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Surface, Catalytic and Magnetic Properties of Small Iron Particles

II. Structure Sensitivity of Ammonia Synthesis

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On Fe/MgO catalysts with metallic iron particles between 1.5 and 30 nm, the ammonia synthesis at atmospheric pressure and between 570 and 680 K was found to be a structure sensitive reaction, with the turnover number of the small particles being an order of magnitude smaller than that for larger particles. The small particles were then treated with ammonia at 680 K to obtain a high virtual pressure of nitrogen with formation of an iron nitride. The latter was then decomposed in a hydrogen/nitrogen gas mixture. After this treatment, the iron particles possessed a higher turnover number which returned to its original lower value after prolonged treatment of the catalyst in pure hydrogen.

The effects of treating the iron particles with ammonia, a hydrogen/nitrogen gas mixture, and pure hydrogen are explained by a nitrogen induced surface reconstruction which can be erased in hydrogen. Hydrogen reduced iron surfaces are rich in sites which are moderately active in ammonia synthesis. Upon exposure to synthesis gas, sites with higher catalytic activity appear on larger particles but hardly on small particles. The surface of the latter can, however, be reconstructed more readily by treatment with ammonia.

INTRODUCTION

Using field electron microscopy, Brill *et al.* (*1*) found that the (100) and (110) planes of iron are transformed into (111) planes in the presence of nitrogen at 670 K. In addition, these authors found that nitrogen is preferentially adsorbed on the (111) plane of iron. Later work by Brill and Kurzidim (*2*) showed that metallic iron from magnetite was more active for the synthesis of ammonia after reduction by a stoichiometric mixture of hydrogen and nitrogen than after reduction in hydrogen. The authors postulated that reduction by synthesis gas ($H_2 : N_2 = 3 : 1$) produces more (111) planes than reduction by pure hydrogen, and that the synthesis of ammonia on iron is more rapid on (111) planes than on other planes.

More recently, it has been reported that the rate of decomposition of ammonia on single crystals of tungsten was higher by at least a factor of 10 on (111) planes than on (100) and (110) planes (*3*). Since tungsten and iron have the same b c c structure, these observations suggest that the symmetry of certain sites on (111) faces of a b c c crystal may be particularly favorable in ammonia synthesis and decomposition. Indeed, Ruch (*4*) has advanced some molecular orbital symmetry arguments to show that such sites would bind nitrogen in a molecular state.

Therefore, it is likely that the ammonia synthesis over iron will be a demanding or structure sensitive reaction, as speculated earlier (*5*), and that its turnover number

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should then depend on particle size in a critical range between 1 and 10 nm where the relative fraction of sites normally found on the (111) faces of b c c crystals changes by an order of magnitude (*6*).

The purpose of this work is to check the structure sensitivity of ammonia synthesis and the beneficial effect of nitrogen induced reconstruction on small particles of iron prepared and characterized as reported in the preceding paper (*7*).

EXPERIMENTAL METHODS

The catalysts used in this study are 1, 5, 16, and 40% Fe/MgO, with surface average particle sizes d equal to 1.5, 4.0, 10 and 30 nm, respectively. In addition, a doubly promoted iron catalyst (Fixed Nitrogen Research Laboratory, FNRL 441) described elsewhere (*8*) was examined; its d value is approximately 150 nm.

The rate of ammonia synthesis at atmospheric pressure was studied using two integral flow reactors (Fig. 1). The reactors were made of quartz, the essential features of each cell being a 200 cm gas preheater, a 10 mm fritted quartz disc over which the catalyst was loaded, and a thermocouple well which descended from the gas preheater through the center of the catalyst bed. The two cells differed only in the diameter of the thermocouple well, this dimension being 4 and 7 mm for each cell, respectively. A Lindberg Hevi-Duty (Model 59544) furnace enclosed the reactor, and temperature control to within ±1 K could be obtained.

