Synthetic Ammonia Iron Catalysts Containing Magnesia as Its Principal Promoter. I. The Catalysts' Performances[1]

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Although the literature contains a few descriptions[3-6] of the synthetic ammonia iron catalysts of the magnesia-promoted type, nothing decisive has ever been reported about the catalysts' performances in relation to the promoter compositions. The present investigation has been undertaken in an attempt to ascertain the kinds and amounts of promoters which are most effective in producing a practicable catalyst of this type. The experimental results here obtained will be able to shed some light on the roles played by the individual promoters.

Experimental

The synthesis gas of $3H_2$-$1N_2$ was compressed into a gas storage vessel (40 l.) and then introduced into another, smaller one (2.5 l.) in which the pressure was automatically controlled at about 110 kg./cm^2 gauge. It was then led, through a needle valve and a high pressure gas flowmeter, into a gas purification train at the fixed pressure of 100 kg./cm^2 gauge. The purification train consisted of a hot nickel-on-kieselguhr plus palladium asbestos deoxidizer, a water cooler, a condenser, and an activated-alumina tower. The gas feed from the train was conducted into a reactor for the ammonia synthesis.

Figure 1 is a simplified diagram of the reactor and its internal parts. The reactor was somewhat different in design from the one which had been used in our previous works (e. g.[7]). An amount (3 cc. in volume, 7.46∼7.54 g. depending upon the kinds of catalyst samples) of a granular catalyst was packed into the annular space between the

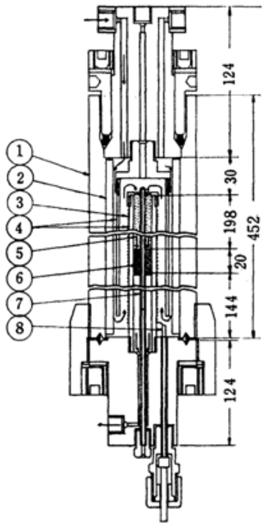

Fig. 1. Reactor for ammonia synthesis.

1 Outer shell 88 mm. O. D. 60 mm. I. D.
2 Quartz tube
3 Heating wire
4 Copper tubes
5 Copper chips
6 Catalyst bed
7 Thermocouple protection tube
8 Lead for heater

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[1] This paper is the 15th in a series of articles dealing with the synthetic ammonia iron catalysts.

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[3] "Ullmanns Encyklopaedie der technischen Chemie," Bd. III, Urban & Schwarzenberg, Muenchen-Berlin (1953), p. 588.

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

[5] C. Bokhoven, C. van Heerden, R. Westrik and P. Zwieterung, "Catalysis," Vol. III, Reinhold Publ. Corp., N. Y. (1955), p. 265.

[6] D. G. Ivanov and N. D. Anastav, *Chem. Tech.*, **15**, 229 (1963).

[7] H. Uchida and M. Kuraishi, This Bulletin, **28**, 106 (1955).

inner wall of a copper tube and the outer wall of a thermocouple protection tube to form a bed (14.4 mm. O. D. and 4 mm. I. D. by 20 mm. high) which was supported on a perforated stainless steel plate. Caution was paid to decrease the axial temperature gradient along the bed. An electric heating wire was wound more closely near the top and the bottom of copper tube, and the whole space above the bed in the tube was filled with copper chips to preheat the synthesis gas to a temperature as close to the bed temperature as possible. The axial temperature profile was measured by means of moving a thermocouple in the protection tube (4 mm. O. D. and 2 mm. I. D.). Throughout all the synthesis runs, the axial temperature difference remained within 2°C. The arrows in the figure indicate the movements of the gas flow in the reactor. The synthesis runs were conducted at several temperatures in the range between 300 and 500°C at a fixed pressure of 100 kg./cm^2 gauge and at a fixed gas flow rate of 5000 ± 50 hr^{-1} in terms of space velocity measured on the basis of the exit gas from the reactor. The exit gas was analyzed for ammonia in the same way as has been stated previously[7] and was metered. Plots of the ammonia concentration in the exit gas vs. the reaction temperature for individual catalysts give their relative activities for the ammonia synthesis.

