Microscopic Studies on Fused Catalysts for Ammonia Synthesis. III. Weak Ferromagnetic Inclusions and Their Isolation for X-ray Study

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Introduction

Iron catalysts for ammonia synthesis have been studied by different workers from different view-points. For these several years in our laboratory, microstructures of the polished surfaces of these catalysts have been examined using the optical, the surface-electron and the surface-ion microscopes.

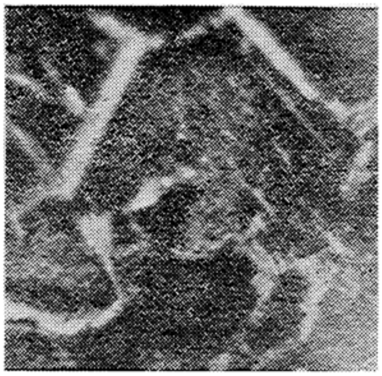
As reported in our first paper[1] the unreduced polished surfaces of usual catalysts with potash addition, when optically observed, consist of two different sorts of grains. A grains are large and each of them is filled with fine regular cleavage surfaces peculiar to magnetite. B grains, much less abundant than A grains, are found mainly along the grain bonudaries of A and are more capable of fine polishing, less markedly changed by hydrogen reduction, but more easily attacked by hydrochloric acid than A grains.

It was found that unreduced surfaces of these catalysts emit enough electrons at about 1000°C to permit observations with the surface-electron microscope. Such observations made with twelve sorts of catalysts showed that potash-promoted catalysts generally gave brightest electronic images, and in particular, those with well developed crystal grains gave almost exact patterns of B grains (Phot. 1a, 1b).

1a ×40

Optical image of polished surface
(Cat. No. 10)

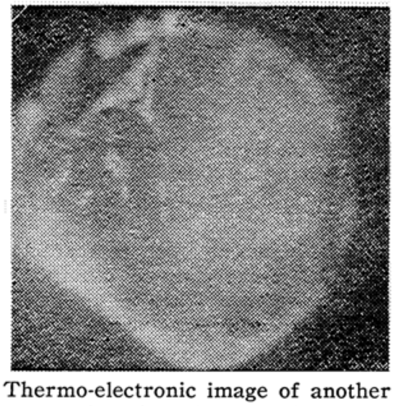
1b ×40



Thermo-electronic image of the same sample using a magnetic lens

The second paper contains observations with the surface-ion microscope of our own construction[2]. The catalysts, when reduced, emit positive ions mainly from B at about the same temperature as they do electrons (Phot. 2a, 2b). These ions could be identified

2a ×20



Thermo-electronic image of another sample using electrostatic lens
(Cat. No. 10)

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[1] N. Sasaki, Y. Ōsumi, *J. Chem. Soc. of Japan*, (Pure Chemistry Section, Japanese), **73**, 808 (1952).

[2] Y. Ōsumi, *J. Chem. Soc. of Japan*, (Pure Chemistry Section, Japanese), **74**, 308 (1953). More details of the results of optical-microscopy and of electron-microscopy are found in 3) and 4) respectively.

2b ×20

Thermo-ionic image of the same sample

with potassium ions, because the application of a magnetic field transversal to the ion path displaced the ionic image to the same extent as the image of a potassium ion source[6].

These potash-rich regions (B grains) seem to have become segregated from the ground magnetite mass of the potassium-promoted catalysts during its solidification.

In the present third paper[5], it will be reported that B grains have been found sufficiently less ferromagnetic than A grains to be magnetically separated from A grains and that they have been studied for their chemical and x-ray crystallographic properties in comparison with A grains.

Isolation of Weak Ferromagnetic B Grains for Surface-electron Microscopic Studies

From the polished surfaces of catalysts no. 4 and 10 (Table I) where B grains were relatively clearly observable, a small amounts of A and B were scraped off with the tip of a needle under an optical microscope. When a pole of a bar magnet whose strength was about 500 gausses was approached from above, it began to attract A powder at the distance of 2–3 cm., while B powder remained unattracted even at the distance of 2–3 mm.