Gases were fed to the reactor through three-way high vacuum stopcocks and a central gas handling manifold. After passing through purification sections, each gas was introduced to the manifold using separate three-way stopcocks which facilitated the switching of various gases to the reactor. While one gas was flowing to the reactor, another gas was flowing to a disposal line while its purification sections were being started. The flow of gases to the

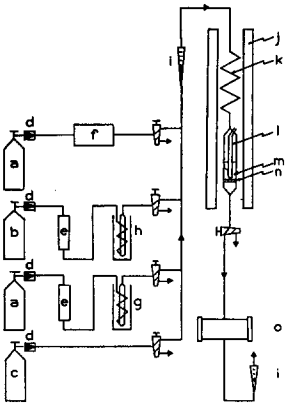

FIG. 1. Apparatus for ammonia synthesis: (a) hydrogen cylinder; (b) synthesis gas cylinder; (c) ammonia cylinder; (d) regulators; (e) Deoxo purifiers; (f) Pd–Ag diffuser; (g) liquid nitrogen 13X molecular sieve trap; (h) dry ice–acetone 13X molecular sieve trap (i) flow meters; (j) reaction furnace; (k) preheating section; (l) thermocouple well; (m) catalyst bed; (n) fritted glass disc; (o) ir cell.

reactor was then switched. While the second gas was flowing to the reactor, the first gas was flowing to a disposal line while its purification sections were being shut down. The bores of each stopcock were flushed with the respective purified gas associated with that stopcock before each experiment began.

Two types of H_2 purification were used for the catalyst reduction and for subsequent treatments. In one case, cylinder H_2 (99.99%) was passed through a Deoxo catalytic hydrogen purifier, and then through a 13X molecular sieve (Linde) trap at liquid nitrogen temperature. In the other case, the cylinder H_2 was diffused through a palladium–silver thimble, and to the manifold without further purification.

A stoichiometric mixture of H_2 and N_2 was obtained from the Matheson Co., and was purified by passage through a Deoxo catalytic hydrogen purifier and a 13X molecular sieve trap at 193 K. This gas mixture was passed over the catalyst at a known flow rate (space velocity of about 7000 hr^{-1} based on void volume), and the gas leaving the reactor was led through a

plastic tube to a Beckman ir spectrophotometer (Model IR-9) in the adsorption mode. The absorption cell for the spectrophotometer was a glass tube 100 mm long and 48 mm in diameter with 6 mm thick sodium chloride windows mounted on each end. The absorbance at 966.5 cm^{-1} as a function of the ammonia concentration was calibrated in two ways. First, a known pressure of ammonia, measured using a Baratron gauge, was introduced into the evacuated absorption cell. Then the cell was filled to 100 kPa with H_2, and the absorbance difference was measured. The second calibration involved the flowing of a stoichiometric mixture of synthesis gas over the catalyst, at a known temperature, and sufficiently low flow rate so that equilibrium conversion to ammonia was obtained (a flow rate 50 times lower than that giving rise to 30% of the equilibrium conversion). The two calibrations agreed within 2% of each other. In both cases, a linear variation of the ammonia concentration versus the absorbance difference was found.

The ammonia used in this study was anhydrous (99.99%), and was connected to the manifold without further purification. Mössbauer spectroscopy was also employed at various stages of this investigation. The details of the spectrometer have been reported elsewhere (*9*), and the results will be presented and discussed when they become necessary for understanding the ammonia synthesis data.

RESULTS

Presentation of Data

The rate of ammonia synthesis is conveniently expressed by the site time yield, $\bar{N}$, an average turnover number. This quantity, which physically corresponds to the average number of ammonia molecules produced per available surface iron atom in a given time, is obtained from the average rate of ammonia formation, $\bar{R}$, and the amount (mol) of metallic iron surface atoms in the catalyst bed, A. The former, $\bar{R}$, (mol NH_3 s^{-1}) was obtained from experimental quantities by:

$$\bar{R} = \bar{v}y/v, \qquad (1)$$

where $\bar{v}$ is the flow rate of synthesis gas leaving the reactor (cm^3 s^{-1}) measured at 298 K and atmospheric pressure, y the mole fraction of NH_3 in the gas mixture leaving the reactor, and v the molar volume of an ideal gas at the conditions of $\bar{v}$ measurement. The value of A was obtained from the CO uptake of the catalyst assuming that one chemisorbed CO molecule corresponds to two surface iron atoms (*10*):

$$A = 2Xw \times 10^{-6}, \qquad (2)$$

where X is the CO uptake (μmol/g of catalyst), and w the mass (g) of catalyst in the reactor. The average turnover number can thus be written in the following form:

$$\bar{N}(s^{-1}) = \bar{R}/A = \bar{v}y \times 10^6/2vXw = 22.1\bar{v}y/Xw. \qquad (3)$$

In general, the average rate of ammonia formation, $\bar{R}$, depends on the mole fraction of ammonia leaving the reactor, y. Because the reaction is limited by equilibrium, values of $\bar{R}$ or of $\bar{N}$ are best given for specified values of efficiency, η, defined as the mole fraction of ammonia leaving the reactor normalized by the equilibrium conversion. Equilibrium conversion was obtained from the literature (*11*).

