# *Effects of Quenching and Annealing in Manufacture of Fused Iron Catalyst upon Activity for Ammonia Synthesis and Potash Distribution*

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## Introduction

In the manufacture of an iron catalyst for the ammonia synthesis a molton oxide of the catalyst is usually allowed to cool in a vessel for melting, and the rates of cooling are mainly determined by the capacities of batches. The different rates are expected to modify grain growth as well as distribution of the promoters and to have considerable effect upon subsequent properties of the catalyst. The adequate rate is, therefore, an important factor to yield the catalyst of superior quality; but no paper, so far as we are aware, has ever been published on this subject.

In the present work, catalysts of four different promoter compositions were subjected to different rates of cooling such as quenching, annealing and normal cooling, and the subsequent activities for ammonia synthesis were measured. In connection with this, the experiment involved the measurements of surface area after reduction of the oxide, and quantities of water-soluble potash, along with the observations of microscopic structure and electronic images.

The quenched catalyst gave nearly the same activity with the normally cooled one, while the annealed catalyst a remarkably low one. The low activity has been to some extent explained in the light of information obtained from the present experiments on distribution state of the promoters in the catalysts. Moreover the present data for characteristic microscopic structures, electronic images and different quantities of water-soluble potash in the catalysts, etc. will provide us with more knowledge for better understanding of the role of the promoters.

## Experimental Procedure

**Preparation of Catalyst.**—The catalyst employed in this work contained the following different promoters; 5% $Al_2O_3$, 1% $K_2O$, for Cat. No. 1; 4% $Al_2O_3$, 1% CaO, 1% $K_2O$ for Cat. No. 2; 3% $Al_2O_3$, 2% $SiO_2$, 1% $K_2O$ for Cat. No. 3; and 3% $Al_2O_3$, 2% $SiO_2$, 1% CaO, 1% MgO, 2.5% $K_2O$ for Cat. No. 4*. They were prepared by burning mixtures of iron powder and promoters to fused iron oxides in oxygen within an iron container capable of holding about 1 kg. of oxides. Immediately after the fusion, the oxides were subjected to different cooling procedures such as: (1) quenching by pouring water on the container, (Cat. No. q,); (2) cooling as usually practised (normal cooling), (Cat. No. c.); (3) annealing for forty hours in an electric furnace kept at about 1000°C before cooling to room temperature, (Cat. No. an.).

**Activity for Ammonia Synthesis.**—The synthesis was carried out with 3 cc. of granules (1 to 2 mm. diameter) of catalyst packed in a previously described converter¹⁾*, under a pressure of 100 kg./cm², at temperatures ranging from 300° to 500°C, at a space velocity of $5\times10^3$; and the exit gas from the converter was analyzed for ammonia content to give relative activity of the catalyst for ammonia synthesis. After a series of measurements, the pressure was reduced to normal pressure, thereafter the temperature being raised to 650°C; and the catalyst was kept at this temperature for five hours, in a current of synthesis gas. Repeated series of measurements gave a measure of thermostability in terms of the decrease of activity before and after heating at 650°C.

**Microscopic Structure.**—A preparation of thoroughly polished catalyst was observed under a microscope in both vertical and oblique illumination, before and after etching by hydrochloric acid. In this observation, concavities produced by etching could more easily be distinguished by oblique illumination.

**Potash Soluble or Insoluble in Water.**—H. Kobayashi²⁾ et al found that part of the potash in the catalyst dissolved in water, and that the remaining quantities were closely associated with the respective activities of the catalysts. In the present work the determination was made by the following procedure: a quantity of fine powder (finer than 100 mesh size) of the catalyst was soaked in water at the room temperature for periods of time, and the aqueous extracts were analyzed for potash content by means of a Perkin-Elmer's flame photometer.

**Surface Area and Potash (+Lime) Concentration in the Surface of Reduced Catalyst.**—The surface area and the potash concentration in the surface of the catalyst reduced at 500°C by hydrogen at normal pressure were determined

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* The compositions are expressed in the weight percentages of promoters in catalysts, on the basis of exact oxidation of iron to $Fe_3O_4$.

1) H. Uchida and M. Kuraishi, This Bulletin, 28, 106 (1955).

* The converter produced ammonia in somewhat higher amount than the one packed with 20 cc. of the catalyst.