The catalysts were prepared by a fusion process in a manner which has been reported elsewhere,[8] starting with a mixture of powders of electrolytic iron supplied by the Showa Denko Co. and promoter materials of the E. P. grade. Lumps of the finished catalysts were crushed, and granules 1.0～1.5 mm. in size were used. The bed of granular catalysts was reduced at 440°C in a current of the synthesis gas at 100 kg./cm^2 gauge at gas flow rates ranging from 1×10^4 to 2×10^4 hr^{-1}. The reduction was continued until no more increase in the ammonia concentration was observed at the temperature of 425°C and at the gas flow rate of 5000 hr^{-1} after successive six-hour periods of reduction.

After the afore-mentioned synthesis runs had been finished, the catalysts were heated at 650°C for five hours in a current of the synthesis gas at atmospheric pressure, and then the synthesis runs were repeated in the same way as before. The change in the ammonia concentration before and after the heat treatment gives a measure of the thermal stabilities of the catalysts.

With a view to calculating the specific activity constant, which corresponds to the specific activity per unit of the catalyst surface area, from the results of the activity measurement, the bed density and the specific surface area of the catalyst sample after the run were determined. The bed density was determined by weighing the catalyst sample, for the bed volume is not changed by the synthesis run. The specific surface area was determined by applying the BET equation to the nitrogen adsorption isotherm at −196°C. It should be noticed that, in general, the surface area determination was made on the catalyst samples after runs at temperatures below 500°C, but that in some special cases where the activity was increased by the heat treatment of the reduced catalyst at 650°C, the determination was made on the catalyst samples after the thermal stability test.

The catalysts in the present investigation seemed more likely to be reduced easily than the catalysts of the alumina-promoted type. In this connection, the increase in the ammonia concentration with the time of reduction was examined in catalysts of particular interest. The catalyst was heated up to 440°C in four hours according to a predetermined schedule at the pressure and at the gas flow rate of the synthesis conditions; it was then kept at this condition until the ammonia concentration in the exit gas became constant.

Results

Catalytic Activity and Thermal Stability.— The activity measurements made on the individual catalysts of different promoter compositions are illustrated in Figs. 2, 3 and 4 as plots of the ammonia concentration in the exit gas vs. the reaction temperature. The promoter compositions, which are summarized in Table I, are expressed in the weight percentages of promoters in the oxide catalysts, on the basis of the exact oxidation of iron to Fe_3O_4. The expression is a conventional one, for the oxidation does not always proceed to, or stop at, the Fe_3O_4 stage, and the ratios between ferrous and ferric irons of the oxide preparations usually show deviations from the 0.5 that corresponds to Fe_3O_4, as the table shows. On the other hand, the expression is rather convenient for defining the promoter composition from the point of view of practical catalyst-manufacturing. To express the promoter composition in the strict sense of the word, the numerals in the table can be corrected by taking the respective ratios into

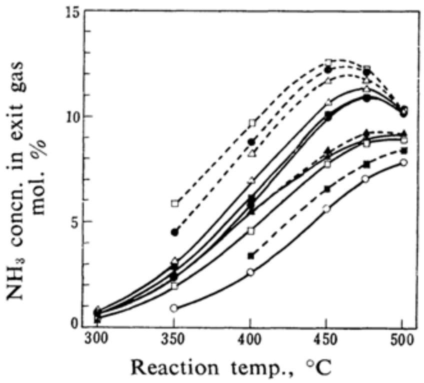

Fig. 2. Activity measurement. I.

Full line, the activity after reduction at 440°C.
Dotted line, the activity after treatment at 650°C for 5 hr.

○ Cat. M-0 ● Cat. M-1 △ Cat. M-2
▲ Cat. M-3 □ Cat. M-5 ■ Cat. M-6

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[8] G. Shima and H. Uchida, *Rpt. Gov't. Chem. Ind. Research Inst. Tokyo*, **45**, 369 (1950).