Collection of Data

Ammonia synthesis data were obtained by first reducing each catalyst with Deoxo-H_2 in one of the flow reactors followed by switching from Deoxo-H_2 to a stoichiometric mixture of H_2:N_2 as the gas flowing through the catalyst bed. The Fe/MgO catalysts were reduced according to the reduction schedule outlined in the preceding paper (*7*), and the doubly promoted iron catalyst (FNRL 441) was reduced for 5

TABLE 1
AVERAGE TURNOVER NUMBERS $\bar{N}$ VS EFFICIENCY η FOR 1% Fe/MgO

T_m (K)	η_{T_m}	$\bar{N}_{T_m}$ (ks^{-1})	η_{T_s}	$\bar{N}_{T_s}$ (ks^{-1})	T_s (K)
		Deoxo-H_2 reduction			
681	0.0908	1.85	0.0844	1.77	678
681	0.0728	2.71	0.0677	2.60	678
681	0.100	1.61	0.0935	1.55	678
682	0.0755	2.72	0.0649	2.57	678
		Ammonia treatment			
678	0.0845	2.98	0.0845	2.98	678
681	0.114	2.11	0.106	2.03	678
679	0.0820	3.31	0.0784	3.27	678
679	0.0916	2.71	0.0876	2.68	678
683	0.0848	3.58	0.0743	3.35	678
682	0.116	2.10	0.100	1.99	678
654	0.0555	1.53	0.0336	1.16	638
555	0.00137	0.321	0.00307	0.517	573
		Deoxo-H_2 treatment			
679	0.0541	4.19	0.0517	4.13	678
679	0.0462	5.22	0.0442	5.15	678
679	0.0529	4.45	0.0505	4.39	678
679	0.0532	4.26	0.0509	4.20	678
665	0.0484	2.47	0.0668	2.96	678
666	0.0358	3.33	0.0487	3.93	678
636	0.0240	1.44	0.0253	1.48	638
583	0.00370	0.335	0.00244	0.262	573
		Pd-H_2 treatment			
682	0.0545	3.65	0.0468	3.46	678
679	0.0742	2.23	0.0709	2.20	678
678	0.0440	4.15	0.0440	4.15	678
642	0.0199	1.36	0.0174	1.27	638
643	0.0216	1.41	0.0184	1.29	638
643	0.0150	2.20	0.0128	2.02	638
644	0.0164	1.99	0.0135	1.79	638
586	0.00450	0.151	0.00263	0.110	573
586	0.00145	0.254	0.000813	0.181	573

days at 720 K prior to the collection of ammonia synthesis data.

The data so obtained are presented in Tables 1–4 under the heading of "Deoxo-H_2 reduction." After switching from Deoxo-H_2 to synthesis gas, stationary state for the ammonia production was reached in less than 1/2 hr, and stayed unchanged after prolonged exposure to the synthesis gas (ca. 3 days). For reasons that will become clear later, pure ammonia was then passed over the catalyst for 1 hr at 670 K, followed by reexposure to the stoichiometric $H_2:N_2$ mixture. In this case, after switching from ammonia to synthesis gas stationary state for ammonia production was reached after a few hours (3–6 hr), and remained unchanged by further synthesis for 4 days. In Tables 1–4 the

