Microscopic Studies on Fused Catalysts for Ammonia Synthesis. IV. Decomposition of Ammonia over Two Different Constituents

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Introduction

Many works on the iron catalyst for ammonia synthesis have been reported by many authors for these forty years. Many interesting results have been obtained about the role of potash added to the catalyst. But, so far as I am aware, no one has ever noticed the microscopic heterogeneity of the fused oxide, both before and after reduction.[1]

As reported in our previous papers[2], the optical, the surface-electron and the surface-ion microscopy revealed that the polished surface of some mixed catalysts in the unreduced state consists of two different sorts of grains. Of twelve catalysts investigated only those with potash or potash-alumina addition belong to this class.

Grains of the one sort (B) are found mainly along the boundaries of grains of the other sort (A), and the total quantity of B is very much less than that of A. B grains were found incidentally to be much less ferromagnetic than A grains. This fact furnished us with a convenient magnetic method of separating B grains from A grains. Chemical analysis showed that B powder was richer in K_2O than A powder. X-ray examination[3] showed that A powders separated from different sorts of catalysts always possessed the pattern of spinel lattice of magnetite, and B powders, on the other hand, highly complicated patterns which differed slightly from each other and probably belonged to slightly modified lattices of magnetite with reduced degrees of symmetry. It was suggested that magnetite would not contain more than about 0.5 per cent of potash in its lattice, so that during solidification B crystals would segregate to take over its

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[1] In one of our previous papers[3] B grains have been considered to be formed only in fused oxides rich in alumina and potash. Later experiments, however, showed that potash exess alone was sufficient for their formation.

[2] N. Sasaki and Y. Ōsumi, *J. Chem. Soc. Japan* (*Pure Chemistry Section, Japanese*), **73**, 808 (1952); Y. Ōsumi, ibid., **74**, 308 (1953). More details of the results of optical-, electron- and ion-microscopy are found in: a) Y. Ōsumi, "*Ammonium sulfate Engineering*" (*in Japanese*) **16**, 13 (1952). b) Y. Ōsumi, ibid., **17**, 8 (1953). c) Y. Ōsumi, ibid., **18**, 11 (1953).

[3] Y. Ōsumi, This Bulletin, **26**, 519, (1953). Y. Ōsumi, "*Ammonium Sulphate Engineering*" (*in Japanese*) **18**, 14 (1953).

exess[4].

The present paper deals with the activities for the decomposition of ammonia at about one atmospheric pressure of A and B powders separated from an ordinary doubly promoted catalyst.

Apparatus, Procedure and Preliminary Test.—Since the separation of B powder is tedious work a very small quantity of it (0.5 g.) was taken for the experiment and accordingly a very low flow rate (3.8 cc. per minute) had to be chosen, so that an unusual type of gas analysis was employed (Fig. 1).

