The Role of Potassium as a Promoter in Iron Catalysts for Ammonia Synthesis

K. ALTENBURG,[1] H. BOSCH,[2] J. G. VAN OMMEN, AND P. J. GELLINGS

Department of Chemical Technology, Twente University of Technology, P.O. Box 217, 7500 AE Enschede, The Netherlands

Five ammonia synthesis catalysts, mainly differing in potassium content, were prepared from a commercial doubly promoted iron catalyst. The activities of these catalysts were measured at 350–450°C and 5–200 atm. The experimental reaction rates were fitted to the modified Temkin rate equation. Increasing the potassium content from 0.1 to 3.8 wt% results in increasing the order in H_2 from 0.7 to 1.5. The change from singly to doubly promoted behavior is gradual. The nature of catalysts with a relatively high K-content is changed, preventing the formation of NH (or NH_2) groups so that N-atoms become the main species on the surface, which explains the higher order in H_2.

INTRODUCTION

The synthesis of NH_3 on promoted iron catalysts has been described in 1940 by Temkin and Pyzhev (1) by the rate equation:

$$r = k_1 \cdot p_{N_2} \cdot \left(\frac{p_{H_2}^{1.5}}{p_{NH_3}}\right)^{2\alpha}$$
$$-k_2 \cdot \left(\frac{p_{NH_3}}{p_{H_2}^{1.5}}\right)^{2(1-\alpha)}. \quad (1)$$

Here α accounts for the nonuniformity of the surface, values between 0.4 and 0.8 being very common (2). This equation describes fairly well the kinetics observed with many industrial catalysts, especially when, at high pressures, the partial pressures are replaced by fugacities (3).

However, the rate constants k_1 and k_2 are often found to be pressure dependent (4), which indicates that the mechanism represented by this rate equation should be modified. In many cases this is also connected with the promoting role of K.

Van Ommen et al. (5) showed that K is probably present on the iron surface as KOH, the stable K-compound under synthesis conditions. It is generally accepted

that K influences the species present on the surface, while the adsorption of nitrogen under synthesis conditions is the rate-determining step (6).

In the critical review of Frankenburg (7) it is suggested that the singly promoted catalyst, containing only Al_2O_3 as addition, has acidic properties, binding the NH- and NH_2-groups stronger than the doubly promoted catalyst containing Al_2O_3 and KOH, on which the acidic centers have been neutralized by K. He did not specify the kinetic consequences of this difference.

Ozaki et al. (8) modified the original Temkin Eq. (1) for the cases that the most abundant species on the surface are N-atoms (or radicals) or NH-groups, respectively. Nielsen et al. (9) combined these results in one equation by introducing a parameter w for the order in H_2. The rate of NH_3 formation is then described by:

$$r = \frac{k \cdot p_{N_2}}{\left[1 + \frac{1}{K_e} \cdot \frac{p_{NH_3}^{2\alpha}}{p_{H_2}^{w}}\right]}. \quad (2)$$

If the surface is covered with N-atoms (or radicals) only, K_e is the equilibrium constant of the reaction:

$$N(a) + 1.5\ H_2\ (g) \rightleftarrows NH_3\ (a) \quad (3)$$
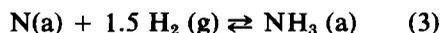
and then $w = 1.5$. The absorbed state is

[1] Present address: Dow Chemical, Terneuzen, The Netherlands.
[2] To whom correspondence should be addressed.

denoted by (a), the gaseous state by (g).

If the surface is covered with NH-groups only, K_e is the equilibrium constant of the reaction:

$$NH(a) + 1.0\ H_2\ (g) \rightleftarrows NH_3\ (a) \qquad (4)$$
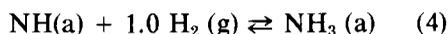
and then $w = 1.0$.