TABLE 2
AVERAGE TURNOVER NUMBERS $\bar{N}$ VS EFFICIENCY η FOR 5% Fe/MgO

T_m (K)	η_{T_m}	$\bar{N}_{T_m}$ (ks^{-1})	η_{T_s}	$\bar{N}_{T_s}$ (ks^{-1})	T_s (K)
		Deoxo-H_2 reduction			
684	0.138	12.0	0.113	10.8	678
684	0.108	16.0	0.0882	14.4	678
681	0.268	6.20	0.246	5.88	678
681	0.186	8.82	0.171	8.36	678
638	0.0808	4.76	0.0808	4.76	638
638	0.104	3.94	0.104	3.94	638
573	0.00741	0.993	0.00741	0.993	573
573	0.00901	0.878	0.00901	0.878	573
573	0.0184	0.605	0.0184	0.605	573
		Ammonia treatment			
682	0.226	9.85	0.191	9.18	678
682	0.223	10.7	0.188	9.97	678
682	0.131	19.3	0.110	18.0	678
682	0.298	8.45	0.252	7.87	678
682	0.282	8.57	0.238	7.98	678
639	0.0877	5.39	0.0849	5.28	638
638	0.108	4.48	0.108	4.48	638
641	0.0391	10.5	0.0351	9.83	638
641	0.0458	9.22	0.0412	8.65	638
570	0.00934	1.40	0.0107	1.52	573
570	0.0123	1.20	0.0141	1.31	573
570	0.0211	0.924	0.0242	1.01	573
		Deoxo-H_2 treatment			
678	0.133	9.66	0.133	9.66	678
680	0.148	10.2	0.134	9.82	678
680	0.229	6.50	0.207	6.27	678
681	0.101	16.0	0.0930	15.2	678
680	0.130	11.5	0.117	11.1	678
		Pd-H_2 treatment			
680	0.0992	10.9	0.0898	10.5	678
680	0.117	10.2	0.106	9.89	678
680	0.157	7.78	0.142	7.51	678
676	0.226	5.36	0.238	5.55	678
680	0.0992	12.7	0.0898	12.3	678
681	0.171	7.98	0.157	7.56	678

TABLE 3
AVERAGE TURNOVER NUMBERS $\bar{N}$ VS EFFICIENCY η FOR 40% Fe/MgO

T_m (K)	η_{T_m}	$\bar{N}_{T_m}$ (ks^{-1})	η_{T_s}	$\bar{N}_{T_s}$ (ks^{-1})	T_s (K)
		Deoxo-H_2 reduction			
676	0.185	28.2	0.190	28.9	678
677	0.260	19.2	0.256	19.5	678
677	0.303	14.4	0.310	14.7	678
678	0.225	22.1	0.225	22.1	678
630	0.0774	11.3	0.102	13.1	638
630	0.110	6.33	0.145	7.38	638
631	0.0552	13.4	0.0701	15.4	638
631	0.0903	9.58	0.115	10.9	638
582	0.0131	3.97	0.00887	3.14	573
583	0.00988	4.93	0.00640	3.80	573
586	0.0117	4.79	0.00670	3.42	573
584	0.0197	3.22	0.0122	2.42	573
622	0.0608	7.76	0.106	10.6	638
625	0.0543	10.1	0.0845	14.2	638
625	0.0410	14.5	0.0641	18.6	638
624	0.0800	7.10	0.130	9.31	638
		Ammonia treatment			
681	0.248	38.3	0.224	36.9	678
679	0.251	33.6	0.241	33.3	678
678	0.285	26.5	0.285	26.5	678
679	0.333	22.2	0.320	22.0	678
679	0.363	19.6	0.347	19.3	678
634	0.0686	22.5	0.0797	24.5	638
633	0.0899	17.2	0.108	19.1	638
632	0.113	12.1	0.141	13.7	638
586	0.0234	4.89	0.0137	3.53	573
589	0.0156	6.69	0.00801	4.65	573
589	0.0126	7.93	0.00631	5.22	573
		Deoxo-H_2 treatment			
674	0.194	32.3	0.211	34.3	678
674	0.226	25.3	0.246	26.8	678
674	0.301	16.2	0.328	17.2	678
674	0.254	22.0	0.276	23.4	678
		Pd-H_2 treatment			
674	0.319	14.8	0.356	15.9	678
677	0.242	26.5	0.238	26.9	678
677	0.290	21.2	0.294	21.4	678
552	0.00395	2.10	0.0103	3.76	573
555	0.00227	3.13	0.00520	5.17	573

pertinent data are summarized under the heading of "Ammonia treatment."

The data show that the ammonia treatment increases the value of $\bar{N}$ at a given temperature and conversion, and in order to test the reversibility of this phenomenon the catalysts were further treated with Deoxo-H_2 at 675 K for 20 hr. Following this treatment, synthesis gas was again flowed over the catalyst, and ammonia synthesis data were collected. As was the case for the freshly reduced catalysts, stationary state ammonia synthesis was established shortly after introduction of synthesis gas (0.5 hr), and the data were unchanged with respect to prolonged ammonia synthesis.

