Microscopic Studies on Fused Catalysts for Ammonia Synthesis. V. Conversion Test with A and B Constituents and Some Studies on "M" Type Crystal

By Yoshio ŌSUMI and Makoto INOUE

(Received February 21, 1957)

Introduction

As reported in our previous papers[1-9]. It was shown, by the aid of the optical[1,5], the surface-electron[1,6] and the surface-ion microscopy[2,7], that some fused catalysts promoted with potash with or without some other additions, consisted of two different sorts of grain. Grains of the one sort (B), much less abundant and magnetic than those of the other sort (A), can be singled out magnetically from the finely pulverized catalyst. "B" powder is richer in potash than "A" powder. "A" powder possesses the magnetite lattice, while "B" powder shows a highly complicated "M"-type diffraction[3,8] pattern of lower degree of symmetry, probably owing to a slight modification of the magnetite lattice. "B" powder is less active than "A" powder towards decomposition of ammonia at the atmospheric pressure[4,9].

The present paper deals with the study on some properties of "B" powder and some comparative studies on "A" and "B" powder with respect to their reducibility in hydrogen, their corrodibility in acid, and their conversion activity and BET surface area in the reduced state.

"M" Type Phase

In ref. 3 it was shown that the content of the water-insoluble potash of A powder attained at most about 0.6 per cent., while that of "M" type "B" powder about five to ten times as much. The chemical analyses were performed after washing out soluble potash with cold distilled water. Recently the amounts of both the soluble and the insoluble potash have been redetermined with new samples. They were washed by boiling in water for one hour. The results are tabulated in Table I (No. II-1, II-4 and II-5) together with the previous ones (No. 3, 4, 10 and 12). The new results confirm the upper limit of potash content in "A" powder at about 0.6 per cent.

The potash content amounting to 0.6 per cent. in "A" powder corresponds to about one atom of potassium for every five unit cells of the magnetite lattice, whereas the potash content in "B" powder about one to two atoms of potassium for each unit cell of the "M" type lattice which is assumed to be equal to that of magnetite.

It is a laborious task to magnetically separate "B" powder from "A" powder. It was attempted to obtain a nearly pure "B" mass by adding as much as 5 per cent. of potash in the usual process of preparing the catalyst. Catalyst II-4 thus prepared gave, however, on magnetic separation, only a small portion of "B" powder comparable in amount with ordinary catalysts. The greater part of potash was found water soluble (Table I).

Of twelve sorts of catalyst previously examined by X-rays, those promoted with potash and alumina always contained "B" powder of the "M" type in which iron is largely in the ferric state. The "B" powder from catalyst II-1 (Table I), however, gives the FeO pattern, instead of the "M" and in fact the iron in it is found mainly in the ferrous state, while the iron in the "A" powder has the usual magnetite composition. The insufficient oxidation of the catalyst in the fusion process seems to affect the oxidation state of iron in the "B" phase rather than in the "A". This fact suggests that the presence of

---

[1] N. Sasaki and Y. Ōsumi, *J. Chem. Soc., Japan (Pure Chem. Sec.)* **73**, 808 (1952).

[2] Y. Ōsumi, ibid., **74**, 308 (1953).

[3] Y. Ōsumi, This Bulletin, **26**, 519 (1953).

[4] Y. Ōsumi, ibid., **28**, 156 (1955).
More details of the results are found in 5) etc

[5] Y. Ōsumi, *Ammonium Sulfate Engineering* (Japanese), **16**, 13 (1952).

[6] Y. Ōsumi, ibid., **17**, 8 (1953).

[7] Y. Ōsumi, ibid., **18**, 11 (1953).

[8] Y. Ōsumi, ibid., **18**, 14 (1953).

[9] Y. Ōsumi, ibid., **23**, 6 (1954).