Nielsen *et al.* (*9*) showed that at NH₃ concentrations >0.1 mol%, $1 \ll 1/K_e \cdot p_{NH_3}/p_{H_2}^w$ in the denominator of Eq. (2). This reduces the rate expression to the original Temkin Eq. (1) with the exception that for the order in H₂ a parameter w has been introduced, dependent on the most abundant species on the surface. Replacing partial pressures by fugacities, and taking into account the reverse reaction, the modified Temkin equation then becomes:

$$r = k_1 \cdot f_{N_2} \cdot \left(\frac{f_{H_2}^w}{f_{NH_3}}\right)^{2\alpha}$$
$$\cdot \left[1 - \frac{f_{NH_3}^2}{f_{H_2}^3 \cdot f_{N_2} \cdot K_{eq}}\right] \qquad (5)$$

with

$$K_{eq} = \left[\frac{f_{NH_3}^2}{f_{H_2}^3 \cdot f_{N_2}}\right]_{at\ equilibrium}. \qquad (6)$$

Brunauer and Emmett (*10*) suggest the presence of NH- or NH₂-complexes on singly promoted catalysts, which retard the rate of NH₃ formation. Nielsen *et al.* (*9*) found for a commercial triply promoted catalyst (K₂O–CaO–Al₂O₃) at 149–309 atm and 370–495°C $\alpha = 0.62$–0.75 and $w = 1.5$, indicating the presence of N-atoms or radicals. Recently Guacci *et al.* (*2*) tested a series of commercial catalysts at 100–300 atm and 380–480°C and found values of α between 0.4 and 0.7 also with $w = 1.5$. Kubota and Shindo (*11*), as quoted by Ozaki *et al.* (*8*), found $w = 1.5$ for doubly promoted and $w = 1.0$ for singly promoted catalysts. From kinetic data as well as from isotope effects at relatively low temperatures and pressures ($\frac{1}{3}$–1 atm), however, Ozaki *et al.* (*8, 12*) conclude that there are NH-radicals on doubly promoted cat-

alysts ($w = 1.0$) and N on singly promoted catalysts ($w = 1.5$).

Three difficulties in comparing the results of activity measurements of different investigators are: (*a*) the different reaction conditions under which the catalysts have been tested, (*b*) the difference in chemical composition of the catalysts, and (*c*) the possible influence of traces of O-containing compounds (see experimental section). To contribute to the explanation of the promoter effect, and especially the influence of K on the nature of nitrogen-containing surface groups, six catalysts, which mainly differed in weight percent K, were investigated under a wide range of synthesis conditions.

EXPERIMENTAL PROCEDURES

Preparation of the catalysts. An industrial Fe catalyst in oxidized form (Al₂O₃ 2.90, K₂O 1.30, ZrO₂ 0.45, and SiO₂ 0.45 wt%) was reduced at 1 bar during about 100 hr in a H₂–N₂-mixture, increasing simultaneously the H₂ concentration and the temperature to 100% and 500°C, respectively. This last condition was maintained overnight (catalyst R, Table 1). After passivation at room temperature part of this catalyst was extracted with boiling water for 6 hr. The resulting K content was found to be 0.1 wt% (Catalyst RE), the Al, Zr, and Si contents being unchanged. Part of the catalyst RE was reloaded with K by soaking it

TABLE 1

Description of the Catalysts

Catalyst[a]	BET (m²g⁻¹)	K (wt%)[b]
R	8.5 ± 0.5	1.20
RE	8.5 ± 0.5	0.10
REL1	5.8 ± 0.1	0.55
REL2	4.3 ± 0.5	0.77
REL3	3.7 ± 0.3	1.20
REL4	2.3 ± 0.2	3.8

[a] The codes are used as follows: R = reduced, RE = R extracted, REL = RE reloaded with potassium.