Since cylinder H_2 usually contains traces of N_2 which are not removed by a Deoxo purifier, the possible effect of this N_2 was eliminated by treating the catalysts with Pd-diffused H_2 for 20 hr at 675 K. Synthesis gas was then readmitted to the reactor and ammonia synthesis data were collected. Quite contrary to what happened after the Deoxo-H_2 treatment, stationary state ammonia synthesis was attained only after several hours of synthesis (ca. 6 hr). As before, however, the stationary state activity for the production of ammonia was not changed by prolonged synthesis. The data obtained after the Deoxo-H_2 and Pd-diffused H_2 treatments are summarized in Tables 1–4 under appropriate headings. A diagrammatic summary of the effects of various gaseous treatments is presented in Fig. 5.

Standardization of Data

For convenience, the data for the different catalysts may be corrected to a set

TABLE 4
AVERAGE TURNOVER NUMBERS $\bar{N}$ VS EFFICIENCY η FOR EMMETT NO. 441

T_m (K)	η_{T_m}	$\bar{N}_{T_m}$ (ks^{-1})	η_{T_s}	$\bar{N}_{T_s}$ (ks^{-1})	T_s (K)
685	0.203	32.1	0.166	28.9	678
684	0.263	21.5	0.218	19.7	678
683	0.229	24.9	0.199	23.1	678
681	0.153	41.1	0.142	39.3	678
619	0.0389	12.7	0.0751	18.4	638
619	0.0377	12.8	0.0728	18.5	638
619	0.0328	14.3	0.0634	20.8	638

of standard temperatures by means of a rate expression, which for the sake of simplicity will be taken to be the classic equation of Temkin *et al.* (*12*):

$$r = kP_{N_2}\left[\frac{p_{H_2}^3}{p_{NH_3}^2}\right]^{\alpha} - \overleftarrow{k}\left[\frac{p_{NH_3}^2}{p_{H_2}}\right]^{1-\alpha}, \quad (4)$$

where the rate, r, is given in terms of the partial pressures of species i, p_i, rate constants $\vec{k}$ and $\overleftarrow{k}$ for the forward and reverse reactions, and an adjustable parameter, α. Neglecting at first the reverse reaction, for plug-flow of a stoichiometric $H_2:N_2$ mixture, the following result obtains:

$$y^{2\alpha+1} = C\vec{k}/\bar{v}, \quad (5)$$

where C is a constant independent of temperature and conversion. Thus, at a given synthesis gas flow rate, the value of y that would result if the reactor were at a standard temperature, T_s, is related to the experimentally measured value of y at some measured temperature, T_m, by the expression:

$$y_{T_s} = y_{T_m}[\vec{k}_{T_s}/\vec{k}_{T_m}]^{1/(2\alpha+1)}. \quad (6)$$

Equation (5) with $\alpha = 0.5$ and an activation energy for $\vec{k}$ of 110 kJ mol^{-1}, provided an adequate representation of the data for each catalyst. Using Eq. (6) coupled with the experimental value of α and temperature dependence of $\vec{k}$, the ammonia synthesis data can be corrected to a set of standard temperatures (Tables 1–4 and Figs. 2–4). It is not implied that Eq. (4) is the rate-law which best fits the data over the studied conversion and temperature ranges (*13*), but it was used for convenience in the temperature correction of the data for comparative purposes.

On the other hand, Eq. (4) is a good rate-law for the ammonia synthesis on iron at high conversions (*12*). Thus, it can be used to ascertain the importance of the reverse reaction as a function of conversion. For $\alpha = 0.5$, the ratio, L, of the rate constant, $\vec{k}$, calculated neglecting the reverse reaction to that calculated considering the reverse reaction is the following:

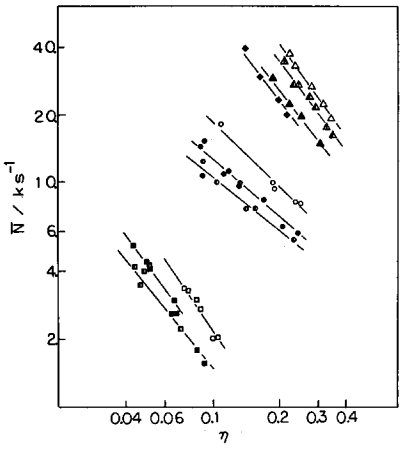

FIG. 2. Average turnover numbers $\bar{N}$ at 678 K vs efficiency η. Symbols for Fe/MgO samples and promoted catalyst: (□) 1% Fe/MgO ($d = 1.5$ nm); (○) 5% Fe/MgO ($d = 4.0$ nm); (△) 40% Fe/MgO ($d = 30.$ nm); (◇) FNRL 441 ($d = 150$ nm). Symbols for treatments: (●) reduced with Deoxo-H_2; (○) treated with NH_3; (◫) treated with Deoxo-H_2; (◐) treated with Pd-diffused H_2.

