Ammonia-Synthesis Iron Catalysts Containing Magnesia as Their Principal Promoter. II. The Texture and Structure of the Catalysts[1]

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The preceding paper[3] discussed the performances of the catalysts which were promoted singly by magnesia and doubly or triply by other oxides besides magnesia. The roles played by the individual promoters were discussed in terms of their effects on the specific activity per unit of specific surface area and on the extent of the specific surface area. The present investigation has been made to obtain a comprehensive picture of the texture and structure of these catalysts and to attain a further understanding of the effects of individual promoters on the catalyst performances from the structural point of view.

Experimental

The catalysts investigated were an unpromoted catalyst (cat. M-O), a couple of singly-promoted catalysts with different magnesia contents (cats. M-1 and -2), three doubly-promoted catalysts containing potash, lime, and silica as the respective second promoters (cats. M-3, -4 and -5, respectively), and two triply-promoted catalysts containing different amounts of magnesia but with fixed amounts of potash and silica (cats. M-7 and -8). For the sake of comparison, one of the catalysts of the alumina-promoted type (cat. A-102) was also investigated. Their promoter-compositions are illustrated in Table I.

The preceding paper[3] presented data on the bed density and the specific surface area of the samples after their use in the synthesis run. In the present study, the total pore volume, the average diameters of pores and particles, the fraction of the surface occupied by free iron, and so forth, all concerning the samples drawn from the same sources, have been determined. The total pore volume, V_{po} (cc./g.), was calculated from the difference between the volumes by the mercury and helium displacement methods, i. e., $V_{po}=V_{Hg}-V_{He}$. The bulk density of the catalyst granule, ρ_b(g./cc.), was given by a reciprocal of V_{Hg}, while the true density of the catalyst material, ρ_t(g./cc.), was given by a reciprocal of V_{He}. The catalyst porosity, or the void

1) This paper is the 16th in a series of articles of dealing with the ammonia synthesis iron catalysts.
2) Present address: Japan Gas-Chemical Co., Enokicho, Niigata.
3) H. Uchida, I. Terao and K. Ogawa, This Bulletin, 37, 653 (1964).

Table I. Physical properties of samples

Catalyst	Promoter-composition wt. %	Hg volume cc./g.	Densities Hg g./cc.	Densities He g./cc.	Surface area $m^2/g.$	Pore volume cc./g.	Porosity	Average pore diameter Å	V_{CO}/V_m
M-O	Unpromoted	0.202	4.95	7.69	1.15	0.072	0.36	2500	—
M-1	2MgO	9.238	4.20	7.52	3.02	0.105	0.44	1390	—
M-2	5MgO	0.253	3.95	7.04	5.57	0.111	0.44	780	0.23
M-3	5MgO, $1K_2O$	0.276	3.69	7.19	1.05	0.137	0.50	5220	0.14
M-4	4MgO, 1CaO	0.251	3.98	7.35	4.63	0.115	0.46	990	—
M-5	4MgO, $1SiO_2$	0.254	3.94	6.90	12.00	0.109	0.43	360	0.23
M-7	2MgO, $1SiO_2$, $1K_2O$	0.256	3.91	7.19	4.67	0.117	0.46	1000	0.14
M-8	4MgO, $1SiO_2$, $1K_2O$	0.267	3.75	6.99	9.37	0.124	0.46	530	0.36
A-102	$2Al_2O_3$, 1CaO, $1K_2O$	0.276	3.62	7.30	6.67	0.139	0.50	820	0.10

fraction of a catalyst granule, was available from V_{po}/V_{Hg}. On the assumption of open-end cylindrical pores, the average pore diameter, $\bar{d}_{po}$ (cm.), was computed from the equation $\bar{d}_{po}=4V_{po}/S$, while, on the assumption that the catalyst granule consists of a loose packing of spherical or cubic particles, the average particle diameter, d_{pa}, was computed from the equation $\bar{d}_{pa}=6/(S\rho_t)$. In the above equations, S ($cm^2/g.$) stands for the specific surface area. Following the method of Emmett and Brunauer,[4] the fraction of surface occupied by free iron was expressed by the ratio of the carbon monoxide volume which was chemisorbed at −78°C, V_{CO}, to the nitrogen volume which formed a monolayer over the entire surface, V_m. The adsorption measurements were conducted by a conventional volumetric method. V_{CO} was determined from the difference between the total carbon monoxide adsorption at −196°C and the subsequent adsorption at this temperature after evaculation at −78°C, while V_m was determined by means of the BET equation applied to the nitrogen adsorption isotherm at −196°C.

