash (+lime)**, the average pore radii*** were also measured on the specimens after the use for the activity measurements[6]. The results are shown again in Fig. 10 and Table I together with those on catalyst No. 5 respectively. A catalyst promoted with alumina, potash and magnesia instead of lime has almost the same activity as catalyst No. 2 (Fig. 10). An attempt will be made to account for promoting action of the additives from the view point of the electron emission image. On adding alumina, potash seems to be stabilized in view of the fact that the emissions were retained over the whole surface on prolonged heating with catalyst No. 2, while

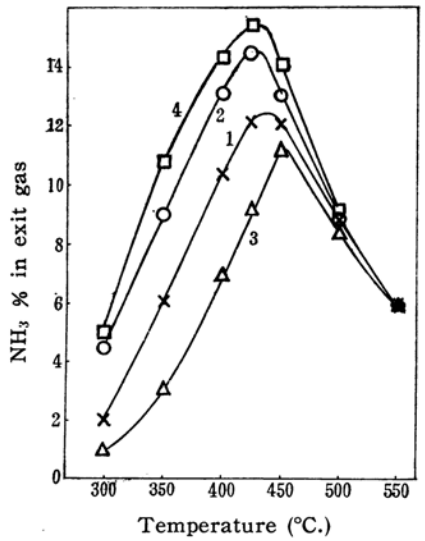


Fig. 10. Ammonia synthesis at 100 kg./cm² and S.V. 5000 in use of 20 cc. Cat. 1; No. 2, 2; No. 3, 3; No. 4, 4; No. 5

they disappeared rapidly with catalyst No. 1. Excellent dispersion of potash is thus observed from the emission image of catalyst No. 2. An addition of lime causes an appreciable increase of the activity as well as the markedly heterogeneous emission which is estimated to be due to the particular subgrains as described above. When magnesia was used instead of lime, there have been found neither the increase of the activity nor the heterogenous emission. The promoting actions of lime for the activity are thus probably ascribed partially to its effect for the formation of the well marked sub-grains in the parent grains, besides that of increasing the surface area (ref. Table I). As for

TABLE I

| Catalyst | No. 2 | No. 3 | No. 4 | No. 5 |
|---|---|---|---|---|
| Surface Area, m²/g. | 6.11 | 8.48 | 7.21 | 6.0 |
| Surface Concentration of Potash | 0.61 | 0.56 | 0.20 | 0.74 |
| Average Pore Radius, Å | 400 | 301 | 322 | 460 |

the addition of lime, A. Nielsen[7] has described that it makes the phase less anisotropic as observed by polarized light and consequently increases the thermostability of the catalyst. On the contrary the surface becomes more heterogeneous on the addition according to our observation and this is consistent with our results[8] that catalyst No. 3 is less thermostable than catalyst No. 2, while the former is superior in the activity to the latter.

** By means of observation under electron microscope on replica of the etched surface, the grains seemed to consist of fine crystallites as small as a few microns in diameter.

* Calculated from isotherms of physical adsorption of $CO_2$ by means of BET method.

** Represented by ratio of value of chemisorbed $CO_2$ to that of monomolecular adsorption at 78°C.

*** Average pore radius is calculated by $r=2\times v/S$, where $v$ is pore volume (volume by mercury displacement-volume by water displacement) and $S$, surface area.

6) H. Uchida and N. Todo, *J. Chem. Soc. Japan* (Industr. Sect.), **56**, 225 (1953).

7) A. Nielsen, "Advances in Catalysis and Related Subjects," Academic Press Inc., New York, **5**, 1 (1953).

8) H. Uchida, *Rep. Chem. Ind. Res. Instit. Tokyo*, **46**, 1 (1951).