$$L = \eta^2/\ln(1-\eta^2). \quad (7)$$

For $\eta = 0.30$, the error made in neglecting the reverse reaction is 5%, and thus the ef-

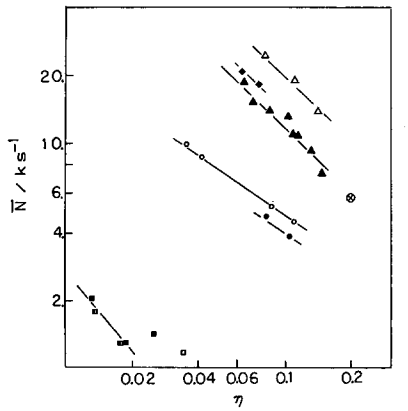

FIG. 3. Average turnover numbers $\bar{N}$ at 638 K vs efficiency η. Symbols for Fe/MgO samples and promoted catalyst: (□) 1% Fe/MgO ($d = 1.5$ nm); (○) 5% Fe/MgO ($d = 4.0$ nm); (⊗) 16% Fe/MgO ($d = 10.$ nm); (△) 40% Fe/MgO ($d = 30.$ nm); (◇) FNRL 441 ($d = 150$ nm). Symbols for treatments: (●) reduced with Deoxo-H_2; (○) treated with NH_3; (◫) treated with Deoxo-H_2; (◐) treated with Pd-diffused H_2.

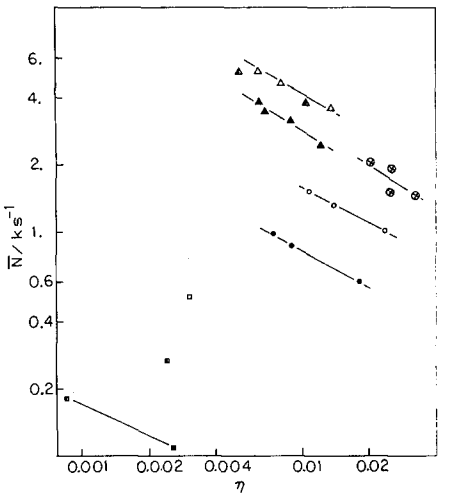

FIG. 4. Average turnover numbers $\bar{N}$ at 573 K vs Efficiency η. Symbols for Fe/MgO samples and promoted catalyst: (□) 1% Fe/MgO ($d = 1.5$ nm); (○) 5% Fe/MgO ($d = 4.0$ nm); (⊗) 16% Fe/MgO ($d = 10.$ nm); (△) 40% Fe/MgO ($d = 30.$ nm); (◇) FNRL 441 ($d = 150$ nm). Symbols for treatments: (●) reduced with Deoxo-H_2; (○) treated with NH_3; (◫) treated with Deoxo-H_2; (◐) treated with Pd-diffused H_2.

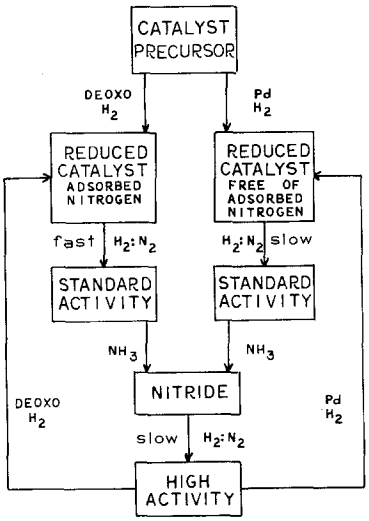

FIG. 5. Summary of catalytic activity dependence on catalyst pretreatment: slow and fast refer to the rate of attainment of stationary state.

fect of the reverse reaction can easily be neglected in the present study.

Transport Phenomena

Ammonia synthesis data were collected for the 5% Fe/MgO catalyst in three separate experiments using catalyst bed lengths of 19, 31, and 54 mm, respectively. In the three cases, values of $\bar{N}$ at a given efficiency were the same. Since the bed length to catalyst grain size ratio was large (> 200), the effect of back-diffusion was expected to be negligible (*14*), and the independence of $\bar{N}$ on the bed length supports this expectation.