TABLE I. PROMOTER COMPOSITION, RATIO OF Fe^{II}/Fe^{III}, BED DENSITY, AND SPECIFIC SURFACE AREA

Catalyst	Promoter composition wt. %	Fe^{II}/Fe^{III}	Bed density g./cc.	Specific surface area $m^2/g.$
M-0	Unpromoted	0.419	1.91	1.15
M-1	2MgO	0.710	1.89	3.02
M-2	5MgO	0.646	1.90	5.57
M-3	5MgO, $1K_2O$	0.545	1.93	1.05
M-4	4MgO, 1CaO	0.611	1.96	4.63
M-5	4MgO, $1SiO_2$	0.674	1.84	12.00
M-7	2MgO, $1SiO_2$, $1K_2O$	0.535	1.95	4.67
M-8	4MgO, $1SiO_2$, $1K_2O$	0.568	1.86	9.37
M-9	4MgO, $1SiO_2$, $0.5K_2O$	0.547	1.96	8.61
M-10	4MgO, $2SiO_2$, $1K_2O$	0.538	1.94	9.12
M-11	4MgO, $0.5SiO_2$, $1K_2O$	0.509	1.91	5.88
M-12	4MgO, $1SiO_2$, $2K_2O$	0.502	1.90	4.44
M-14	2MgO, $1SiO_2$, $1Al_2O_3$, $1K_2O$	0.537	1.89	7.88
A-102	$2Al_2O_3$, 1CaO, $1K_2O$	0.405	1.87	6.76

The bed density and specific surface area refer to the catalyst samples after use in the synthesis runs.

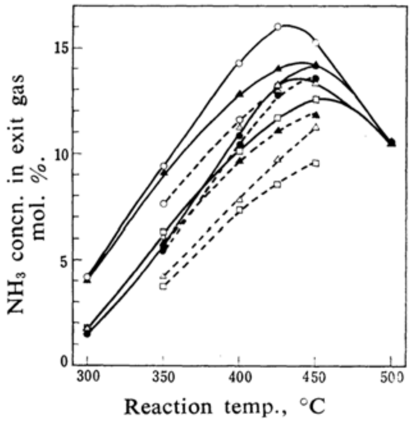

Fig. 3. Activity measurement. II.

Full line, the activity after reduction at 440°C. Dotted line, the activity after treatment at 650°C for 5 hr.

○ Cat. M-8 ● Cat. M-9 △ Cat. M-10
▲ Cat. M-11 □ Cat. M-12

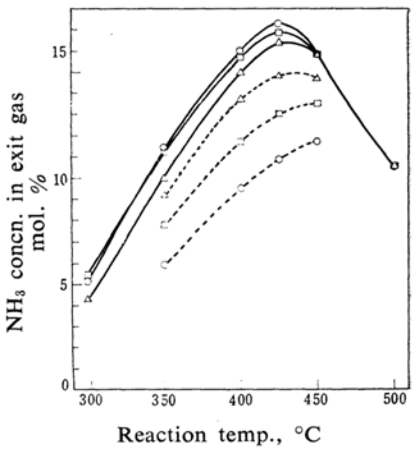

Fig. 4. Activity measurement. III.

Full line, the activity after reduction at 440°C. Dotted line, the activity after treatment at 650°C for 5 hr.

○ Cat. M-7 △ Cat. M-14 □ Cat. A-102

account. The figures include the thermal stability measurements for the individual catalysts also.

Figure 2 indicates the results on the catalysts, including an unpromoted one (cat. M-0), a couple of magnesia-promoted ones (cats. M-1 and -2), and three doubly-promoted ones, containing potash, lime, and silica (cats. M-3, -4 and -5 respectively) as the second promoter. After reduction, the magnesia-promoted catalysts give essentially the same activity as an alumina-promoted catalyst.[9] A remarkable difference between the above two catalysts, however, appears in their activities after heat treatment at 650°C; the activities of the magnesia-promoted catalyst becomes greater after the heat treatment, whereas that of the alumina-promoted catalyst decreases somewhat (cf.[10]). The increased activity after the heat treatment of the former catalyst stays at the same level, even after prolonged heat treatment for the succeeding five hours, thus demonstrating its excellent thermal stability. Both potash and lime act not as promoters but as moderately effective inactivators (cf. the results on cats. M-3 and -4) insofar as the activities.

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[9] H. Uchida and N. Todo, *J. Chem. Soc. Japan, Ind. Chem. Sec. (Kogyo Kagaku Zassi)*, **60**, 1235 (1957).