[b] The potassium content is based on passivated catalysts.

under reduced pressure in water containing the desired amount of KOH. Subsequently the water was slowly evaporated and the catalyst was dried *in vacuo* during 3 hr at 550°C (catalysts REL1 to REL4). The amount of K present was then determined by atomic absorption before the activity measurements. From Table 1 it is clear that the surface area of a catalyst decreases when it is loaded with an increasing amount of K, as is well known from the literature (*13*). Some preliminary ESCA experiments were performed with the reduced forms of catalysts R and RE.

Activity measurements. About 4 g of catalyst (particle size 0.3–0.6 mm) was placed in a tubular reactor (length, 75 cm; internal diameter, 6 mm). The remaining volume was filled with γ-Al_2O_3. Two of these reactors were fitted parallel in an aluminium block and placed in a furnace. The temperature was measured in the center of the aluminium block, the axial difference over this block being always less than 2°C. From a supply vessel the 1 : 3 N_2–H_2-mixture was purified over columns of active carbon, a copper catalyst, and molecular sieves. The last purification step was a prereactor containing some Fe catalyst, which also made it possible to adjust the inlet concentration of NH_3. To obtain a constant degree of purification (<1 ppm O-containing compounds) the total flow rate through the purification train was kept constant (100 1/hr). The NH_3-concentration at the inlet and outlet of the reactors was measured by absorption in water and titration with 0.1 N HCl. Dilution with γ-Al_2O_3 of catalyst R gave no significant differences, as compared to experiments with the same catalyst without dilution, so that temperature gradients in the catalyst bed do not play a noticeable role.

Prior to activity measurements each catalyst was reduced again in synthesis gas (H_2/N_2 = 3), increasing both pressure and temperature to 200 atm and 500°C and maintaining this condition for 5 hr.

Activity measurements were performed with catalysis R and RE at 350 and 450°C and 5–200 atm. Measurements with the reloaded catalysts REL1, 2, 3, and 4 were performed at 400°C and 5–150 atm. All measurements were performed in a randomized sequence with respect to pressure and temperature. The catalyst performance was stable and reproducible for a period of at least some weeks during all measurements.

RESULTS

The Pressure Dependence of the Reaction Rate Constant

The reaction rate constant was calculated at a certain pressure and temperature from the integrated form of the rate Eq. (5):

$$k_1 = \frac{\phi_0}{W} \cdot \int_{x_{in}}^{x_{out}} \frac{dx}{(1 + x)^2 \cdot f(x)} \qquad (7)$$

where ϕ_0 is the molar flow rate at the inlet of the reactor based on 0% NH_3, W is the weight of catalyst, and x is the mole fraction NH_3. $f(x)$ follows from Eq. (5) written as $r = k_1 \cdot f(x)$, and K_{eq} is calculated as a function of temperature according to Gillespie and Beattie (*14*). Figure 1 shows the reaction rate constant as a function of the total pressure, computed for $w = 1.5$ and for $w = 1.0$ according to Eq. (7). In both cases α was chosen to be 0.7 as a reasonable, representative value (*2*). Not all catalysts can be described with either $w = 1.5$ or $w = 1.0$. The activities of R and RE were measured as a function of pressure at 350 and 450°C. The promoting effect is not influenced very much by the temperature, as shown in Fig. 2. The dotted lines in Fig. 1 have been obtained by interpolation from the appropriate Arrhenius plots.