TABLE I

Catalyst No. and (promoter in per cent)	species of powder isolated	weight per centage	X-ray diffraction pattern	per centage of oxide found in the powder: K_2O water soluble	K_2O water insoluble	K_2O total	CaO	MgO	Al_2O_3	Fe-oxides*	T°C
II-1	A	99.0	magnetite	0.4	0.5	0.9	0.5		4.2	94.1	530
(1 K_2O, 1 CaO, 5 Al_2O_3	B	1.0	FeO	0.8	0.9	1.7	1.1		5.6	89.0	465
II-4	A	89.8	magnetite	3.0	0.6	3.6			5.1	90.8	550
(5 K_2O, 5 Al_2O_3)	B	10.2	M	6.8	3.1	9.9			6.0	82.5	550
II-5	A	90.5	magnetite	0.2	0.6	0.8	0.3		5.3	94.1	515
(1 K_2O, 1 CaO, 5 Al_2O_3)	B	9.5	M	0.7	5.4	6.1	1.0		4.4	90.4	505
3	A	96.1	magnetite		0.58					—	—
(1 K_2O)	B	3.9	FeO		2.13					—	—
4	A	96.9	magnetite		0.40				4.8	92.8	510
(1 K_2O, 5 Al_2O_3)	B	3.1	M		4.00				6.3	84.5	515
10	A	95.0	magnetite		0.52		0.46		11.3	84.4	520
(1 K_2O, 1 CaO, 10 Al_2O_3)	B	5.0	M		3.49		2.41		25.0	71.6	515
12	A	92.0	magnetite		0.34			0.70	4.9	93.7	515
(1 K_2O, 1 MgO, 5 Al_2O_3)	B	8.0	M		1.98			0.61	3.4	93.1	515

* These figures are obtained by conveniently assuming all Fe exists as Fe_3O_4 in "magnetite", as Fe_2O_3 in "M" and as FeO in "FeO". Actually, for example, $Fe^{2+}/Fe^{3+} = 36/67$ for Cat II-1, A ("magnetite" type), $Fe^{2+}/Fe^{3+} = 9/91$ for Cat II-4, B ("M" type) and $Fe^{2+}/Fe^{3+} = 71/29$ for Cat II-1, B ("FeO" type).

alumina is not sufficient for the formation of the "M" type "B" phase and the state of oxidation of iron is rather essential. It may be that alumina is even unnecessary in this connection and the formation of the "FeO" type instead of the "M" type in ctalyst 3 (Table I) is a result of the insufficient oxidation and not of the absence of alumina.

TABLE II
THERMOSTABILITY OF B POWDER ("M" type)

temperature C°	period of heating hr.	X-ray diffraction pattern	T°C
550	1	"M", (Hematite)	
750	1	"M", (Hematite)	505
880	1	"M", Hamatite	
960	1	Hematite, "M"	500
1000	2	"M", Hematite	
1040	1	"M", Hematite, Magnetite	
1130	1	Magnetite, Hematite, "M"	520
1220	1	Magnetite, Hematite	
1340	2	Magnetite, (Hematite)	540

X-ray figures are listed in the order of decreasing intensity and braketed ones are very weak.

TABLE III
POTASH FUSION OF IRON OXIDE

temperature °C	type of oxide	X-ray diffraction pattern
700	Fe_3O_4 Fe_2O_3	Magnetite, "M" "M"?
880	Fe_3O_4 Fe_2O_3	"M", Magnetite "M"?, (FeO)
930	Fe_3O_4 Fe_2O_3	"M", Magnetite Magnetite, FeO
1010	Fe_3O_4 Fe_2O_3	FeO, Magnetite, FeO FeO
1200	Fe_3O_4 Fe_2O_3	Magnetite, FeO FeO Magnetite

Each oxide was fused with potassium nitrate of half the weight of the oxide for three hours in a nitrogen stream.

Attempts have been made to synthesize the oxide having the "M" type structure by heating,in an iron boat in nitrogen atomosphere, at temperatures given in Table III, a certain quantity of pure magnetite or hematite with half the weight of potassium nitrate and without any addition of alumina. The X-ray examination of specimens after washing with water shows that the "M" type structure can be obtained when the heating temperature was not higher than 1000°C. The conclusion is that for the synthesis of "M" phase the excess of potash alone is necessary, alumina and other additions being unessential. The "M" particles thus synthesized, however, are not at all attracted by the magnet while the "M" type

" B " particles are feebly attracted.

Further attempts were made to synthesize the " M " type crystals containing alumina by potash fusion of mixtures of magnetite and alumina in more or less intimate mixture (Table IV). The structure aimed at was obtained in products fused at about 900°C with a sufficient quantity of potash (the products were also non-magnetic).

The following experiments were performed with " A " and " B " powders prepared from catalyst II-5 (Table-I) with alumina, lime and potash as promoters.