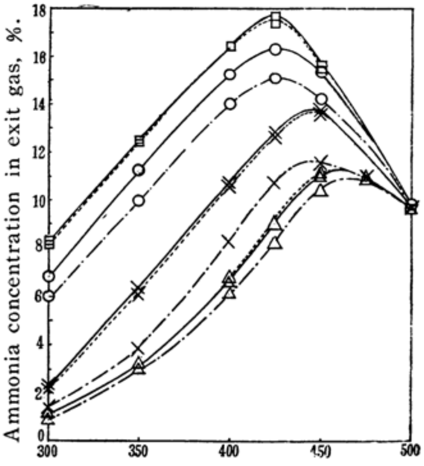
2) H. Kobayashi and O. Nishijima, *J. Chem. Soc. Japan (Ind. Sect.)*, 57, 189 (1954).

from the results of measurements of carbon dioxide adsorption. The former was evaluated by the usual BET method applied to the physical adsorption isotherm at −78°C and the latter was expressed as a ratio of the amount of chemisorbed carbon dioxide to that of physically adsorbed at −78°C.

**Electronic Image.**—An electronic image from the polished surface of the oxide was observed at successive stages in the reduction of the oxide, by means of an emission electron microscope described in a previous paper[3]. The reduction was carried out at 450°C in the electron microscope, through which hydrogen was passed. Immediately after the observation the specimen was removed therefrom to an optical microscope to contrast the emissive regions with the optical images in oblique illumination.

## Experimental Results

**Activity for Ammonia Synthesis.**—The results are summarized in Fig. 1, and show an outstanding common trend of activity among four kinds of catalysts different in promoter composition. Generally, the annealed catalyst tended to reveal much lower activity than the normally cooled one for the ammonia synthesis, but the quenched catalyst revealed the same.



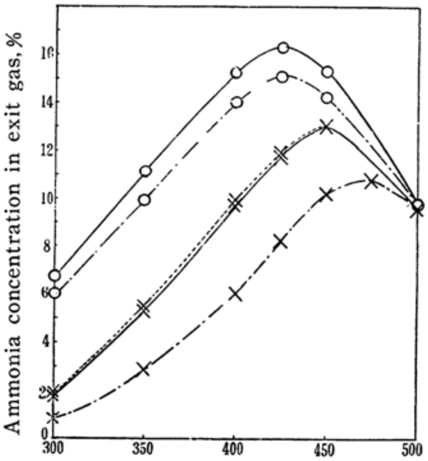
Pressure, 100 kg./cm², space velocity, $5\times10.^3$

×, Cat. No. 1, ○, Cat. No. 2,
△, Cat. No. 3, □, Cat. No. 4.
········ quenched catalyst,
——— normally cooled catalyst,
—·—· annealed catalyst.
(The activity of Cat. No. 2q coincided just with that of Cat. No. 2c.)

Fig. 1. Results of ammonia synthesis.

Catalyst No. 4 revealed the highest activity, while catalyst No. 3 the lowest.

The measurement of thermostability of catalysts subjected to different rates of cooling indicated that three catalysts of No. 2 series . . . No. 2q, No. 2c and No. 2an . . . were nearly the same in thermostability (Fig. 2).



Pressure, 100 kg./cm², space velocity, $5\times10^3$.

○, ×, before and after heating at 650°C respectively.
········ quenched catalyst,
——— normally cooled catalyst,
—·—· annealed catalyst.

Fig. 2. Thermostability for Cat. No, 2.

**Microscopic Structure.**—Cleavage facets of individual grains were visible, even by the naked eye, in catalysts No. 1, No. 2 and No. 4, but scarcely any were visible in No. 3. Catalysts No. 3 and No. 4 revealed microscopic structures very different from those of catalysts No. 1 and No. 2, which might be ascribed to the presence of silica in the former.

In the case of catalysts No. 1 and No. 2, the grain growth was not markedly restrained by quenching (Phot. 1 of catalysts No. 1q), and the individual grains were locally etched to result in concavities in their interior (Phot. 2). Annealing modified the structure to develop large grains, whose diameter sometimes attained to 10 mm., and to make the oxide so resistive against etching as to be hardly ever attacked by hydrochloric acid but aqua regia causing figures seen in Phot.'s 3 and 4 of catalysts No. 1an and No. 2an. These photographs show the preservation of a comparatively homogeneous structure* over the whole grain.