[10] H. Uchida, *Rpt. Gov't. Chem. Ind. Research Inst. Tokyo*, **46**, 1 (1951).

after reduction are concerned. Of the above two catalysts, only the one containing lime as the second promoter shows an increase in the activity after the heat treatment at 650°C to such a high level as to be comparable with that after the reduction of a catalyst doubly-promoted by alumina and potash.[9] No such phenomenon was observed in the case of the corresponding catalyst of the alumina-promoted type. Silica added as the second promoter has an unfavorable effect on the thermal stability but has little effect on the activity after reduction.

Figure 3 shows the results on a series of triply-promoted catalysts containing varying amounts of silica and potash with a fixed amount of magnesia (4%). The activities of the triply-promoted catalysts can be much higher than those of the doubly-promoted ones, provided that the added amounts of silica and potash are appropriate. Among the three catalysts (cats. M-8, -10, and -11) with the same magnesia (4%) and potash (1%) content, the catalyst with 1% silica (cat. M-8) exhibits a higher activity than any of the catalysts with 0.5% (cat. M-11) and 2% silica (cat. M-10). Moreover, the activity of the catalyst M-10 with a greater silica content, or with a higher ratio of potash to silica, is apt to descend more rapidly with the lowering of the reaction temperature than do the activities of the catalysts with smaller contents, or with lower ratios. This is also the case for the two catalysts with the same magnesia and silica content but with different amounts of potash (cf. cats. M-9 and -12). Of all the triply-promoted catalysts under investigation, a catalyst (cat. M-7) with a minor magnesia content (2%) and with the same content of silica and potash as that of cat. M-8 gives the highest activity, as is shown in a separate figure of Fig. 4. Unfortunately, the highly active catalysts here obtained have poor thermal stability, the catalyst of the highest activity being the poorest.

Triply-promoted catalysts containing alumina, potash, and lime are in current use in industrial ammonia synthesis. One such catalyst (cat. A-102) is compared with one of the present triply-promoted catalysts (e. g. cat. M-7) for activity and for thermal stability in Fig. 4. The former catalyst exhibits a little more activity than does the latter one, with nearly the same thermal stability. The poor thermal stability of cat. M-7 can be improved by the further addition of a small amount of alumina, accompanying a small decrease in the activity (cf. the plot of cat. M-14).

Bed Density and Specific Surface Area.—The results are summarized in Table I. The bed densities are in a narrow range from 1.84 to 1.96 (g./cc.). As regards the present catalysts, the bed densities may be considered to be of a constant value without bringing about any serious errors in the discussion of the promoters' effects on the catalyst performances. A brief outline of the promoters' effects on the change in the specific surface area of the iron catalysts can be obtained from the data in the table. A detailed description will, however, be made in the next chapter in connection with their contributions to the activities of the individual catalysts.

Reduction of the Catalysts.—The results concerning the five kinds of catalysts, an unpromoted catalyst (cat. M-0), a magnesia-promoted catalyst (cat. M-1), two triply-promoted catalysts of different principal promoters (cats. M-7 and A-102), and a quadruply-promoted catalyst containing magnesia, alumina, potash, and silica (cat. M-14), are illustrated in Fig. 5 as the plots of the ammonia concentration in the exit gas vs. the reduction time. It is almost certain that the increase in the ammonia concentration runs parallel to the extent of reduction except for the final stage, where the removal of the last traces of oxygen causes a considerable increase in the activity.

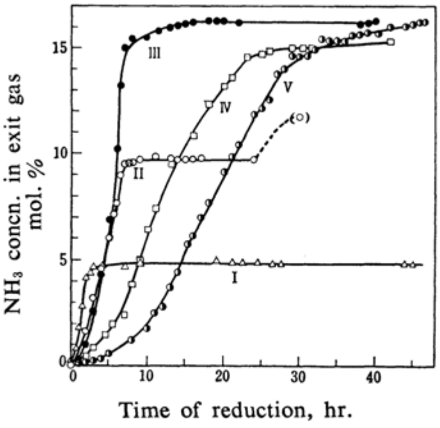

Fig. 5. Increase in ammonia concentration with time of reduction.
Reduction temp., 440°C. ○ in parenthesis indicates the activity after treatment at 650°C for 5 hr.
△ Cat. M-0 (I) ○ Cat. M-1 (II)
● Cat. M-7 (III) □ Cat. M-14 (IV)
◑ Cat. A-102 (V)

The results disclose that the addition of magnesia serves to retard the reduction rate of a magnetite only to a very small extent (compare curve I with curve II), whereas the reduction rate is greatly reduced in the presence of alumina (compare curves IV and V with curve II). Potash and silica, when simultaneously added in addition to magnesia, seemingly have no effect on the rduction rate at the earlier stage, but they have the effect of enabling the resulting catalyst to be reduced more easily toward the end of the reduction (compare curve II with curve III[11]).