Thermostability of the " M " type Phase

The thermostability of the " M " type lattice mentioned above was tested as follows. About 0.5 g of B powder placed on a piece of platinum plate was heated in a porcelain tube in the nitrogen stream at temperatures given in Table II and after cooling subjected to the X-ray examination. Table II shows that the " M " type phase becomes unstable at about 1000°C, to change into the magnetite lattice (the powder becomes strongly magnetic). This change is probably caused by the loss of potash and oxygen at high temperatures so that the " M " type phase can survive much higher temperatures when it cools down from the solidifying point as the constituent in the matrics of the " A " phase. It will be noted in this connection that the electron-emission characteristics of " B " grains as revealed by the surface electron microscope¹⁾ may be related to the potash liberated accompanying this lattice transformation.

As to the possible mechanism of the formation of the " M " type phase in fused catalysts, it may be suggested that at higher temperatures fused oxide probably forms a homogeneous phase with potash, which on solidifying yields magnetite crystals with about 0.6 per cent. of potash, the remaining potash being enriched at the crystal boundaries to form " M " type crystals.

Corrosion in Acid Solutions and Reduction in Hydrogen Gas

The change in appearance of the polished surface of " B " grains, as the optical microscope observations showed¹⁾, was less marked on reduction in hydrogen and more marked on attack in hydrochloric acid than that of " A " grains. But the loss in weight in both cases of " A " powder does not differ much from that of " B " powder.

The action of the acid was observed with 1.5 g of the specimen by dipping in hydrochloric acid at room temperature. In 1 N-acid dissolved 6 per cent. of both " A " and " B " in one day, and in 6 N-acid 17 per cent. of A and 15 per cent. of " B " in three hours.

The weight change during reduction in hydrogen was followed with a quartz fiber torsion balance carrying 0.1 g. of the specimen in powder form (~200 mesh) in a heated tube through which hydrogen gas at atmospheric pressure was passed at the rate of 40 cc. per minute. The temperature was raised at the rate of 100°C per 40 minutes.

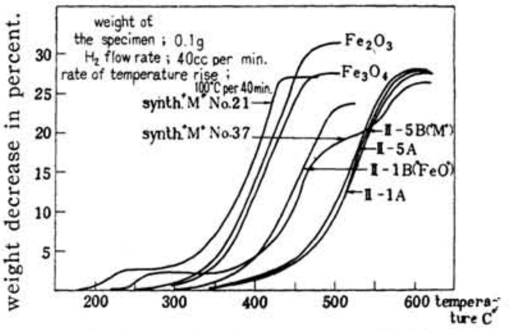

Fig. 1. Rate of weight decrease by hydrogen reduction for A, B powder and some other iron oxides.

The reduction curve of " B " (Fig. 1) is nearly the same in form as that of "A". The temperature T (Table I) at which half the oxide has been reduced to iron is almost the same for "A" and "B" powders from one and the same catalyst. Different values of T were obtained for catalyst II-1, whose "B" powder shows the FeO pattern.

It is a matter of well-established fact[1,5,10] that alumina in magnetite raises the temperature of beginning reduction. It may, therefore, be concluded that the aluminium atoms in the " M " type lattice are situated essentially in the same manner as in the magnetite lattice. But the T values of those " M " type products (No. 37 and 43 in Table IV) prepared by potash fusion of alumina-promoted magnetite are lower than that of the "M" type "B" powder separated from catalysts. This fact may be explained by the assumption that the excessive potash

---

10) A. Mittash u. E. Kennecke, Z. Elektrochem., **38**, 666 (1932).

TABLE IV

POTASH FUSION OF IRON OXIDE WITH ALUMINA

No. of specimen	temperature °C	materials and mixing ratio in brackt		X-ray diffraction pattern	T°C
21	850	$Fe_3O_4(10)\,Al_2O_3(0.5)$	KNO_3 (5)	"M"	395
22			KOH (5)	"M"	425
23			K_2CO_3 (5)	FeO	410
34	520	catalyst promoted with 5% Al_2O_3 (10)	KNO_3 (5)	Hematite	490
35	610			Hematite	485
36	730			Hematite	465
37	900			"M"	465
79	970			FeO	425
39	900	catalyst promoted with 5% Al_2O_3 (10)	KNO_3 (0.5)	Hematite	490
42			KNO_3 (1)		490
43			KNO_3 (2)	"M"?	490
41			KNO_3 (5)		480
58	700	catalyst promoted with 5% Al_2O_3 (10)	K_2CO_3 (3)	Hem, Mag	480
59	810				480
60	900				485
77	1000			FeO	470
73	1150			FeO	465
52	900	catalyst promoted with 5% Al_2O_3 (10)	K_2CO_3 (0.2)	Mag, Hem	480
53			K_2CO_3 (0.7)		475
56			K_2CO_3 (2)		460
57			K_2CO_3 (5)	Magnetite	450

Specimens were fused for about three hours in air.

during the fusion process has extracted alumina from magnetite to form potassium aluminate.