TABLE I

Catalyst	Promoter Added in %				Polished Surface as Observed		X-ray Diffraction Pattern of Powder	
No.*	Al_2O_3	K_2O	CaO	MgO	Optically	Surface-Electronically	A	B**
1	—	—	—	—	no B	faint emission from whole surface	magnetite with slight α-Fe_2O_3	—
2	5	—	—	—	ditto	ditto	magnetite	—
3	—	1	—	—	B	strong emission from B	magnetite with slight FeO	FeO with slight magnetite
4	5	1	—	—	ditto (distinct)	ditto	magnetite	M
8	4	—	1	—	no B	somewhat bright emission from whole surface	ditto	—
9	4	—	—	1	ditto	faint emission from whole surface	ditto	—
10	10	1	1	—	B (distinct)	strong emission from B	ditto	M
11	4	1	1	—	ditto	ditto	ditto	M
12	4	1	—	1	ditto	ditto	ditto	M

* The catalyst numbers are the same as those used in the first report.

** In the column of X-ray diffraction pattern of B powder, blanks mean that weak ferromagnetic substance is not separable, and M indicates a peculiar diffraction pattern mentioned in the text.

A small piece of the catalyst as a whole was ground in an agate-mortar to a fine powder. It was then all attracted to the underside of a sheet of paper horizontally held, by placing the end surface of the magnet pole on the upper side of it. When the magnet was then moved about slowly along the sheet, weakly magnetic particles fell down from the paper, while the strong magnetic ones remained attached to it. From the powder made from pure magnetite no particles fell off during this treatment irrespective of the

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[3] Y. Osumi, "Ammonium Sulphate Engineering" (Japanese) **16**, 13 (1952).

[4] Y. Osumi, ibid., **17**, 8 (1953).

[5] Details about this work will soon be published in "Ammonium Sulphate Engineering" (Japanese).

[6] N. Sasaki, K. Mitani, *Proc. Imp. Acad.*, (Tokyo) **17**, 36 (1941); N. Sasaki, *J. Applied Phys.*, **19**, 1050 (1948).

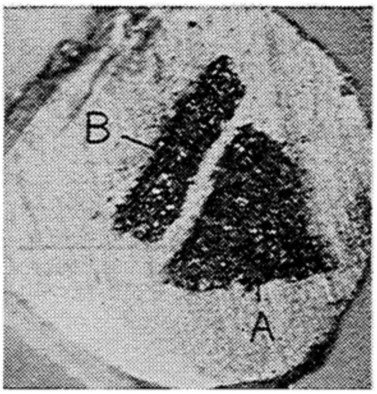
way and degree of pulverization. All the fallen particles must have come from B grains. Actually these were not attracted by the magnet 2–3mm from them.

One may suppose that B grains are inherently non-magnetic and the observed weak magnetism of B particles is due to the presence of a very small amount of A not separated from B particles by the process of pulverization. But the fact that even extrafine powder of B can finally be attracted to the last particle shows the magnetism is inherent in B. Incidentally the Curie point has been estimated to about 520°C for A powder and about 580°C for B powder made from catalyst no. 4.

By the magnetic separation, no. 4 and 10 catalysts respectively gave 3 and 5 per cent of B powder. These figures almost agreed with those calculated from the relative areas of A and B in the optical photographs of the polished surfaces.

A and B powders each in a small amount were kneaded with a drop of liquid paraffin, and placed side by side on a small disc cathode of nickel in our surface-electron microscope. Phot. 3a and 3b show that B powder is as good an emitter as B grains on the polished surface of the original catalyst.

3a ×25



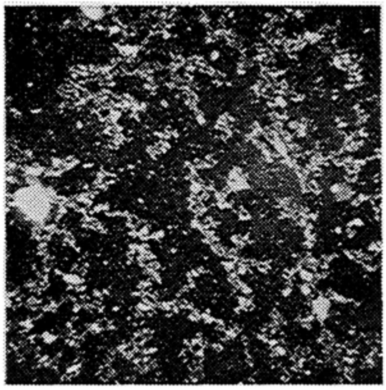
Optical image of powders on Ni-plate
(Cat. No. 4)

3b ×50

Thermo-electronic image of the same sample using a magnetic lens

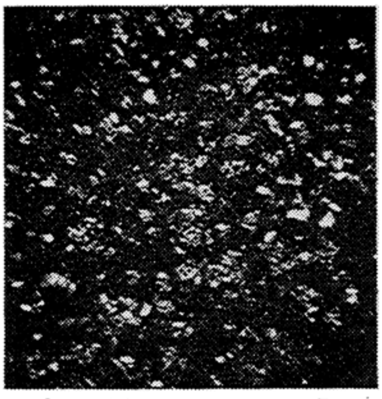
Under the optical microscope fine particles of A powder are seen aggregated in arabesque figures, dispersed with difficulty probably due to mutual attraction between the magnetized particles (Phot. 4a), while B powder is seen as separated particles with rather sharp facets and edges, a fact unexpected from the mere appearance of B grains on the polished surface (Phot. 4b).