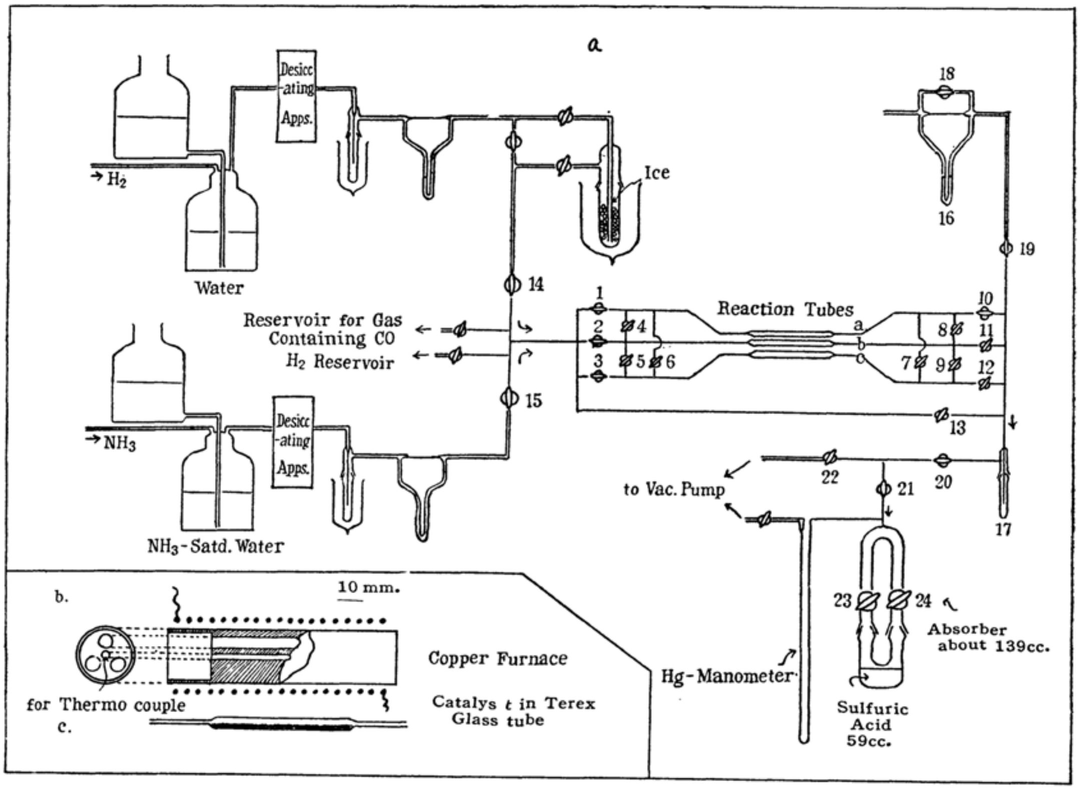

Fig. 1.

Electrolytic hydrogen gas was purified by passing through the solutions of potassium permanganate and potassium hydroxide, and over red hot copper, potassium hydroxide, and phosphorus pentoxide. Synthetic ammonia gas was dried over solid potassium hydroxide. The flow rate of each gas was kept nearly constant by inserting a buffer gas holder with large liquid levels before a capillary tube maintained at 25°C. In Fig. 1 straight lines beginning at stop cocks 14 and 15 show a system of capillary tubes, 1.5mm. in inner diameter. The gas can flow through three reaction tubes a, b and c in six different orders, i. e. a ⟶ b ⟶ c,……c ⟶ b ⟶ a.

Catalyst powders were placed in the lower halves of horizontal reaction tubes, which were of terex glass, 4.3 mm. in inner diameter and 60 mm. long (Fig. 1c). Each was inserted in one of three tunnels bored through a copper block which could be heated electrically (Fig. 1b). The size of capillary tube 17 is such that while the largest part of the gas coming from the reaction tubes is sucked into the absorber where high vacuum prevails at the beginning, a certain small fraction of it still flows through stop cocks 18 and 19 into the atmosphere. This can be ascertained by means of flowmeter 16 by closing stop cock 18 for a short time. Thus the pressure inside the reaction tubes can always be kept slightly higher than one atmosphere.

The analysis of the gas from the reaction tubes is carried out in the following way: after evacuating the absorber (with stop cocks 21–24 open and 20 closed), the gas is sucked into the upper part of the absorber (with stop cocks 22–24 closed and 20–21 open) up to the pressure of about 400 mm Hg, and stop cock 21 is closed. Cock 23 is then opened as slowly as possible and then 24 is opened. The gas now begins to circulate in the absorber and ammonia is absorbed rapidly.

A certain amount of unreduced catalyst powder was divided into three parts. Each was placed in one of the reaction tubes connected in series and reduced at the same time. Our purpose was

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[4] From thermomagnetic measurements the possible existence of more than one magnetic phase in highly promoted catalysts has been concluded by L. R. Maxwell, J. S. Smart and S. Brunauer, *J. Chem. Phys.*, **19**, 303 (1951).