As previously described[4], catalyst No. 3q containing silica with a small amount of potash revealed slag inclusions (according to Z. W. Wilchinsky[5], a potassia-silica glass) (Phot. 5), which with an increased addition of potash were apt to take a more precise crystalline outline as shown in Phot. 7 of catalyst No. 4 q. When the

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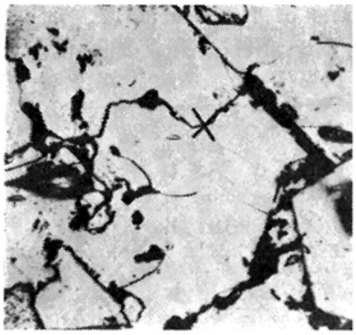
[3] H. Uchida and N. Todo, This Bulletin, **27**, 585 (1954).

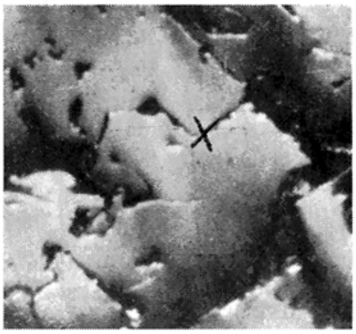
* "Homogeneous structure" means the structure uniformly resistive against etching.

[4] H. Uchida, N. Todo and K. Ogawa, *Rpt. Gvn't. Chem. Ind. Research Inst. Tokyo*, **46**, 11 (1951).

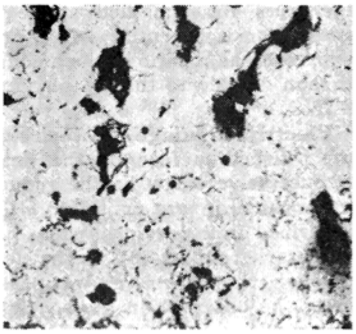
[5] Z.W. Wilchinsky' *Analyt. Chem.*, **21**, 1188 (1949).



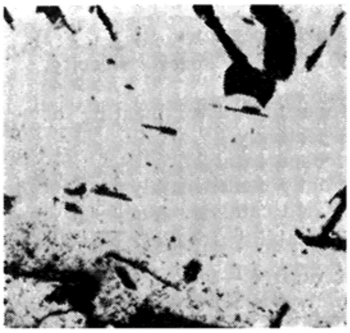
Phot. 1. Cat. No. 1q, etched by HCl. ×100



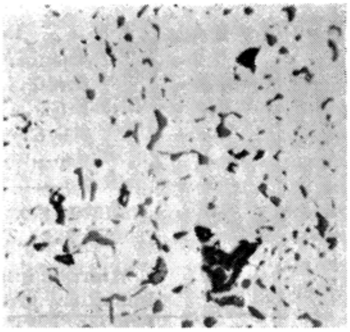
Phot. 2. Phot. 1 in oblique illumination.



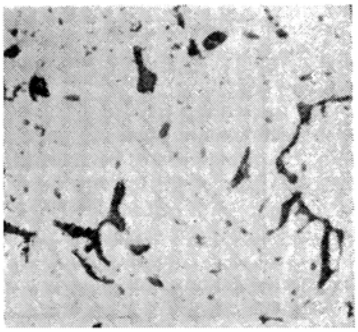
Phot. 3. Cat. No. 1an, etched by aqua regia.



Phot. 4. Cat. No. 2an, etched by aqua regia.

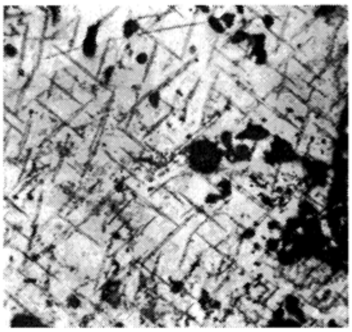


Phot. 5. Cat. No. 3q, unetched.



Phot. 6. Cat. No. 2an, unetched.

Phot. 7. Cat. No. 4q, unetched.



Phot. 8. Cat. No. 4an, etced by HCl.