In order to obtain additional information on the catalyst texture, the catalysts were examined by optical and electron microscopy. The oxide catalyst samples were polished on one surface by ordinary methods, finishing with a final buffing of soft cloth with wet alumina; they were then observed under an optical microscope before and after etching with hydrochloric acid. In some particular cases, the etched samples were reduced with hydrogn at temperatures between 380 and 500°C in a cell attached to a high-temperature microscope, and the structural changes in the surface with time of reduction were observed under a microscope. The hydrogen flow rate was approximately 5 l./hr. Electron microscopic observations were made by a JEM-6A electron microscope on replicas of the etched surfaces shadowed with chromium-carbon and also on finely ground powders of the catalyst samples before and after their use in the synthesis run. The samples were ground in castor oil.

X-Ray diffraction patterns were taken on powdered samples less than 200 mesh in size as well as on the samples after their use in the synthesis run, by means of a Geigerflex D-3F X-ray diffractometer. Fe $K\alpha$ radiation from a sealed-off X-ray tube equipped with berylium windows and with a manganese dioxide filter was used at 30 kV. and 7.5 mamp.

Results and Discussion

The Texture of Catalysts after Use in the Synthesis Run. — Table I summarizes the data on the mercury volume, mercury and helium densities, pore volume, porosity, average pore diameter, the fraction of the surface occupied by free iron, and the specific surface area. The comparison between the mercury volumes of cat. M-O and cat. M-1 shows that magnesia alone is already effective in preventing the catalyst granules from shrinking during the reduction process and subsequent synthesis run. The porosity values of the promoted catalysts fall in a narrow range from 0.43 to 0.50, all values being higher than the 0.36 of cat. M-O. In view of the fact cat. M-3 gives a higher porosity than cat. M-O, it is likely that the individual granule of the former catalyst consists of particles more loosely packed than those of the latter in spite of nearly the same extent of the specific surface area. In fact the average pore diameter is twice as large as that of cat. M-O. With regards to other catalysts, the average pore size depends mainly on the extent of the specific surface area, since their pore volumes are within the narrow range. The effects on the particle size of the addition of promoters will be described later in connection with the effects on the crystallite dimension.

The fraction of the surface occupied by the free iron of catalysts of the magnesia-promoted type, including the catalyst singly promoted by magnesia, is always small; this result is similar to that with catalysts of the alumina-promoted type. The result is, however, opposite to that of Kobosev et al.,[5] who stated that magnesia was entirely surface-inactive in the

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

5) N. I. Kobosev, B. V. Erofeev, I. B. Kaverin and A. N. Bogoyavlenskaya, *Acta Physicochim, U. S. S. R.*, 1, 483 (1943).

Table II. Lattice constant of oxide catalyst (a), crystallite width of reduced catalyst (D), and average particle diameter ($\overline{d}$)

Catalyst	M-O	M-1	M-2	M-3	M-4	M-5	M-7	M-8	A-102
a, Å	8.396	8.395	8.395	8.393	8.402	8.393	8.396	8.393	8.391
D, Å	560	300	310	640	280	250	300	290	390
$\overline{d}$, Å	6760	2640	1530	7950	1760	730	1790	920	1220

course of the reduction of an iron oxide. One explanation of these apparently different results may be that magnesia is surface-inactive in the earlier reduction stage, where the iron particles poduced by reduction remain extremely small in size, but that magnesia is apt to accumulate on the surface with the particle growth. This explanation is not contradictory to the facts that the reduction of cat. M-1 in the earlier stage takes place at a rate nearly as fast as the reduction of a pure magnetite, but that the last traces of oxygen can be removed only with difficulty.[3] The other promoters besides magnesia play scarcely any significant role in the change in the fraction; e. g., the fraction of cat. M-4 is of almost the same extent as that of cat. M-2.[6]