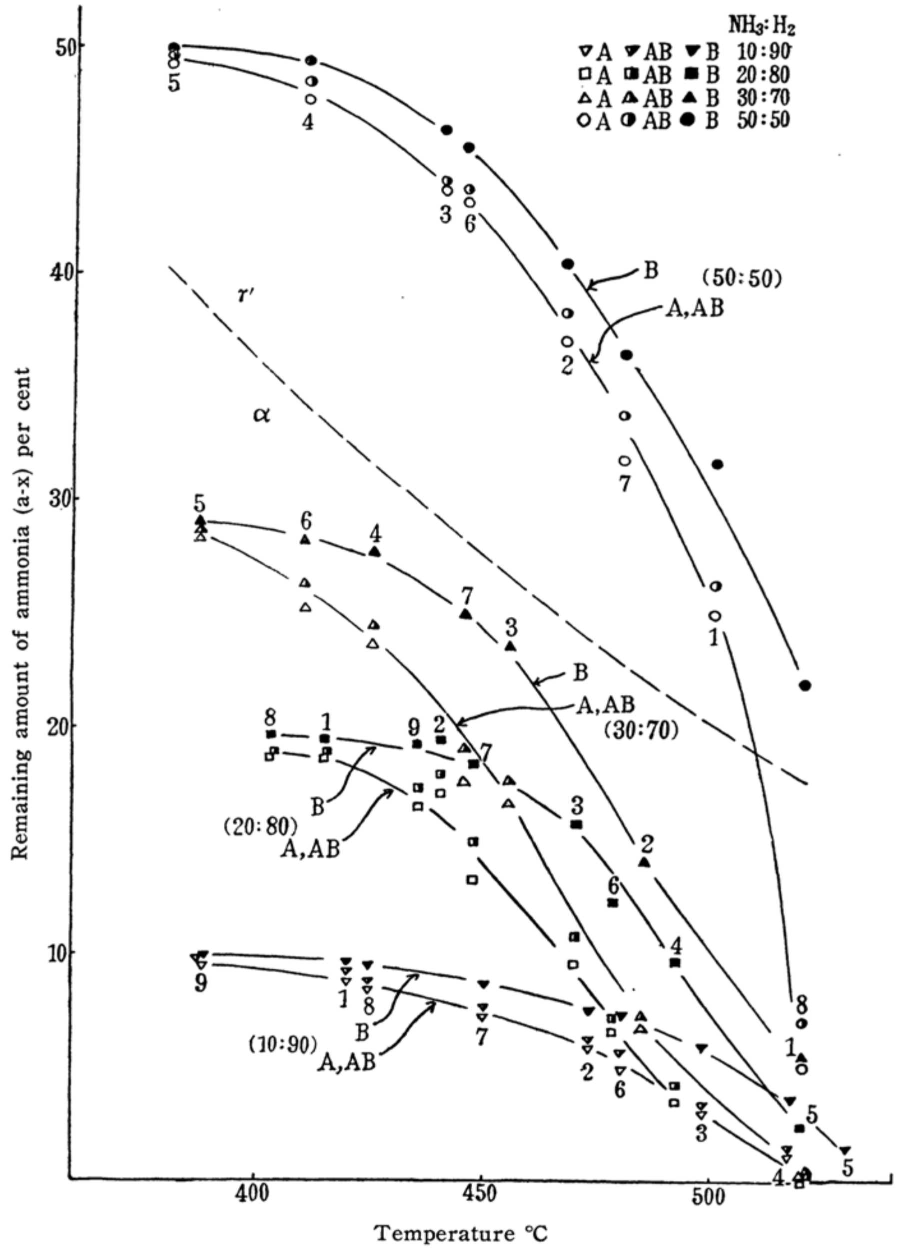

Fig. 2. Activities of A, B and AB powders for decomposing ammonia in NH_3-H_2 mixtures of various compositions.

(1, 2, 3, ...and a, b, c......in the figure indicate the chronological order of data.)