Measurements of Conversion Activity and BET Isotherms

Seven g. of "A" (or "B") powder were pressed into small tablets, 3 mm. in diameter and 3 mm. high, and sintered at about 700°C in nitrogen stream. At this temperature the disintegration of the "M" type crystal does not occur. The tablets were placed in a layer, 18 mm. thick and 18 mm. in diameter, in the convertor shown in Fig. 2, and following a fixed schedule (Table V) reduced in hydrogen stream at

TABLE V

REDUCTION SCHEDULE FOR CONVERSION TEST

temperature °C	reduction period, day	amount of water caught in the trap placed at the outlet of the converter, g A	B
250	1/4	0.275	0.241
275	1/4		
300	1/2		
325	1	0.779	0.676
325	1	0.500	0.253
325	1	0.260	0.277
350	1	0.207	0.404
375	1	0.100	0.275
400	1/2	0.088	0.172
425	1/4		
450	1/4		
total	7	2.209	2.298

The trap was kept at dry-ice temperature.

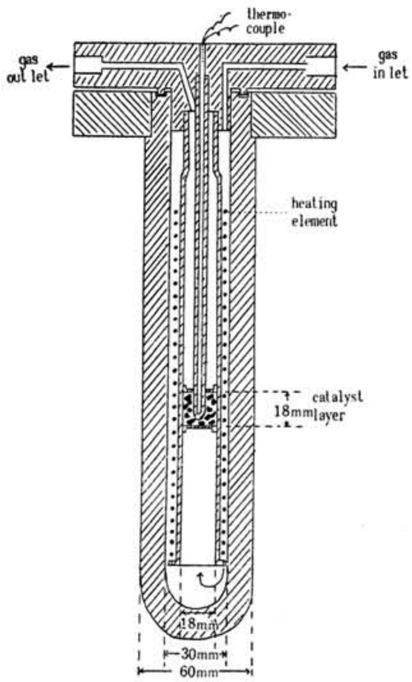

Fig. 2. Experimental convertor.

atmospheric pressure at the space-velocity of about 15000. Hydrogen was purified by being passed through a nickel catalyst, potassium hydroxide and phosphorus pentoxide. The progress of reduction was followed roughly by weighing at intervals the water captured from the issuing hydrogen gas in a trap cooled at −78°C(Table V).

For the conversion tests hydrogen and nitrogen from 150 atm. cylinders were mixed in the ratio of 3 : 1 in a gas holder, and passed over a copper catalyst and compressed into a storage vessel at 100 atm. pressure. For the conversion test at ordinary pressure the raw gas mixture from the storage vessel was reduced to