The Crystal Structure of the Catalysts before and after Use in the Synthesis Run.—The lattice constants of oxide catalysts were calculated on the basis of the α_1-line from the (553) or (731) plane of Fe_3O_4, the Bragg angle of which could be measured with a reasonable accuracy. The results are summarized in Table II. The addition of magnesia does not cause any changes in the lattice constant of a pure magnetite. This is quite different from the finding with the alumina addition by Westrik,[8] who pointed out that the lattice constant appears to decrease linearly with the ratio $Al^{3+}/(Fe^{3+}+Al^{3+})$ and who concluded that alumina is dissolved in the magnetite lattice. The linear relationship just referred to, on the other hand, can be interpreted in terms of the Vegard equation of $a=a_1M_1+a_2M_2$, where a is the lattice constant of the promoted catalyst, a_1 and a_2 are the lattice constants of Fe_3O_4 and Al_2FeO_4 spinel respectively, and M_1 and M_2 are the respective contents in mole fraction. Accordingly, Al_2O_3 and FeO in Fe_3O_4 combine to form the Al_2FeO_4 spinel, and the resulting spinel is in a solid solution with Fe_3O_4. If an identical mechanism is applied to the addition of magnesia, the lattice constant of cat. M-1 or cat. M-2 is expected to decrease with the magnesia content because the lattice constant of the $MgFe_2O_4$ spinel ($a=8.36$ Å) is smaller than that of pure magnetite. It is more likely, according to Goldschmidt,[9] that the Mg^{2+} ions cannot enter the lattice as substituents of the Fe^{2+} ions but that they can occupy the empty interstices in the magnetite lattice. Cat. M-4 gives the larger lattice constant, as can be expected from the larger size of Ca^{2+} ions.

From the broadening of the X-ray diffraction lines, which can be almost entirely accounted for by the occurrence of small crystallites,[10] the crystallite width of the samples after the synthesis run was calculated by means of the Scherrer formula: $D=C\lambda/B\cos\theta$. In this formula, D is the crystallite width, λ is the wave length of an X-ray radiation (1.937 Å for the Fe-K line), B is the true half-breadth (angular) of the diffraction line, θ is the Bragg angle, and C is 0.9. The graphs given by Jones[11] were used to make correction for the $\alpha_1\alpha_2$-doublet and to evaluate the true diffraction breadth on the basis of the experimental data. The calculations were made on the basis of the line from the (110) plane. The results are compared in Table II with those on the average particle diameter.

Apart from the results concerning cat. M-3, the crystallite widths of the catalysts of the magnesia-promoted type fall in a narrow range between 250 and 310 Å, whereas the average particle sizes of these catalysts fall in a far wider range from 700 to 2600 Å (cf. Table II). These facts indicate that the individual particles of these catalysts consist of from about 10 to several hundred crystallites and that the particle size is more strongly dependent on the promoter-composition than is the crystallite width. It is worthwhile to notice that not only the individual particles of cat. M-O but also those of cat. M-3 consist of more than 1000 crystallites. The comparison of the crystallite width and the particle size of cat. M-O with the respective values of cat. M-1 clearly

6) In connection with this finding, we want to call attention to the results of Hall et al.[7] who measured on this kind of catalyst the changes in the specific surface area and in the carbon monoxide chemisorption with the reduction progress in a hydrogen flow at atmospheric pressure and found a much higher value of the fraction after the complete reduction. The disagreement may perhaps be due to the different treatments to which the catalyst samples have been submitted.

7) W. K. Hall, H. Tarn and R. B. Anderson, *J. Am. Chem. Soc.*, **72**, 5436 (1950).

8) R. Westrik, *J. Chem. Phys.*, **21**, 2094 (1953).

9) H. J. Goldschmidt, *Nature*, **137**, 478 (1946).

10) A. Nielsen, "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," Jul. Gjellerups Forlag, Copenhagen (1956), p. 165.