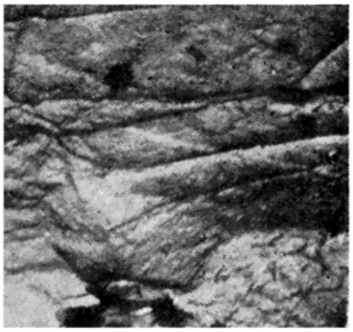


Photo. 9. Replica from surface of Phot. 4. ×5000

catalysts were annealed the inclusions tended to diminish their size and they partially disappeared, and the structure in the grain became more homogeneous. These catalysts did not, however, attain to so homogeneous a structure as those of catalysts No. 1an and No. 2an (refer to Phot.'s 6 and 8 of catalyst No. 3an and No. 4an respectively).

**Potash Soluble or Insoluble in Water.**—The rate of solution of soluble potash from catalyst No. 3 was found to be much slower than that from catalyst No. 2, requiring twenty hours for completion. Therefore, insoluble potash contents listed in Table I are given as ratios of the amount of potash remaining in catalyst soaked in water for twenty hours to the total amount originally contained.

TABLE I

INSOLUBLE POTASH, SURFACE AREAS, AND SURFACE CONCENTRATION OF POTASH (+LIME)

| Catalyst | Total potash wt. % | Insoluble potash %[a)] | Surface area $m^2/g.$[b)] | Surface concentration of potash |
|---|---|---|---|---|
| No. 1q | 0.91 | 18.8 | 15.6 | 0.64 |
| No. 1c | 0.88 | 56.4 | 15.9 | 0.68 |
| No. 1an | 0.89 | 7.8 | 11.7 | 0.42 |
| No. 2q | 0.90 | 30.0 | 17.1 | 0.49 |
| No. 2c | 0.93 | 88.9 | 17.5 | 0.53 |
| No. 2an | 0.87 | 17.0 | 12.7 | 0.51 |
| No. 3q | 0.94 | 87.0 | 12.0 | 0.36 |
| No. 3an | 0.95 | 63.8 | 7.4 | 0.35 |
| No. 4q | 2.43 | 93.2 | 17.4 | 0.54 |
| No. 4an | 2.40 | 68.6 | 14.1 | 0.58 |

a): ratio of the amount of potash remaining in catalyst soaked in water for 20 hours to the total potash.

b): surface area per g. of reduced catalyst.

Catalysts No. 1 and No. 2, when normally cooled, contained the greatest quantity of insoluble potash, whereas annealed ones the least. Similarly, in the case of catalysts No. 3 and No. 4, the quenched catalyst contained a greater quantity of insoluble potash than the annealed one. In addition, it is here worth noticing that the quantity varied remarkably according to the promoter composition, namely, it was somewhat or considerably increased by the addition of lime or silica respectively.

Soluble potash seems to come from potash existing as a separate phase[6,7] in the catalyst. The soluble potash gave no sign of dissolving as an aluminate, for no aluminium ion could be detected in the aqueous extracts. Potassium may also be present as potassium ferrite[6,7] but its dissolution as such seems to be improbable*.

**Surface Area and Potash (+Lime) Concentration in the Surface of Reduced Catalyst.**— The results are presented in Table I. For all kinds of catalysts, the slightly less was found on the quenched and the remarkably small on the annealed. So far as a catalyst of a definite promoter composition was concerned, the surface area as well as the activity remained nearly constant independently of the varying quantities of insoluble potash till the quantity lowered to a certain value (18.8% and 30% of the total potash with catalysts No. 1 and No. 2 respectively), but both of them diminished remarkably with the further decreasing quantity (7.8% and 17%).

Among catalysts No. 1, No. 2 and No. 3, the catalysts No. 3 gave abnormally small values of surface concentration of potash, despite their equal potash contents.

Both quenching and annealing exerted so slightly important an effect upon the surface concentration, that the concentration remained nearly unchanged by these procedures (Table I). This result may be interpreted to indicate that the soluble potash in the annealed catalysts hardly at all segregates along the grain boundaries but the greater part remains in the interior of grains, since the segregation would give rise to a decrease inpotash content in the interior and consequently the smaller surface concentration*.

How could the potash dissolve into water from the interior of such large grains as those of the annealed catalysts? To solve this problem the following observations were conducted.