Discussion

Rate Constant and Specific Activity Constant. —A quantitative comparison of the catalyst activities at a fixed temperature can be made in terms of the rate constant, k, of the ammonia synthesis reaction. In this paper, k is calculated by the aid of the expression derived from the Temkin-Pyzhev rate equation:

$$k=\left(\frac{\nu_{H_2}{}^{3/2}}{\nu_{NH_3}}\right)P^{1/2}\cdot SV_0\int_0^z\frac{z(1-z)^{3/2}\,dz}{(1+z)^2\{L^2(1-z)^4-z^2\}} \tag{1}$$

where

$$k=273(3/4)^{-3/2}k_2 \tag{2}$$

and

$$L^2=z_{eq}/(1-z_{eq}) \tag{3}$$

In the above equations, ν is the fugacity coefficient, P (atm. abs.) is the total pressure, SV_0 (hr^{-1}) is the space velocity based on the inlet gas,[12] R (atm. m^3/mol. °K) is the gas constant, and k_2 is the rate constant of the reverse reaction. It should be noticed that k ($atm^{0.5}\,hr^{-1}$) is based on the unit bed volume. Table II lists the values of k at 400°C with the various individual catalysts. Unless otherwise stated, k in this paper will hereafter denote the rate constant at this temperature. On the assumption that the entire catalyst surface is available to the catalytic reaction, the specific rate constant, k', ($atm^{0.5}$ cc./hr. m^2) at 400°C is then calculable from the relation of

$$k=k'\rho S \tag{4}$$

where ρ (g./cc.) is the bed density[13] and where S(m^2/g.) is the specific surface area of the catalyst after use in the synthesis run. In view of the findings of Bokhoven et al.,[14] who calculated the effectiveness factor, i. e., the ratio of the experimental rate constant in the absence of retardation due to diffusion effects in pores of the catalyst, and in view of previous activity measurements by other investigators, the assumption seems to be reasonably applicable to the present results at 400°C. The values of k' thus calculated are summarized in Table II. On the basis of the data available on the k' as well as on the S values of the individual catalysts, a better insight into the promoter effects on the activity or k can be obtained.

Magnesia as a promoter contributes to the increase in k' as well as to the establishment and stabilization of a large S. The smaller amount of 2 wt. % in the oxide catalyst is preferred because the greater amount of 5 wt. % accompanies such a considerable decrease in k' as to result in the smaller k, even though S becomes larger to a small extent. Potash, as the second promoter, increases k' to a certain degree, but it reduces S to so extremely small a value that its effect on k is rather unfavorable. As it is, the effect of potash addition on k appears to be of the opposite kind to that with the catalyst of the alumina-promoted type. Lime as the second promoter has little effect on S, but it contributes to the increase in k', and, as a result, the higher k is established. Silica as the second promoter behaves in a peculiar way; while it is remarkably effective in producing a large S, it reduces k' to such a low level as to be below that of a pure iron catalyst.

In view of the information just obtained on the promoting action of potash and silica, an attempt will be made to interpret the high activity that appears with a few of the present triply-promoted catalysts. Figure 6 gives plots of k, S and k' as a function of the ratio of K_2O/SiO_2, with respect to the series of catalysts containing different amounts of potash