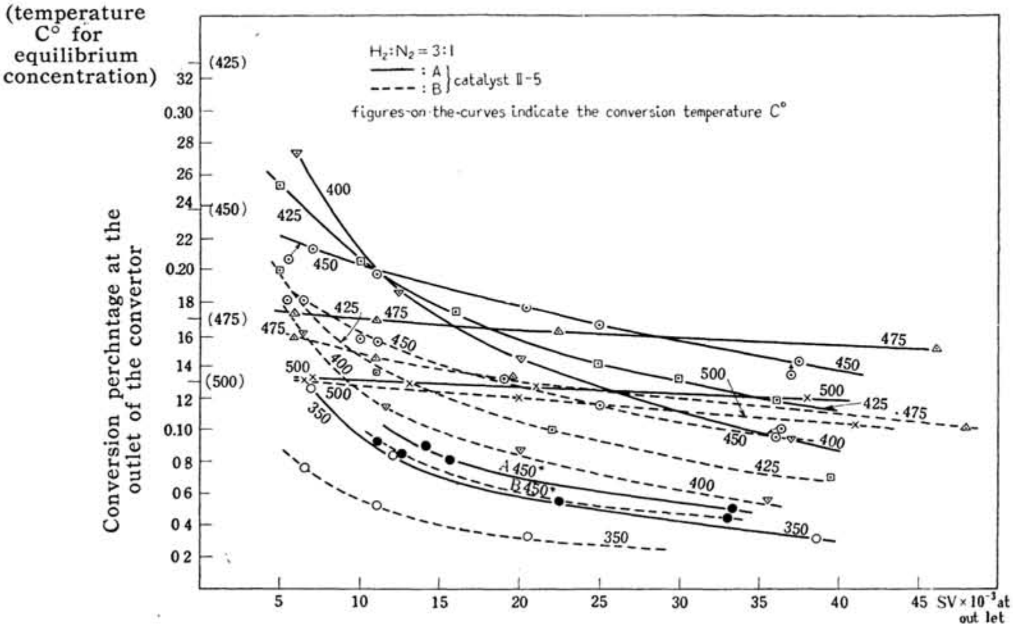

Fig. 3. Conversion activities of A and B powder at atmospheric pressure.
* These curves of low activities were obtained after the experiment of high pressure conversion

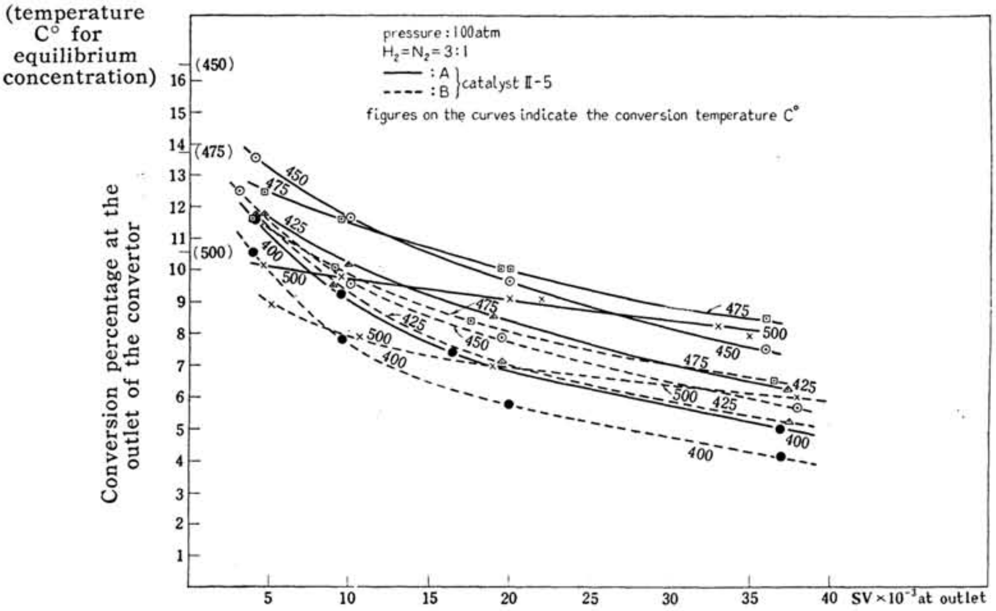

Fig. 4. Conversion activities of A and B powder at a high pressure.

atmospheric pressure and purified in the same way as for the reduction test. For the higher-pressure conversion test, the raw gas at 100 atm. was passed over a nickel catalyst and led through silica-gel and alumina-gel for dehydration.

The results represented in Figs. 3 and 4 clearly show that the conversion activity of "B" powder is lower than that of "A" powder for the whole range of space velocity and particularly at low temperatures.

The influence of water vapor upon the activity was tested by passing the raw gas through a water saturator kept at 0°C. The results (Table VI) show that the water vapor has a similar poisoning effect on the conversion activity as on the decomposition activity at ordinary pressure.

In order to investigate the surface condition of "A" and "B" powders after reduction, BET measurements were carried out by using carbon dioxide and carbon monoxide. Brunauer and Emmett[11,12] state that at the first stage of adsorption at −78°C a rapid chemisorption of carbon dioxide occurs on the surface alkali molecules, followed by the usual physical adsorption on the whole surface (the "total" isotherm).

Seven g. of "A" or "B" powder were reduced in the adsorption bulb made of pyro-glass (about 10 cc.) following the same reduction schedule in the conversion test. Fig. 5 represents adsorption isotherm of carbon dioxide at −78°C on "A" and "B" powders. The isotherm designated as "van der Waals" was obtained at −78°C with the sample outgased for one hour at 0°C after the "total" isotherm measurement. At this temperature all carbon dioxide molecules adsorbed physically are to be removed without the chemisorption being affected, so that from the difference between the two isotherms the amount of chemisorbed carbon dioxide "V_c" may be obtained, while from the van der Waals isotherm the amount of the gas forming the monomolecular layer "V_m". Since "V_m" values for "A" and "B" powders are essentially equal, the total surface of the iron crystallites formed by the reduction seem to be almost the same for the two types of oxides. From "V_c" and "V_m" values we obtain the coverage by the alkali molecules amounting to about 86 per cent. of the total surface for "B" and 58 per cent. for "A" powder. The difference is apparently not great enough to account for the large difference in the potash content.