11) F. W. Jones, *Proc. Roy. Soc.*, **A160**, 16 (1963).

shows that the addition of magnesia largely contributes to a retardation of the growth of crystallites and particles, though not so much as does alumina (as for the particle growth, cf. Ref. 12), during the periods of reduction and synthesis. The effect is considerably pronounced when silica is added as the second promoter, but it is cancelled out in the presence of potash. Lime added as the second promoter scarcely affects the growth.

It is generally accepted[13] that the iron crystallites and particles probably unite quite easily to grow in size whenever they come in contact wihthout a barrier of promoter oxides. Marked growth, however, does not always take place because there is an interfacial layer of promoter oxides, as in the case of cat. M-3. Accordingly, the interfacial oxide layer capable of retarding the particle growth requires certain characteristics as regards the melting point of the oxide material; the crystallites are apt to combine more easily when the interfacial layer contains potash, which has a lower melting point than magnesia. The relatively small particle sizes of the triply-promoted catalysts, cats. M-6 and -8, are probably due to the fact (cf. Ref. 14) that silica acts to keep potash within the particles; as a consequence, the small fraction of potash coverage is established.

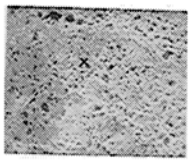
In view of the above picture of the catalysts, one might expect, at first glance, a lower specific activity per unit of the surface area, k' (atm.$^{0.5}$ ml./hr. m^2), with a larger size of the particles, for the particle growth is accompanied by the formation of crystallographic planes more closely packed than the (111) α-iron plane, whose specific activity is higher than that of any other planes. However, the situation is sometimes reversed; e. g., k' at 400°C of cat. M-3 (2.10×10^2), with a large particle size, is higher than that (2.4×10) of cat. M-5, with a much smaller particle size[3].

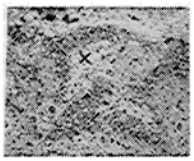
Microscopic and Electron Microscopic Structures of the Oxide Catalysts. — One can make easily finish the polishing of the catalysts of the magnesia-promoted type than those of the alumina-promoted type.[15] Photographs 1, 4 and 7 show the respective optical micrographs of the polished surfaces of cats. M-1, A-102 and M-7, while Phots. 2 and 5 show those after the etching of M-1 and A-102 catalysts. As is evident from the microphotographs, cats. M-1 and -7 of the magnesia-promoted type possess a larger number of holes and cavities than cat. A-102 of the alumina-promoted type, being more porous in structure. A close examination of Phots. 1 and 2 of cat. M-1 reveals that the etched figures are apt to appear in the region which is light gray on the polished surface. The etched figure appears to be a hill-and-valley structure on an electron micrograph (Phot. 8). Magnesia may be more concentrated in the light gray region, and it may give rise to the etching or the faster dissolution of the oxide material. In contrast, cat. A-102 gives an etched figure characterized by a mosaic structure of well-developed grains, across which a number of clear-cuts run in parallel (Phot. 5), and the individual grains consist btoh of a great many plate-shaped subgrains and a few single crystallites of the octahedral type (Phots. 9 and 10). Additional information on the shape of subgrains can be obtained from the respective electron micrographs (Phots. 11 and 12) taken of the finely ground powders of cats. M-1 and A-102. The powders from cat. M-1 are massive and irregular in shape, whereas the great majority of powders from cat. A-102 are plate-shaped. Cat. M-7 gives a polished surface which includes more pores and after the etching, shows grains of an irregular shape surrounded by narrow cracks. This catalyst gives both the plate-shaped and massive powders.[16]

The Change in the Structure of the Catalysts with the Progress of the Reduction.—In connection with our previous finding[3] that the reduction of the catalysts of the magnesia-promoted type in a current of synthesis gas at a high pressure proceeds more rapidly than that of cat. A-102 of the alumina-promoted type, the change in the surface of the etched samples with the progress of reduction was pursued for each catalyst under a high-temperature microscope. The rusults are exemplified in Phots. 3 and 6 for cats. M-1 and A-102 respectively.