Although the optical microscopic structure of the grain in the annealed catalyst seems homogeneous (Phot. 4), a replica stripped from the etched surface revealed in an electron microscope many finer grains (sub-grains) as well as narrower grain boundaries between those grains (Phot. 9). These boundaries, considering their poor resistance to acid, seemed to be rich in potash and might be considered to offer paths for potash to dissolve out from the interior of the grain. This hypothesis could be confirmed with the results given in Table II, which revealed marked increase of the surface area and simultaneously appreciable decrease of the surface concentration after dissolution of soluble potash.

TABLE II

CHANGE OF SURFACE AREA AND SURFACE CONCENTRATION OF POTASH (+LIME) AFTER DISSOLUTION OF POTASH

| Catalyst | Surface area $m^2/g.$ oxide | Surface concentration of potash |
|---|---|---|
| No. 1an | 0.58 | 0.89 |
| No. 1an after dissolution | 2.02 | 0.06 |
| No. 2an | 0.50 | 0.62 |
| No. 2an after dissolution | 1.72 | 0.19 |

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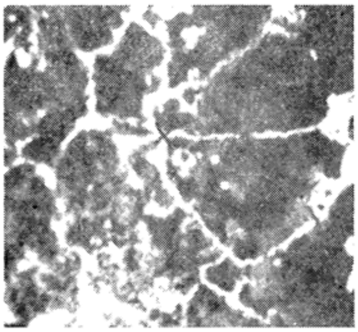
[6] L.R. Maxwell and J.S. Smart, *J. Chem. Phys.*, **19**, 303 (1951).

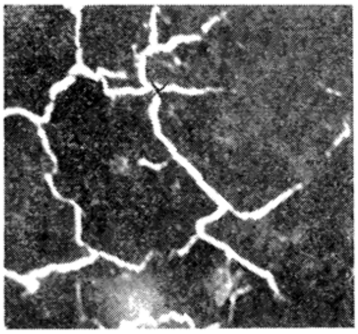
[7] R. Brill, "Structure and Properties of Solid Surfaces", The University of Chicago Press (1953), p. 437.

* The potash in a catalyst containing potash only (0.93%) also comprised two kinds, i.e. soluble and insoluble. The insoluble potash amounted to 70.6% of the total potash.

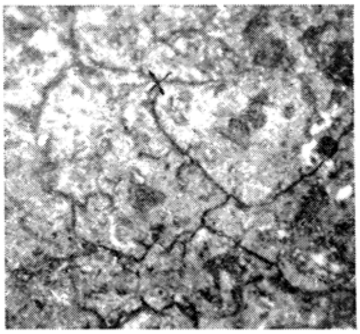
* As the grain interiors, not the grain boundaries, occupy the major part of the catalyst, the measured surface concentration may be chiefly dependent on the surface concentration of the individual fine particles of iron produced by reduction in the interior.



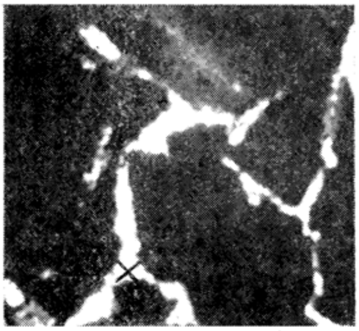
Phot. 10. Electronic image, Cat. No. 1q, oxide, 800°C. ×50



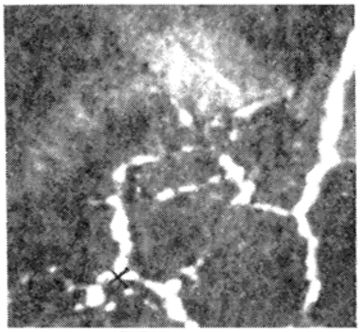
Phot. 11. Electronic image, Cat. No. 1q, after reduced for 5 min., 880°C.



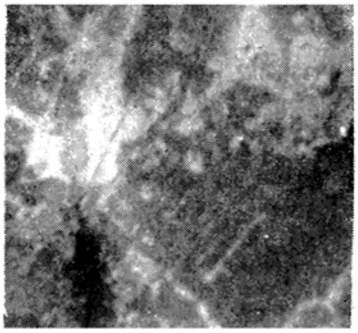
Phot. 12. Optical image, Cat. No. 1q, after electr. image observation.