On the microscopic examination of catalyst No. 4 containing sillca, glassy grains are present. As potash is liable to segregate in these grains as described, potash is poorer in the major surface free from these grains than it is in catalyst No. 2 and 3, since the total content is almost the same in every three. The part played by the addition of silica may therefore reduce the surface concentration of potash and consequently cause a decrease of the activity. From this view point, a simultaneous addition of potash sufficient to spread in every grain of catalyst with addition of sillica will probably contribute to a recovery of the activity. The estimation is confirmed with the results with catalyst No. 5.

H. Kobayashi et al[9] have found recently that potash can be divided into those soluble in water and those insoluble and that the larger the content of the latter the higher the activity for ammonia synthesis. They have also described a relation between them, according to which a rapid linear increase of the activity is accompanied with the insoluble potash content till to 0.4% potash, beyond which the increase becomes gradually more slow, showing a bend at this content. The value of 0.4% has been considered by them as a limiting content of potash in A part by Y. Osumi. As has been indicated by H. Kobayashi, the activity remains quite low as far as the insoluble content dose not exceed 0.4%. It is therefore necessary to increase the content more and more to obtain any catalyst appropriate for the industrial use. On the basis of our results on the optical as well as the electronic emission images, potash in excess of that possessed by the catalyst distributed homogeneously in the bulk is found locally in the following three kinds of the regions such as, 1 grain boundaries, 2 particular sub-grains in the parent grains, 3 interfacial grain (glassy or crystlline) especially in the particular case where promoters such as silica are used. On reducing the catalysts, they afford a large surface area as shown in Table I respectively. Among the above three, the grain boundaries might contribute to a very small area even if the grains were of the dimension of a few microns. Secondly, the interfacial grains occupy only a small fraction of the total number of the grains and their presence seems not to contribute to an increase of the surface area as well as the activity as it is proved on the latter with catalyst No. 4. In contrast, the particular sub-grains may most contribute to the surface area, as they occupy a wide region of the grains wherein numerous fine pores appear on reduction. It may therefore be probable that the insoluble potash exceeding the limiting value of 0.4% may exist in these sub-grains, so this fact may contribute most to the activity. These sub-grains are liable to appear markedly on addition of lime, and, ndeed the catalyst shows high activity. The authors would finally like to mention that the appearance of the particular sub-grains may be accelerated not only in use of adequate promoters, but may also be favored by maintaining the temperature during the fusion as high as possible so that the segregation of potash in the grain boundaries may be avoided.

9) H. Kobayashi and O. Nishijima, *J. Chem. Soc. Japan* (Industr. Sect.), **57**, 189 (1954).

## Summary

The electronic images have been observed on 5 types of the catalysts for ammonia synthesis, which are different in promoter-composition. On heating the oxides from 750 to 900°C, the images of different kinds which were characterized by their respective promoters compositions appeared after a few minutes. On reduction, some of the images remained, while the others disappeared, and during the periods of five to thirty minutes of the reduction, the images turned to the respective characteristic ones again, sometimes being quite different from those of the oxides. On the additional observations, a part of the images weakened or disappeared and rather the homogeneous images over the whole sections became to be observed by raising thetemperature.

Comparing the image with the optical, the net work of the emission after the reduction corresponds to cracks on the section. When the microscopic structure of the section thoroughly polished and etched with hydrochloric acid is adopted for comparison with the above optical image, grain boundaries in the oxide always correspond to the cracks. Therefore, the electronic images on the oxide are not always related to the grain boundaries.

Qualitative explanations on respective promoting effect of alumina, lime and silica are yielded from view point of the electronic image.

It has been proved from the observations of the electronic as well as the optical images that there are the following 3 types of regions which are rich in potash, i.e. the grain boundaries, particular interfacial grains and some of the sub-grains into which the

parent grains are divided. When references are made to the results of the activity for ammonia synthesis, surface area and etc., together with that by H. Kobayashi who has described that the activity is greatly enhanced by the larger amount of potash insoluble in water, the estimation shows that probably potash existing in the sub-grains above may most contribute to the activity for ammonia synthesis.

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*Government Chemical Industrial Research Institute, Tokyo*