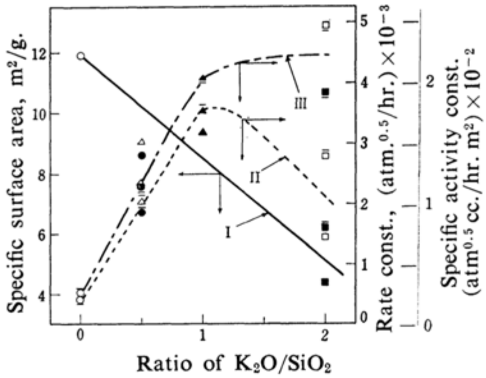

Fig. 6. Specific surface area (I), rate constant (II), and specific activity constant (III) as function of ratio between contents of potash and silica in weight percentage.
Upper barred mark, rate constant: Under barred mark, specific activity constant.
○ Cat. M-5 ▲ Cat. M-8 ● Cat. M-9
△ Cat. M-10 □ Cat. M-11 ■ Cat. M-12

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[11] The final activity was a little low as compared with the activity in the synthesis run. This catalyst of particularly poor thermal stability may have exhibited lower activity because of the lower gas flow rate during the reduction process.

[12] SV_0 is given by $SV_0=SV_z(1+z)$, where SV_z is the space velocity based on the exit gas.

[13] In the present discussion, ρ requires little consideration, since it remains almost constant for all the catalysts.

[14] C. Bokhoven and W. van Raayen, *J. Phys. Chem.*, **48**, 471 (1954).

TABLE II. RATE CONSTANT (k), SPECIFIC RATE CONSTANT (k') AT 400°C, ACTIVATION ENERGY FOR AMMONIA DECOMPOSITION (E), FREQUENCY FACTOR (A), AND FREQUENCY FACTOR PER UNIT OF CATALYST SURFACE AREA (A')

Catalyst	k atm$^{0.5}$/hr.	k' atm$^{0.5}$ cc./hr. m^2	E kcal./mol.	A atm$^{0.5}$/hr.	A' atm$^{0.5}$ cc./hr.m^2
M-0	9.18×10	0.42×10^2	56	1.2×10^{20}	5.5×10^{19}
M-1	1.15×10^3	2.01×10^2	45	5.9×10^{17}	1.0×10^{17}
M-2	1.05×10^3	0.99×10^2	44	1.4×10^{17}	1.3×10^{16}
M-3	4.25×10^2	2.10×10^2	44	5.7×10^{16}	2.8×10^{16}
M-4	1.54×10^3	1.70×10^2	42	5.1×10^{16}	5.6×10^{15}
M-5	5.38×10^2	0.24×10^2	48	1.5×10^{18}	7.0×10^{16}
M-7	4.71×10^2	5.18×10^2	41	7.7×10^{16}	8.5×10^{15}
M-8	3.57×10^3	2.05×10^2	44	4.8×10^{17}	2.7×10^{16}
M-9	1.91×10^3	1.15×10^2	46	1.4×10^{18}	8.4×10^{16}
M-10	2.08×10^3	1.18×10^2	45	7.3×10^{17}	4.1×10^{16}
M-11	2.78×10^3	2.48×10^2	39	1.2×10^{16}	1.1×10^{15}
M-12	1.62×10^3	1.92×10^2	41	3.9×10^{16}	4.6×10^{15}
M-14	4.01×10^3	2.69×10^2	41	9.6×10^{16}	6.4×10^{15}
A-102	4.57×10^3	3.61×10^2	39	2.8×10^{16}	2.2×10^{15}

and silica, besides a fixed amount of magnesia. In the figure, k' rises rapidly with the ratio at first but much more slowly beyond a ratio of ca. 1, whereas S descends almost linearly as the ratio rises. Accordingly, the high activity, or the high value of k, in the intermediate range of the ratio may be ascribed to a sufficiently high k' and a moderately large S.

Activation Energy and Frequency Factor. — The substitution of Arrhenius equation with reference to k' into Eq. 4 results in the following expression of k:

$$k=k'\rho S=A'\exp(-E/\boldsymbol{R}T)\rho S \tag{5}$$

where E (kcal./mol.) as defined by Eq. 2 stands for the activation energy of ammonia decomposition, and A' (atm$^{0.5}$ cc./hr. m^2) is the frequency factor per unit of the catalyst surface area, namely, $A'=A/\rho S$. Accordingly, the catalyst activity at a reaction temperature of T (°K) is expressed as a function of A', E, ρ, and S, which are parameters independent of the reaction temperature, T. and E and A' were determined from the Arrhenius plot of k' between 300 and 425°C. The results are summarized in Table II. A rough examination of the table shows that both E and A' change in the same direction as the promoter compositions are changed, both of them being highest with the unpromoted catalyst and lowest with one of the triply-promoted catalysts (cat. M-11).