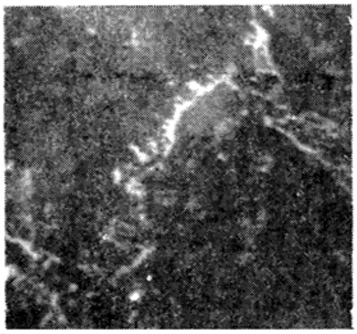
Phot. 13. Electronic image, Cat. No. 2an, oxide, 840°C.



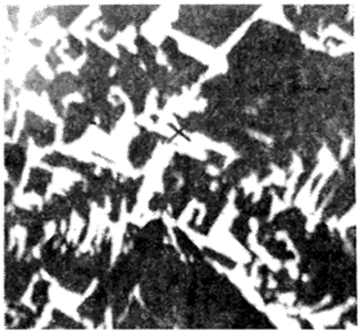
Phot. 14. Electronic image, Cat. No. 2an, after reduced for 5 min., 760°C.



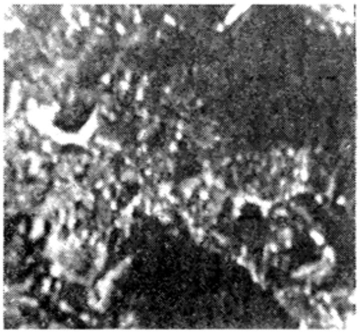
Phot. 15. Electronic image, Cat. No. 3q, oxide, 900°C.



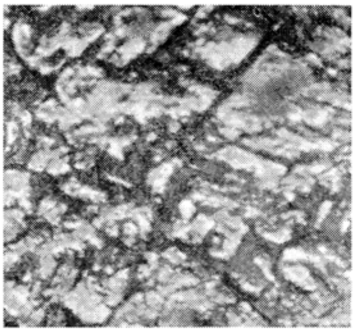
Phot. 16. Electronic image, Cat. No. 3an, oxide, 940°C.



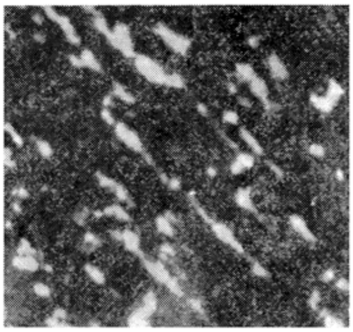
Phot. 17. Electronic image, Cat. No. 4q, oxide, 760°C.



Phot. 18. Electronic image, Cat. No. 4q, after reduced for 5 min., 780°C.



Phot. 19. Opitical image, Cat. No. 4q, after electr. image observation.



Phot. 20. Electronic image, Cat. No. 4an, oxide, 800°C. ×50

**Electronic Image.**—The oxide, even after comparatively prolonged heating, gave substantially unchanged electronic images. After reduction of the catalysts, the brighter images still remained without any remarkable change, but the new weaker images appeared homogeneously over wide regions on the section.

The electronic images of the normally cooled catalysts No. 1 and No. 2* were not markedly different from those of the respective quenched catalysts, but the appreciably different ones were observed with the annealed. The electronic images of the quenched catalysts of No. 1 and No. 2 are exemplified by Phot.'s 10 and 11 of catalyst of No. 1q. The images from the oxide appeared not only in regions where cracks were produced by reduction but also in the interior enclosed by the cracks (compare Phot. 10 with Phot. 12). With the progress of reduction the images from the interior tended usually to become weaker and simultaneously to impart homogeneous appearance to the grain, as is seen in Phot. 11, and exhibit strong emission coming from the cracks. In the case of annealed catalysts, the emission hardly ever took place in the interior of grains, but mainly in the grain bound aries and/or narrower grains existing between the well grown grains as shown in Phot. 13 of catalyst No. 2an. After reduction of the catalysts, the weaker homogeneous images appeared in the interior of grains (Phot. 14).

The electronic images from the catalysts containing silica were previously3) indicated to be very different from catalysts No. 1 and No. 2. Catalysts No. 3q did not easily emit the electrons and higher temperatures were required to produce the image. The catalysts gave weaker and homogeneous images from all over the section, together with slightly stronger emissions from the slag inclusions (Phot. 15). The images from catalysts No. 3an (Phot. 16) were not very different from those from catalyst No. 3q, which would be expected from comparatively smaller difference between their microscopic structures.