4a ×50



Optical image of powder A
(Cat. No. 4)

4b ×50



Optical image of powder B
(Cat. No. 4)

The weak ferromagnetic substances can be obtained from all potash-promoted catalysts which give distinct optical and electronic images of B grains. (Table I)

Chemical Compositions of A and B

In the foregoing reports the possible segregation of potash in B grains has merely been assumed from the study of some properties of polished surfaces. This can now be confirmed by analysing A and B powders separately. The results are given in Table II.

TABLE II

Catalyst No.		Weight Percentages of A & B	Oxide Percentages Found in Powder				
			Fe-oxides	Al_2O_3	K_2O	CaO	MgO
3	A	96.1	99.42*	—	0.58	—	—
	B	3.9	97.87*	—	2.13	—	—
4	A	96.9	92.8 (Fe_3O_4)	4.8	0.40 (0.29)**	—	—
	B	3.1	84.5 (Fe_2O_3)	6.3	4.00 (2.95)**	—	—
10	A	95.0	84.4 (Fe_3O_4)	11.3	0.52	0.46	—
	B	5.0	71.6 (Fe_2O_3)	25.0	3.49	2.41	—
12	A	92.0	68.0 (Fe_2O_3) 25.7*** (FeO)	4.9	0.34	—	0.70
	B	8.0	93.14 (Fe_2O_3)	3.4	1.98	—	0.61

* These figures were obtained not by analysis but by subtraction of the weight percentage of potash from one hundred.

** These figures were obtained by the analysis of the sample after boiling for 4 hours in water.

*** These figures obtained by analysis correspond very roughly to Fe_3O_4, so that in other samples shown qualitatively to contain both Fe^{++} and Fe^{+++}, total Fe is assumed to exist in the form of Fe_3O_4.

The alkali content of B is definitely greater than that of A for all the catalysts studied. Here we may tentatively assume that the crystal structure of A is not capable of containing more than about 0,5 per cent of potash, and in the solidifying process B crystals separate out to take over the excers of it. Calcium oxide behaves similarly (Catalyst no. 10), but magnesium oxide does differently (Catalyst no. 12).

X-ray Studies of A and B

Of all A and B specimens listed in Table I, X-ray diffraction photographs were taken using unfiltered Fe-K radiation (Camera diameter: 90 mm). Specimens A from the non-promoted iron oxide (Catalyst no. 1) and from singly promoted catalyst with potash addition (Catalyst no. 3) gave patterns characteristic of magnetite intermingled with some of the strongest lines of α-Fe_2O_3 and FeO respectively, while specimens A from catalysts with alumina addition (Catalyst no. 2, 4, 8–12) always gave the pattern of magnetite only, irrespectively whether they contained other promoters or not. Alumina addition seems to facilitate the formation of spinel lattice of magnetite⁷⁾.

Specimen B from a singly promoted catalyst with potash addition (Catalyst no. 3) gave patterns of FeO intermingled with some very strong lines of magnetite. Potash addition seems to favour the formation of FeO, for Fe_2O_3 fused with K_2CO_3 (1 : 1 in weight) for one hour at about 1100°C also contains FeO in an amount detectable by X-ray.

Specimens B from catalysts containing K_2O and Al_2O_3 (Catalyst no. 4, 10–12) all exhibit complicated diffraction patterns of similar type (denoted by M in Table I). The lattice spacings calculated from these lines and the relative intensities do not correspond to any compound listed in the A. S. T. M. or the Hanawalt tables.⁸⁾ However, the comparison of the lines of A and B of catalyst 4 (Phot. 5a, 5b) shows that these two crystal structures are not essentially different.