From the ammonia per cent in original gas mixture (a) and that in decomposed gas mixture (b), the decomposed or remaining amount (x or a-x) was calculated as following:

$$H_2 + NH_3 \longrightarrow H_2 \quad + NH_3 + N_2$$

$$100-a \quad a \quad 100a-+3/2x \quad a-x \quad 1/2x$$

therefore $b/100=(a\text{-}x)/(100+x)$, $x=100\ (a\text{-}b)$.

to see whether the catalysts so prepared were equally active toward ammonia decompositions. Hydrogen gas was passed through the tubes in the order a ⟶ b ⟶ c for seven hours each at 350°C, 400°C, 450°C, 500°C successively and then for fourteen hours at 530°C, the flow rate being 2.7 cc. per minute. After the reduction the activity of the catalyst at several temperatures between 400°C and 500°C was measured separately for each tube by passing a mixture of ammonia and hydrogen gas (3: 7 in volume) at the rate of 3.7 cc. per minute through it. It was found that the activity decreased in the order a ⟶ b ⟶ c.

The reduction was then further continued by passing hydrogen gas at 2.7 cc. per minute in the order c ⟶ b ⟶ a for seventeen hours and then in the order b ⟶ c ⟶ a for twenty-eight hours at 530°C. The three reaction tubes showed almost no difference in activity. The same was also the case when hydrogen gas at the rate of as high as 40 cc. per minute, was passed over the fresh oxide powder in one direction a ⟶ b ⟶ c only, the time and temperature schedule being the same as in the first instance. It may be inferred that the existence of a small amount of water vapour in hydrogen gas has a detrimental action.

Between runs the cold catalysts stood in hydrogen at about 800 mm Hg in order to prevent the intrusion of air.

Activity of A and B Powders toward Decomposition of Ammonia in Ammonia-Hydrogen Mixtures of Various Composition.—B powder amounting to about 3 per cent was separated from catalyst No. 4[5]. 0.5 g.[6] of each powder A, B and the original unseparated powder AB of the same mesh size (under about 300) was placed in three different tubes and reduced at the flow rate of 40 cc. per minute for 6 hours each at 300°C, 350°C, 400°C, 450°C, 470°C, 500°C and 520°C. In order to make the condition of reduction in each tube as equal as possible, the order of gas flow was altered every hour from one to another of the six ways. The ammonia-hydrogen gas mixtures for the decomposition test had the mixing ratios in volume, namely, 10: 90, 20: 80, 25: 75, 30: 70 and 50: 50. The results are shown in Fig. 2, the remaining amount of ammonia being expressed in % of the undecomposed original mixture. For all gas mixtures A and AB powders showed similar activity which was higher than that of B powder. The decomposed amount of the gas mixture 50: 50 is smaller than that of the mixture 30: 70 below about 500°C, but the situation is reversed above that temperature. This fact can be related to the work of Lehrer[7], who showed that four sorts of nitrides are formed by the action of mixtures of ammonia and hydrogen when the gas composition and temperature are suitably varied. It is significant that the broken line in Fig. 2 showing the boundary of α and γ' nitrides crosses the curve for the 50: 50 mixture at about 500°C. The apparent energy of activation roughly calculated from the curves for the mixture 30: 70, was found to be 30 kcal. for B powder and 25 kcal. for A powder.

The Poisoning Effect of Water Vapour and Carbon Monoxide.—The influence of water vapour upon the activity was tested with three sorts of powders A, B and AB of catalyst No. 4. Hydrogen was passed through a bottle filled with crushed ice and placed in a bath kept at −7°C and then mixed with ammonia to the composition $NH_3 : H_2 = 1:3$ (Fig. 1a, Water vapour pressure over ice at