The absence in this work of internal and external mass and heat transfer limitations, is assured by the almost identical values (Figs. 3 and 4) of $\bar{N}$ at the same η, at both 573 and 638 K, for the catalysts containing 16 and 40% Fe. Note that the Fe particle size, d, for these two catalysts is at least 10 nm so that, although they have different values of d, no effect of particle size on the rate was expected and none was found. Details of the experimental criterion for the absence of transport phenomena as used here, can be found elsewhere (*15*).

DISCUSSION

Particle Size

Under the experimental conditions of this study, the ammonia synthesis has a turnover number which varies with particle size (Figs. 2–4). At each temperature, the data for the catalysts with 1.5, 4.0, and 30 nm particle sizes cluster in three distinctive groups irrespective of the nature of the pretreatments, and at a given efficiency, the turnover number increases with particle size. One possible origin of this behavior is that of metal–support interaction, which may be expected to increase in importance as particle size becomes smaller. This interaction might modify the electronic structure of the metal by electron transfer between metal and support, and therefore the catalytic activity of very small particles. Such an

explanation receives no support from the Mössbauer spectra of the iron particles in all samples, with Mössbauer parameters indistinguishable within experimental error from those of bulk metallic iron (*7*).

Rather it is tempting to ascribe the dependence of turnover on particle size to structure sensitivity, according to which the relative proportion of sites with enhanced activity for ammonia synthesis would decrease as particle size becomes smaller. This interpretation receives a great deal of support from the effects of pretreatment on catalytic activity, the dependence of these effects on particle size, and the surface reconstruction of small iron particles discussed further in the third paper of this series (*10*).

Let us now discuss the effects of pretreatment of the catalysts in various gases, and show how these results confirm and amplify the early speculations of Brill and Kurzidim based on limited data (*2*).

Ammonia Treatment

As evidenced by Mössbauer spectroscopy, the exposure of the metallic iron particles to ammonia at 670 K completely transforms the iron to an iron nitride phase. The reexposure of this phase to a stoichiometric $H_2:N_2$ mixture at 670 K completely reduces the nitride to metallic iron (*10*). As a result of the phase changes accompanying the ammonia treatment, a modification of the iron particles may take place. In addition, Mössbauer spectra show an increase in the amount of metallic iron caused by the ammonia treatment. It was shown in the preceding paper (*1*) that the Fe/MgO catalysts used in this study contain iron in essentially two different chemical states. One form of iron is metallic iron, and the other form is Fe^{2+} in MgO, the fraction of the iron in the metallic state being about 0.5. Any changes in the fraction of metallic iron accompanying the ammonia treatment can be determined by measuring the spectra areas of the respective iron phases. Thus, following the ammonia treatment the amount of metallic iron increases by 3% for the 1 and 5% Fe/MgO catalysts, but by 20% for the 40% Fe/MgO catalyst. When the respective increases in the amounts of metallic iron accompanying the ammonia treatment are taken into account for the various catalysts, there appears to be a significant increase in the catalyst activity accompanying the ammonia treatment for 1 and 5% Fe/MgO, while for 40% Fe/MgO the enhancement in activity is small. Clearly, these results are consistent with the view that the ammonia synthesis on iron is a structure sensitive reaction. With the small particles of 1 and 5% Fe/MgO, exposure of the hydrogen reduced surfaces to a stoichiometric $H_2:N_2$ mixture seems to bring about a reconstruction to a more active surface according to the ammonia synthesis data, as discussed in the next section. This reconstruction, however, is not complete, since the turnover numbers on the small particles are much smaller than those on the large particles. Ammonia treating the iron particles and decomposing the nitride in synthesis gas provides a method for achieving more extensive reconstruction of the surface of the small particles.

In contrast, for the large iron particles the effect of the ammonia treatment is small. This indicates either that reconstruction of the hydrogen reduced surface upon exposure to synthesis gas is complete, or that the hydrogen reduced surface is in fact the most stable surface in the presence of nitrogen. These two possibilities will be discussed further in the next section.