Since the activity measurements were made mainly on the catalysts promoted doubly and triply, the effects of individual promoters on the change of E and A' can not be clarified separately. However, within certain limits, it is possible to say that magnesia, potash, and lime act similarly to reduce E and A', whereas the situation is the reverse with silica. The differences in effects on E and A' between potash and silica can be seen in a more concrete way from the findings available on the series of triply-promoted catalysts containing varying amounts of potash and silica besides a fixed amount of magnesia. In this connection, Fig. 7 shows the plots of E and A' as a function of the ratio of K_2O/SiO_2. Both E and A' tend to diminish almost linearly with the ratio. Further, the highest value of k' is found at the highest ratio, at which E and A' are lowest (cf. the plot III in the figure). This, however, does not necessarily mean that silica is useless as a promoter, for the large S that contributes to the establishment of a high k does not develop until the catalyst contains

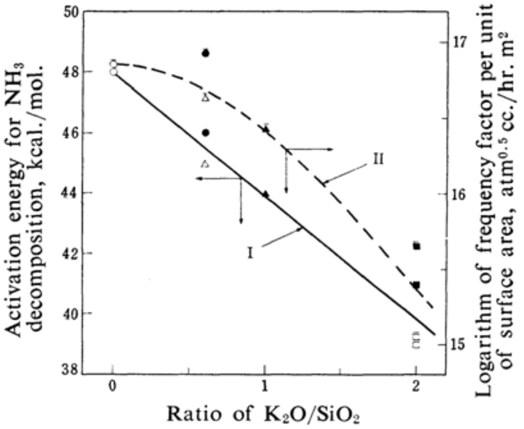

Fig. 7. Activation energy (I) and logarithm of frequency factor per unit of surface area (II) as function of ratio between contents of potash and silica in weight percentage.
Symbol with bar to the top: Frequency factor per unit of surface area.
◑ Cat. M-5 ▲ Cat. M-8 ● Cat. M-9
△ Cat. M-10 □ Cat. M-11 ■ Cat. M-12

some silica.

Reduction Rate and Catalyst Activity.— Kobosev[15] stated that magnesia added as a promoter to a ferrous oxide had rather an accelerating effect on the reduction rate and that it was not at all effective in increasing the catalyst activity. The above statement differs from the present results; the addition to a magnetite does retard the reduction rate, even though to a very small extent, and between the two series that of catalysts containing magnesia as the principal promoter and that of catalysts containing alumina as the principal promoter, no essential differences appear in their activities notwithstanding the fact that their reduction rates differ greatly. A triply-promoted catalyst belonging to either one of the two series can, similarly, be highly active provided appropriate kinds and amounts of promoters are added. Moreover, nothing remarkably different between the two series is recognizable with respect to the factors of S, k', E and A'. Accordingly, the generally accepted opinion (cf.[5]) that oxides which greatly retard the reduction rate are good promoters can not always be true.

Summary

A catalyst promoted singly by magnesia can be as active as one promoted singly by alumina. The activity of the former catalyst is increased by a succeeding reduction at 650°C to a higher level; the increased level is preserved even after the prolonged heating at this temperature. Potash, lime, and silica added as second promoters behave in their respective peculiar manners. Among the catalysts under investigation, a triply-promoted catalyst performs in nearly the same way as one of the catalysts of the alumina-promoted type in current use in industrial ammonia synthesis, provided the amounts of such kinds of promoters as magnesia, potash, and silica are appropriate.

The activity or the rate constant is expressed as a function of the temperature-independent parameters, which are the bed density, the specific surface area, activation energy, the frequency factor per unit of the catalyst surface area, and the reaction temperature. The effects of individual promoters have been discussed in view of the changes in magnitude of each parameter which result from their additions.

The catalysts of the magnesia-promoted type can be reduced much more easily than the catalysts of the alumina-promoted, type, but the reduction rate is only a little below that of the unpromoted catalyst.

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[15] N. I. Kobosev, *Acta. Physicochim. U.R.S.S.*, **4**, 829 (1936).