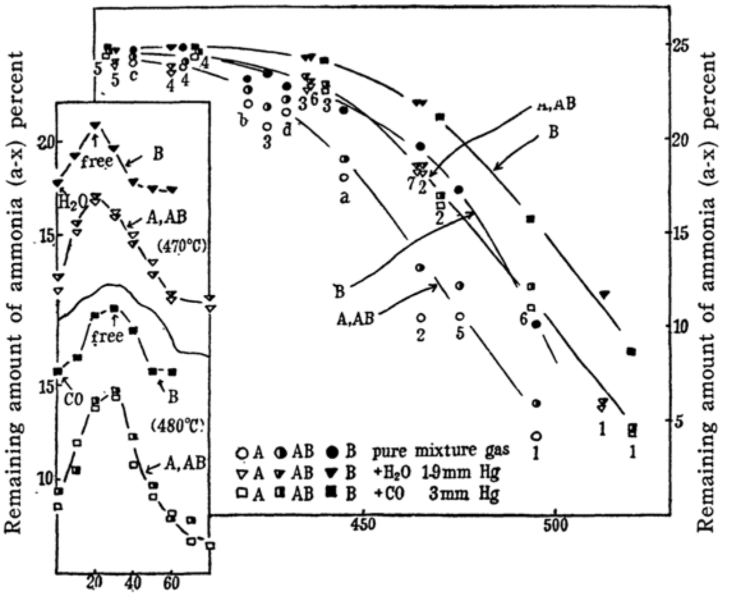

Fig. 3b.

Fig. 3a. Poisoning effects of water vapour and carbon monoxide.

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[5] An iron catalyst including Al_2O_3 (5%), and K_2O (1%).

[6] For the scientific purpose activity per unit area of catalyst would be more significant than activity per unit mass. The measurement of the surface area is planned.

[7] E. Lehrer, *Z. Elektrochem.*, 36, 383 (1930).

-7°C is 2.54 mm Hg). The results are shown in Fig. 3a. A (AB) and B powders all show similar decreases in activity.

Carbon monoxide affected the activity to nearly the same extent, when the gas mixture was led to the reaction tubes from a gas holder in which 3 mm Hg of carbon monoxide had been diluted to the atmospheric pressure with the ammonia-hydrogen mixture 1: 3 (stop cocks 14, 15 and 19 being held closed).

The progress of poisoning and recovering were also studied by measuring the decomposition rate every ten minutes. These processes went on also similary on both powders (Fig. 3b). It is to be noted that the activity of A (and AB) powder is somewhat greater after recovering than before poisoning.

The Effect of Thermal Treatment.—After the activities of new samples of catalyst No. 4 were determined at temperatures between about 400 and 500°C using the gas mixture 30 :70 (Fig. 4), the temperature was raised to about 740°C and kept for one hour in the hydrogen stream. No change in activity was observed on the next day. The catalysts were further heated at about 830°C for one hour. The powder now showed a lower activity at the beginning of the measurement, but later recovered the activity to the value before the heat treatment. B showed, however, less activity throughout the whole measurement.

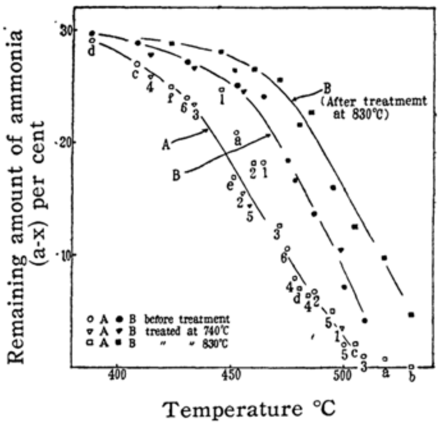

Fig. 4. Effect of heat treatment.

It seems that reduction at temperatures ranging from 300 to 520°C has caused a considerable grain growth of iron, and the heating at 740°C after the reduction does not effect any further change in the surface structure. The decrease in activity of B powder heated at 830°C may be considered, apart from the effect of simple sintering, in conjunction with our previous ion-microscopical observation that potassium in B powder above 800°C migrates through grain boundaries and evaporates from the surface.