On both diagrams we notice a few lines exactly in the same positions which may be attributed to indices (044), (004) and (022), or some of the planes most densely packed with O atoms in magnetite structure. The strong lines in Phot. 5a with indices (113) and (115) seem in Phot. 5b to have split into many closely situated lines. Potash added in sufficient quantity seems to change the spinel lattice of magnetite into a slightly modified lattice with reduced degrees of symmetry

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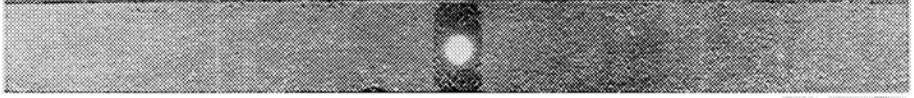
7) A possibility of solid solution formation between Fe_3O_4 and γ-Al_2O_3 has been reported by R. W. G. Wyckoff, E. D. Crittenden, *J. Am. Chem. Soc.*, **47**, 2866 (1925); R. Brill, *Z. Elektrochem.*, **38**, 669 (1932).

8) They also do not correspond to $KFeO_2$ or $KAlO_2$, T. F. W. Barth, *J. Chem. Phys.*, **3**, 323 (1935); L. T. Brownmiller, *Am. J. Sci.*, **29**, 260 (1935).

5a

powder A (Cat. No. 4)

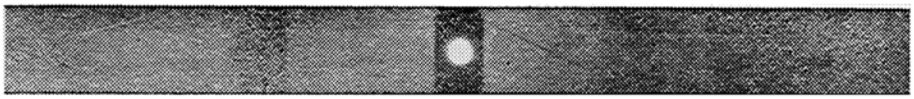


5b

powder B (Cat. No. 4)

(thereby probably leaving the closely packed configuration of oxygen atoms almost intact).

Attempts were made to reproduce this interesting M type structure in specimens directly synthesized by fusing for 3 hours at about 1000°C Fe_3O_4 (Catalyst no. 1) with an equal amount of potash and 1, 5, 10, and 20 per cent of Al_2O_3. Of these only one with 5 per cent Al_2O_3 addition gave the M pattern (Phot. 5c).



5c

potash fusion product of Fe_3O_4 with 5% Al_2O_3

These facts make highly probable our above-mentioned assumption that potash added in the course of melting to usual doubly promoted catalysts with K_2O and Al_2O_3 is retained in the spinellattice of magnetite in high dilution and in the M type lattice of B grains in much higher concentration. By the way, when boiled for 4 hours in water, B powder lost about a quarter of the total potash but still retained the M pattern unaltered.

Formerly Okamoto and Kobayashi⁹⁾ measured the activation energy for high pressure ammonia synthesis on various kinds of usual doubly promoted catalysts in relation to the amounts of K_2O retained after washing with water at room temperature for one day. They found that the activation energy was large for catalysts with K_2O content less than about 0.5 per cent, and it decreased with increase of K_2O content to a constant minimum value of about 15 Kcals for the K_2O content larger than 0.5 per cent. This fact may be explained by the assumption that the activity of catalysts is determined by A grains which constitute almost the whole mass and can contain K_2O to at most about 0.5 per cent and K_2O soluble in water at room temperature is contained not in A and B but in some other unidentified potassium compounds.

Summary

On the basis of our new finding that B grains on the polished surface (Report 1 and 2) of usual iron synthetic ammonia catalysts are less ferromagnetic than A grains, we attempted to separate magnetically B grains from A grains. The more magnetic fraction (called A powder) and the less magnetic fraction (called B powder) have the following properties:

1. B powder as observed by the surface-electron microscope is as strongly electron-emissive as B grains on the polished surface. This suggests a successful separation.
2. Chemical analysis shows that B powder is far richer in K_2O and CaO than A powder.
3. X-ray diffraction patterns of A powders separated from usual doubly or triply promoted catalysts are identified with that of magnetite, and those of B powders are all similar and complicated, whether they contain CaO or MgO or not. The product of potash fusion of Fe_3O_4 with 5 per cent Al_2O_3 gave the same diffraction pattern as B. Some relation of this new crystal structure to the spinel lattice of magnetite was discussed.

In the next paper will be reported the results of ammonia decomposition tests carried out with A and B powders under atmospheric pressure.

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9) T. Okamoto, *J. Soc. of High Pressure Gas Industry* (Japan), **16**, 216 (1952).