As for cat. A-102, reduction takes place along the grain boundaries and sub-boundaries to result in the deeper grooves; hence, the reduction on the individual grains with only a few sub-boundaries proceeds at a very slow rate, probably because of the rapid accumulation of alumina on these surfaces. In contrast to this, the reduction of cat. M-1 starts at a great many domains scattered rather homogeneously over the whole surface, and a large number of small pores and narrow cracks appear before the reduction penetrates through the wall surfaces of the pores as well as of

12) H. Uchida and N. Todo, *J. Chem. Soc. Japan, Ind. Chem. Sec.* (*Kogyo Kagaku Zassi*), **60**, 1235 (1957).
13) A. Nielsen, Ref. 10, p. 175.
14) H. Uchida and N. Todo, This Bulletin, **29**, 20 (1956).
15) The hardness on the Vicker's scale was 345 kg./mm^2 for cat. M-1 in contrast to 390 kg./mm^2 for cat. A-102.
16) The microphotographs taken after the etching and electron micrographs of cat. M-7 will be illustrated elsewhere.


Phot. 1. 100×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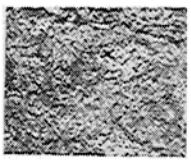
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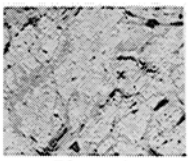
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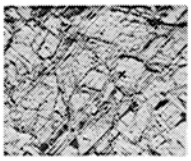
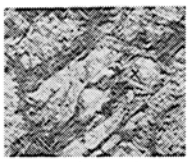
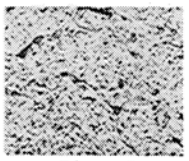
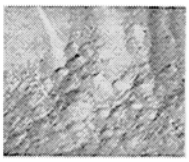

Phot. 5.


Phot. 6.


Phot. 7.

Phots. 1—7: Microphotographs of oxide catalysts. Phots. 1—3: Cat. M-1. Phots. 4—6: Cat. A-102. Phot. 7: Cat. M-7. Phots. 1, 4, and 7: Polished surface. Phots. 2 and 5: Polished and etched surface. Phot. 3: After reduction for 5 hr. at 380°C and 4 hr. at 500°C. Phot. 6: After reduction for 2 hr. at 400°C and 4 hr. at 510°C.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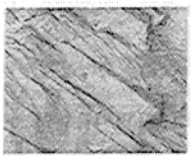
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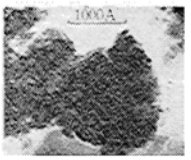
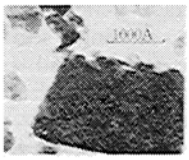
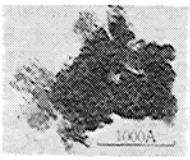


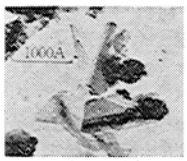
Phot. 11.



Phot. 12.



Phot. 13.



Phot. 14.

Phots. 8—10. Electron micrographs of replicas of polished and etched surface of oxide catalyst. Phot. 8: Cat. M-1. Phots. 9—10: Cat. A-102. Phots. 11—14: Electron micrographs of catalyst powders before and after use in the synthesis run. Phot. 11: Cat. M-1 before the use. Phot. 12: Cat. A-102 before the use. Phot. 13: Cat. M-1 after the use. Phot. 14: Cat. A-102 after the use.

the cracks into the interior. In this way, the reduction of cat. M-1 in the earlier stage proceeds more rapidly than that of cat. A-102. This finding gives additional support to Kobosev's view that magnesia is ineffective in retarding the reduction rate. Nevertheless, one must keep in mind the fact that magnesia acts as an effective stabilizer for the catalysts.