After evacuation for about one day at

TABLE VI

EFFECT OF WATER VAPOR ON CONVERSION ACTIVITY AT 450°C, 100 ATOM AND S.V.: 23000

	percentage of NH_3 in the outlet gas	
	A	B
Pure gas	9.2	7.5
Gas containing H_2O	2.0	0.5

Gas was bubbled through water saturator kept at 0°C.

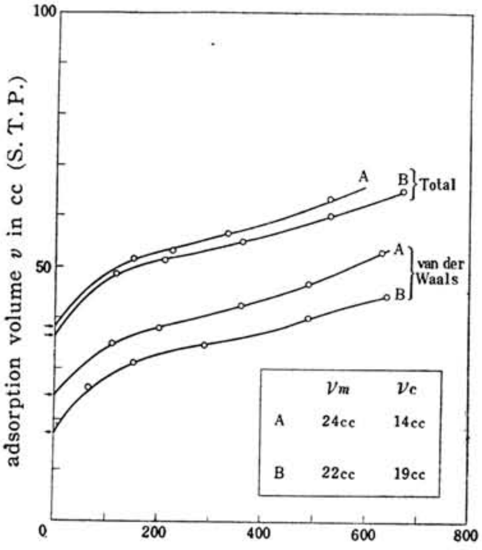

Fig. 5. Adsorption isotherms for carbon dioxide at −78°C on A and B powder.

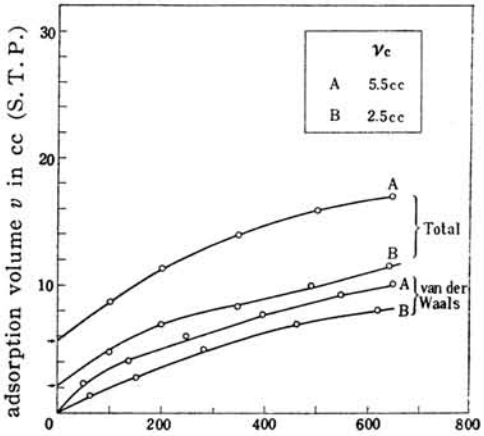

Fig. 6. Adsorption isotherms for carbon monoxide at −78°C on A and B powder.

---

[11] P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, **59**, 310 (1937).

[12] Idem., ibid. **59**, 1553 (1937).

400°C, adsorption isotherms were determined with carbon monoxide which is adsorbed on the metallic iron surface only[7,8]. The isotherm may more or less be affected by the carbon dioxide still remaining on the iron surface. Fig. 6 shows that the area of the iron covered surface is smaller for "B" than for "A". The sum of the potash-covered and iron-covered areas is nearly equal to the total area ("V_m") for "B" powder, but smaller for "A" powder. This probably is, as Brunauer and Emmett suggested, due to the occupation of the iron surface by alumina.

Summary

Iron synthetic ammonia catalyst (No. II-4) promoted with aluminium oxide, potassium oxide and calcium oxide was separated magnetically into two different sorts of powder, "A" with magnetite structure and "B" with "M" type structure. As to their catalytic activities for normal and high pressure conversion at temperatures between 400 and 520°C, it was found that "B" was less active than "A" particularly for the low temperature conversion. Some other properties of these powders are as follows:

(1) "B" powder becomes unstable when heated above 1000°C and changes into magnetite. Powder with the lattice structure of "M" type can be synthesized by sintering iron oxide at about 900°C with a sufficient amount of potassium nitrate or hydroxide, but it is completely non-magnetic.

(2) "A" and "B" powder showed almost equal rate of weight decrease when reduced in hydrogen gas or treated with acid solutions.

(3) The BET measurement carried out with "A" and "B" powder reduced in hydrogen revealed that the total specific surface area is almost equal for both "A" and "B" whereas the portion occupied by alkali molecules is larger for "B" powder.

We owe our deep gratitude to Dr. A. Uchida, Tokyo Industrial Research Institute for providing us with Cat. II-5 in this study and also to Mr. Z. Ujino in our Laboratory for his help in chemical analysis.

Mitsubishi Kasei Laboratory
Kawasaki, Kanagawa