The Effect of Mixing B Powder to the Catalyst Singly Promoted with Alumina.—As reported previously A and B powders

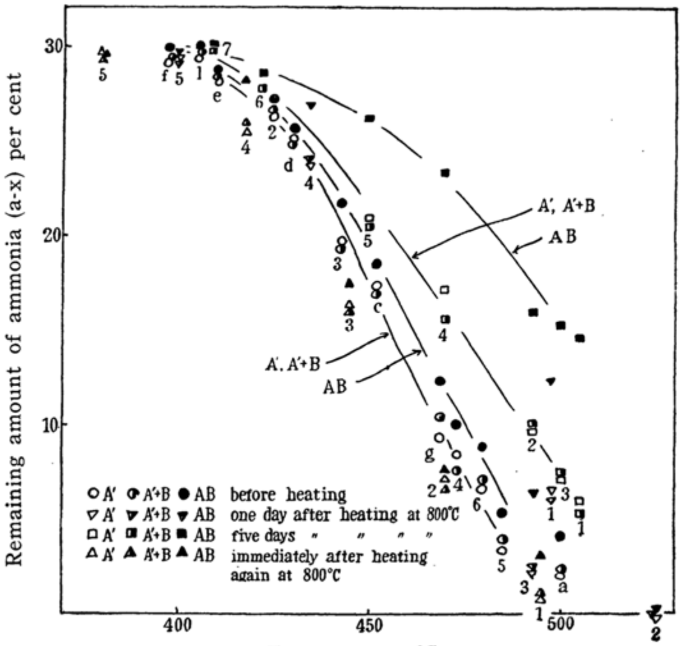

Fig. 5. Effects of adding B powder to alumina-promoted catalyst.

contain about 0.4 and 4 per cent of potash respectively. If potassium at the temperature of ammonia synthesis could now migrate from B powder to A powder, which has in some way lost potassium, B powder could play the role of potash source and contribute to the maintenance of activity of the catalyst. The idea was tested by the possible change in activity toward the ammonia decomposition of an alumina-promoted catalyst (A'), in which a small amount of B powder had been added before reduction.

The samples filled in the three tubes were respectively

(A') catalyst No. 2 (promoter: 5% Al_2O_3)
(A'+B) mixture of 97 parts of catalyst No. 2 and 3 parts of B powder from catalyst No. 4
(AB) catalyst No. 4 (promoters: 5% Al_2O_3 and 1% K_2O)

The result is that A′ and A′+B are almost equally and AB somewhat less active (Fig. 5). They were then heated for one hour at 800°C. On the following day A′ and A′+B were found to be as active as before the heating (though they showed lower activities at the beginning of measurement), while AB showed somewhat less active (Fig. 5). If left for five days after reduction both A′ and A′+B showed similar decreases in activity, and AB a greater decrease. These catalysts were again subjected to the same heat treatment and their activities were immediately measured. They were found to be rather greater than before the first heat treatment. As to the mechanisms of the recovery of activity during the decomposition tests and the diminution of activity during preservation at room temperature, various explanations are possible, but none of them has yet been tested experimentally.

In any case we may conclude that potassium in B grains probably does not play any important role in the commercial synthesis of ammonia.

Summary

An unreduced iron synthetic ammonia catalyst promoted with potash or potash and alumina was separated into two different sorts of powders (A and B). Some of their properties were mentioned in the previous reports. Their catalytic activities for decomposing ammonia mixed with hydrogen were studied at atmospheric pressure by a specially devised flow method. The results are:

1. Between about 400°C and 500°C and for the gas mixtures of several compositions, A powder is more active than B.
2. The actions of the gas mixture laden with water vapour over ice kept in a −7°C bath and of that with 0.4% carbon monoxide are much the same in the rate and extent of poisoning as well as in the rate of recovering when the admixing of the poisoning gases is discontinued. As to the liability to the effects, one sort of powder scarcely differs from another.
3. Heating at 740°C for one hour has no effect. Heating at 830°C for one hour makes B powder less active and A powder also less active at first, but its activity before heating is soon recovered in the course of a run.
4. The activity of a potash-free alumina-promoted catalyst is not affected by adding before reduction a small amount of potash-rich B powder.

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