The Electon-microscopic Structure of the Catalysts after the Synthesis Run. — Electron microscopic investigations of the ammonia synthesis iron catalysts have been made by McCarty and Anderson[17] and more recently by Schaefer[18]. Their results are of much interest, because they gave us a direct concept of the catalyst structure. However, their results refer mainly to the pore structure of the catalysts after reduction under rather mild conditions at atmospheric pressure; they do not permit a detailed consideration of the particle structure of the catalysts in use at a high pressure. The present observations, therefore, have been made on finely ground powders from the catalyst samples after ammonia synthesis.[19]

The results are exemplified in Phots. 13 and 14 for cats. M-1 and A-102 respectively, revealing that the powders from cat. M-1 are massive and irregular in shape, whereas the powders from cat. A-102 are mainly thin-plated. The photographs, when compare with the corresponding photographs of the oxide catalysts (Phots. 11 and 12), indicate that the subparticles after the synthesis run can still retain their original shape. This finding seems to support the view of Westrik and

17) J. T. McCarty and R. B. Anderson, *J. Appl. Phys.*, **22**, 1441 (1957).
18) K. Schaefer, *Z. Electrochem.*, **64**, 1190 (1960).
19) The catalyst samples subjected to ammonia synthesis at a high pressure differ considerably in texture from the samples reduced at atmospheric pressure (cf. Ref. 12).

Zwietering[20] that both the habit and the orientation of the iron formed are very strongly affected by the oxide from which it has originated. For the plate-shaped subparticles, a thickness of 410 Å is calculated by means of the $\bar{d}_{pa}=2/\rho_t S$[21] formula, a value which is in good agreement with the crystallite width of 390 Å computed from the X-ray line broadening.

A highly active catalyst is usually furnished with both a moderately large specific surface area and a high specific activity per unit of the surface area.[22] However, the high specific activity is sometimes accompanied by a small extent of the specific surface area, and vice versa. In this connection, the above-mentioned finding suggests that a structure of the raw catalyst such as that revealed by the photographs of highly active cat. A-102 is favorable for establishing a large extent of the specific surface area of the high specific activity. The optical and electron microscopy of the catalysts may thus provide a convenient means for us to search for promoter-compositions which would be able to produce high-activity of catalysts.

Summary

This paper has presented data on such textures as the specific surface area, the pore volume, the average diameter of particles and pores, the fraction of the surface occupied by free iron and so forth, and on such structures as the lattice constant in the oxidic state and the crystallite width after the synthesis run of individual catalysts of the magnesia-promoted type, together with data on both a pure magnetite and a catalyst of the alumina-promoted type. It has also included the results of the examination of the catalysts by means of optical and electron microscopy.

Although the magnesia used as a promoter may be surface-inactive at the earlier stage of reduction, it tends at the later stage to cover the major portion of the particle surface and acts to retard the particle growth as well as the crystallite growth. The retarding effect on the growth is cancelled out when potash is added as the second promoter, but it is considerably pronounced in the presence of silica. Apart from the catalyst doubly promoted by magnesia and potash, the particle size of the promoted catalysts ranges from 700 to 2600 Å, but the crystallite widths lie in a far narrower range, between 250 to 390 Å. The specific activity per unit of the surface area is not always higher for the catalysts of the smaller particle sizes.

The lattice constant of a pure magnetite is not changed by the addition of magnesia, indicating that the Mg^{2+} ions occupy the empty interstices in the magnetite lattice.

The microscopic and electron-microscopic structures of the polished and etched surfaces of oxide catalysts of the magnesia-promoted type are very different from those of the alumina-promoted type. In view of the change in the microscopic structure of the surface with the reduction progress, an explanation in terms of the different reduction rates between the two types of catalysts is probable.

On the basis of the fact that the subparticles of the catalyst after the synthesis run still retain the original shape of the corresponding oxide catalyst, either plate-shaped or massive, the electron-microscopic as well as the microscopic observation of the polished and etched surface of the oxide catalyst can afford a means for predicting the promoter-composition which will produce a highly active catalyst.

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20) R. W. Westrik and Z. Zwietering, *Proc. Kon. Ned. Akad. v. Wetenschappen*, B56, 492 (1953).
21) On the assumption of plate-shaped subparticles, the thickness, $\bar{d}_{pa}$, is calculated from this formula.
22) Strictly speaking, the bed density should be taken into account, but it varies only a little among the catalysts under investigation.