Catalyst No. 4 gave the images at the temperature considerably lower than that for catalyst No. 3. The images of quenched catalyst No. 4q appeared in the crystalline inclusions seen in the microscopic structures (Phot. 17), and even after reduction they were invariably visible together with newly appearing weaker images from other regions (Phot. 18). The reduction, however, produced cracks around the inclusions (Phot. 19), which might be interpreted as indicating the grain boundaries to exist in the immediate neighbourhood of the inclusions. When the catalyst was annealed, the electronic images varied from those of the quenched, corresponding to the variation in microscopic structure, thus appearing at new etch marks of parallel orientation shown in Phot. 8 and simultaneously in the remaining inclusions (Phot. 20).

## Discussion

**Catalytic Activity and Surface Area.**—The catalytic activity is to be directly correlated with the surface structure of the reduced catalysts. Actually, the surface area was found to be remarkably diminished by an-

TABLE III

RELATION BETWEEN DECREASE OF ACTIVITY AND DECREASE OF SURFACE AREA BY ANNEALING

| Catalyst | Apparent energy of activation kcal./mol. | Aan/Aq (425°C) | San/Sq |
|---|---|---|---|
| No. 1q | 50.1 | 0.669 | 0.750 |
| No. 1an | 49.8 | | |
| No. 2q | 37.4 | 0.716 | 0.739 |
| No. 2an | 39.4 | | |
| No. 3q | 51.1 | 0.803 | 0.616 |
| No. 3an | 49.6 | | |
| No. 4q | 37.1 | 0.672 | 0.810 |
| No. 4an | 39.7 | | |

Aan, Aq: values of A at 425°C for annealed and quenched catalysts respectively.

San, Sq: surface areas for annealed and quenched catalysts respetively.

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* Refer to photographs in our preceding paper3).

* Values of *A* were obtained by substituting in Arrhenius' Equation values of *k* calculated by Temkin-Pyzhev's Equation, and *E* from Arrhenius' plots of *k*'s at 350, 400 and 425°C.

nealing, with simultaneous decrease of the activity. More quantitatively speaking, the degree of activity decrease with the diminishing surface area may be more reasonably expressed by the ratio of the frequency factors, $A$, of Arrhenius' Equation ($k=Ae^{-E/RT}$) than by the ratio of the rate constants, $k$, since the frequency factor term involves the number of active sites which is intimately correlated with the surface area of catalyst. The ratios of $A$'s* are listed in Table III. In the case of catalyst No. 1, No. 2 and No. 4, it appeared from the table that the activity was decreased by annealing, approximately in proportion to the decrease in surface area*. Compared with these catalysts, the catalysts No. 3 also showed a decrease in activity but it was less than the decrease in surface area.

The difference in surface area between individual reduced catalysts is mainly due to the difference in size of fine particles produced by reduction in the interior of grains rather than in the grain boundaries, because the grain boundaries occupy only a part of the catalyst. Within the grains, the extent of particle growth during reduction is expected to be differently restrained by the distribution states of the promoter such as alumina and silica.

Unfortunately, details of the distribution can not be established with certainty from the available experimental results, but the observations on the electronic images from the catalysts can give some knowledge of the potash distribution, and further, when combined with the other results, may lead us to a better understanding of the different extents of particle growth between the quenched (+normally cooled) and annealed catalysts.

**Potash Distribution and Surface Area.**— From the fact that the oxide gives substantially unchanged electronic images after prolonged heating, it may be reasonably assumed that the insoluble potash, i. e. potash combined strongly as potassium aluminate[7,8], silicate[5] and ferrite[6,7] in the oxide, is responsible for the images. Under this assumption, it follows that the interior of grains in the quenched and normally cooled catalysts ... the interior where the images were frequently observed ... must be abundant in insoluble potash, while the same regions in the annealed catalysts, No. 1an and No. 2an must hardly contain any insoluble potash*.

To the extent that the catalysts No. 1 and No. 2 are concerned, the results obtained in the present experiment are summarised with a special regard to the insoluble potash, as follows: the catalysts comparatively rich in insoluble potash, such as the normally cooled and the quenched, reveal the inhomogeneous microscopic structure as well as the electronic images in the interior of grains; and when reduced, larger surface area. This fact may be interpreted to mean that the insoluble potash of the quenched and normally cooled catalysts, existing probably as aluminate and ferrite within the grain, prevents the formation of a perfect solid solution of $Fe_3O_4$ and $FeAl_2O_4$ spinel, resulting in the less homogeneous structure**, but its practical absence within the grains of annealed catalyst favours the formation. The less homogeneous structure may be considered to offer more obstacles against free migration of reduced iron atoms during reduction than the homogeneous and to restrain the particle growth, resulting in the larger surface area. However, since the structure of the mixed crystal of $Fe_3O_4$ and ferrite or aluminate of potassium has not yet been clarified at present, a satisfactory explanation can not be expected.