Hydrogen Treatment

Upon reexposure of the catalyst to Deoxo-H_2, a catalytic activity corresponding to that surface initially formed after original Deoxo-H_2 reduction is expected, and is experimentally observed. For the 1 and 5% Fe/MgO catalysts the turnover

numbers obtained after Deoxo-H_2 treatment of the ammonia treated particles are only slightly higher than those obtained on the freshly Deoxo-H_2 reduced catalysts. It must be remembered, that for these two catalysts there was no significant increase in the amounts of metallic iron accompanying the ammonia treatment. For the 40% Fe/MgO catalyst, there was a 20% increase in the amount of metallic iron produced by the ammonia treatment, and from Mössbauer spectroscopy it can be shown that this increase in the amount of metallic iron is not destroyed by further treatment of the catalyst with hydrogen. Thus, for the 40% Fe/MgO catalyst there is only a small decrease in the turnover number produced by the Deoxo-H_2 treatment, the final synthesis rate being about 30% higher than that of the freshly reduced catalyst. This result is quite consistent then, with the previous conclusion that, over and above a mere increase in the amount of metallic iron, there is only a small effect of the ammonia treatment on the large iron particles.

The experimental results indicate that the structure of the iron surface is quite sensitive to the partial pressure, or virtual pressure, of nitrogen over the catalyst. This point is further emphasized by the effect of the Pd-diffused H_2 treatment. During this treatment, the iron surface is exposed to nitrogen-free H_2 and another surface reconstruction may occur. Since it is known that the small amount of nitrogen in cylinder hydrogen is enough to cover a substantial fraction of an iron surface after reduction with the impure hydrogen (*16*), there may be a significant difference between a treatment of the catalyst with Deoxo- and Pd-diffused hydrogen, since the former still contains nitrogen and the latter does not.

For all of the Fe/MgO catalysts, there was a long period of time after the Pd-diffused H_2 treatment before the catalysts reached stationary state with respect to the rate of ammonia synthesis (ca. 6 hr). This time period was much longer than that required for the surface to chemisorb the steady state amount of nitrogen at a rate corresponding to the final stationary state synthesis rate. Thus, this long induction period must be due not to the build-up of the steady state concentration of surface nitrogen, but to a slow nitrogen induced surface reconstruction initiated by the switch from Pd-diffused H_2 to the synthesis gas mixture. The hydrogen reduced surface is not, therefore, the most stable surface in the presence of nitrogen. Consequently, for the 40% Fe/MgO catalyst, the reconstruction of the Pd-diffused H_2 reduced surface in the presence of synthesis gas, appears essentially complete since the corresponding surface structure gives a turnover number approximately equal to that of a surface obtained after the ammonia treatment. On the other hand, for the 1 and 5% Fe/MgO catalysts the nitrogen induced surface reconstruction is far from complete as evidenced by the low turnover numbers on these catalysts after the Pd-diffused H_2 treatment. The experimental observation that the catalysts approached their stationary state ammonia synthesis rates in a short time after the Deoxo-H_2 treatments must now point to the conclusion that the amount of nitrogen present in Deoxo-H_2 (40 ppm) is enough to affect significantly the structure of the iron surface.

The true effect of the ammonia treatment is obtained by comparing the turnover numbers after the ammonia treatment with those collected after the Pd-diffused H_2 treatment. This comparison properly takes into account the effect of the increase in the amount of metallic iron accompanying the ammonia treatment, and it provides a reproducible measure of the effect on the iron surface of the amount of nitrogen present during the surface formation. In one case, there is no nitrogen present during the surface formation (Pd-diffused H_2), and in the other case, there is

an intimate interaction between the nitrogen and surface during its formation (ammonia treatment). For the 1 and 5% Fe/MgO catalysts, small particle effects are present, and the effect of the ammonia treatment is significant. However, on the 40% Fe/MgO catalyst, small particle effects are absent, and the iron surface has a turnover number almost identical to that of a doubly promoted iron catalyst. This interesting observation will not be discussed any further at this stage of our work.

Kinetics and Mechanism

The next question is the origin of the structure sensitivity of ammonia synthesis. Early kinetic work (*17*) indicating the same apparent activation energy on very small and larger particles of iron, could not be reproduced in a more extensive study of the kinetics which reveals a rather complex behavior (*13*). There are several questions which necessitate further investigation. What is the best rate equation, if there is only one, that correlates data on small and large particles? While the surface of larger iron particles appears nonuniform (*12*), is this also the case for very small particles? Should we consider the possibility that the most abundant surface intermediate is not the same at low (below 650 K) and/or high temperatures, or on the special sites created as a result of nitrogen induced surface reconstruction? Finally, of course, what is the nature of these special sites? While a kinetic answer to this question cannot be given now, a reasonable and hopefully even convincing assignment for these special sites can be proposed on the basis of other data involving magnetic susceptibility, Mössbauer spectroscopy and chemisorption of carbon monoxide. This information will be discussed in the next paper of this series (*10*).

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