**Promoting Effect of Lime and Silica.**— An addition of lime has made the microscopic structure as well as electronic images of the interior of grains more heterogeneous and potash more insoluble. For the reason described in the preceding paragraph, a large surface area is what can be expected of catalyst No. 2 containing lime.

Silica exerted upon the structure of catalysts peculiar effect such as, marked decrease of surface concentration of potash, appearance of slag inclusion and a peculiar X-ray diffraction line between (333) and (440) lines on Debye-Scherrer's diagram of $Fe_3O_4$, and so forth. The results obtained with the catalysts containing silica gave sometimes a contradictory evidence (the higher activity of catalysts No. 4 than catalyst No. 2 of equal surface area, the comparatively small surface area of catalyst No. 3 containing a

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* This does not necesarily means the nearly constant intrinsic activity, irrespective of annealing, per unit surface area. However, the surface concentration of potash and the apparent activation energy (Table II & III), remaining unchanged by annealing, are suggestive of this constant activity.

8) S. Brunauer and P.H. Emmett, *J. Am. Chem. Soc.*, **62**, 1732 (1940).

* After reduction, the two kinds of potash, soluble and insoluble, in the oxides seem no longer to behave differently in the interior of grain, both giving the stable and homogeneous images over the grain and accumulating, as described in the foregoing chapter, on the surface of fine particles of reduced iron.

** In this respect unmixed solid solution of potassium aluminate in $Fe_3O_4$ was pointed out by Wyckoff and Crittenden (*J. Am. Chem. Soc.*, **47**, 2866 (1925), refer to 6)).

great amount of the insoluble potash) against the phenomena that were observed with catalysts No. 1 and No. 2. From these results, promoting effects quite different from those of alumina may be expected of silica, and further they show promise for their fruitful application in the catalyst manufacturing, as realized with the highly active catalyst No. 4. However, since the experimental data so far obtained remain insufficient to permit close insight in its promoting action, further investigation is now in progress.

## Summary

Catalysts of four different promoter compositions . . . 5% $Al_2O_3$, 1% $K_2O$ for catalyst No. 1; 4% $Al_2O_3$, 1% CaO, 1% $K_2O$ for No. 2; 3% $Al_2O_3$, 2% $SiO_2$, 1% $K_2O$ for No. 3; and 3% $Al_2O_3$, 2% $SiO_2$, 1% CaO, 1% MgO, 2.5% $K_2O$ for No. 4 . . . were subjected, immediately after their fusion, to different cooling rates such as quenching, annealing and normal cooling.

Among the differently cooled catalysts, the annealed catalyst tended to reveal much lower activity for ammonia synthesis than the normally cooled one, but the quenched catalyst revealed the same.

The characteristic microscopic structures of catalysts of different promoter compositions were more or less markedly modified by annealing to develop large and structually more homogeneous grains, and part of the potash in these catalysts dissolved in water more or less remarkably according to the promoter composition as well as the cooling rate. In other words, the amount of insoluble potash in the catalysts was increased somewhat or considerably by the addition of lime or silica respectively, and the greatest quantity was found in the normally cooled catalysts while the smallest was in the annealed. After the reduction of differently cooled catalysts, the largest surface area was exhibited by the normally cooled catalyst, and the smallest by the annealed, but the surface concentration of potash (+lime) was nearly the same for three differently cooled catalysts. The catalysts of different promoter composition revealed also their characteristic electronic images. After annealing, the images from the interior of grains disappeared in the case of catalysts No. 1 and No. 2. but such disappearance was less remarkably found with catalysts No. 3 and No. 4.

From the results obtained, the interpretation of the decrease due to annealing of catalytic activity has been intended on the basis of the distribution state of the promoters. Some of the effects exerted by the addition of lime can be explained on the same basis, but the peculiar effects of the addition of silica on both activity and structure remains unexplicable despite the promising effect for manufacture of the highly active catalyst.

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