Evaluation of the Experimental Data

The different pressure dependence of the reaction rate constants shown in Fig. 1 suggests that the value of w varies with the potassium content because a true reaction rate constant of a particular catalyst is a function of temperature only and must be
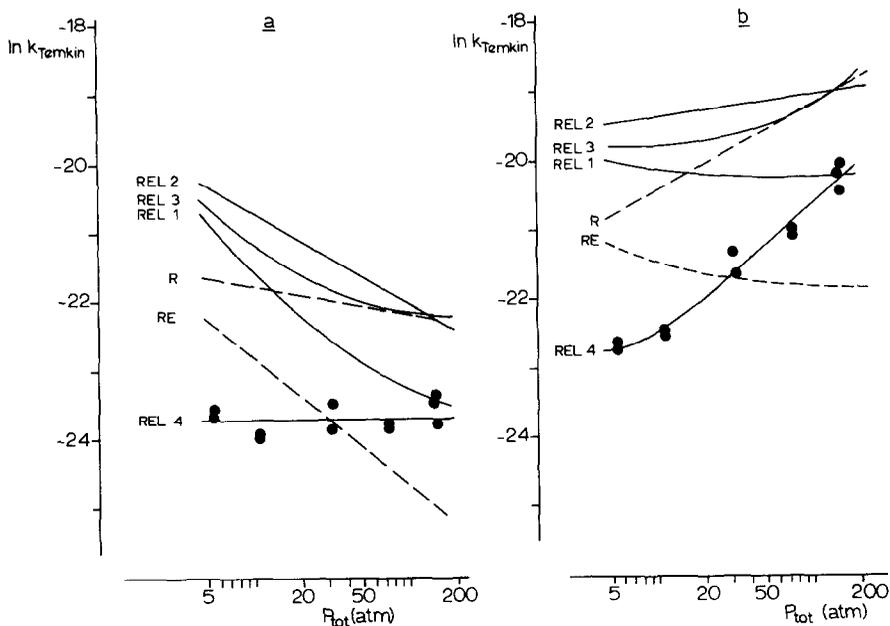
FIG. 1. The pressure dependence of k_{Temkin} at 400°C: (a) $\alpha = 0.7$ and $w = 1.5$; (b) $\alpha = 0.7$ and $w = 1.0$. For the sake of clarity only the experimental points of catalyst REL4 are given. The dotted lines are calculated by interpolation from Arrhenius plots (see text).

independent of pressure. For a series of experiments ($i = 1, \ldots, n$) with a certain catalyst at a chosen temperature over a wide range of pressures the optimum values of k_1, α, and w were calculated by a nonlinear least-squares method, mini-
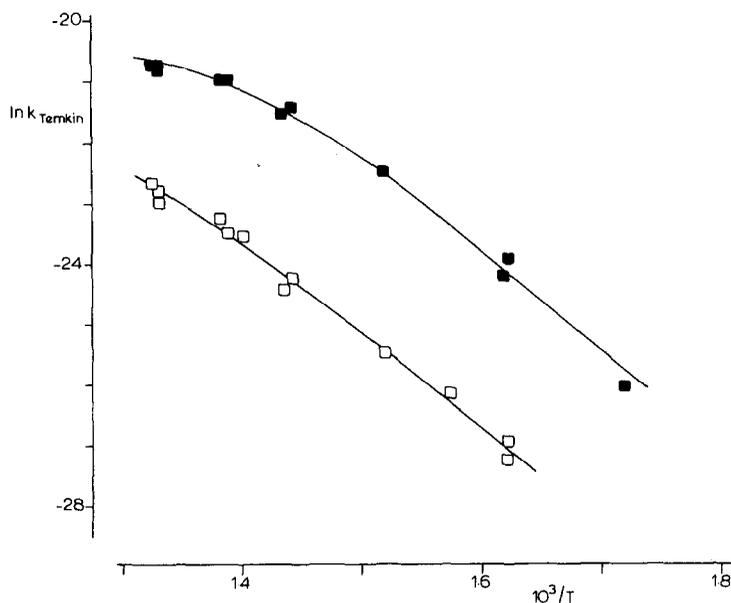

FIG. 2. Arrhenius plots of two catalysts at $P = 150$ atm. ■, R (1.2% K); □, RE (0.1% K). k_{Temkin} is calculated according to Eq. (7) with $\alpha = 0.7$ and $w = 1.5$.

mizing the function:

$$F = \sum_{i=1}^{n} \left[1 - \frac{\phi_{0,i}}{W \cdot k_1} \cdot \int_{x_{\text{in},i}}^{x_{\text{out},i}} \frac{dx}{(1+x)^2 \cdot f(x)} \right]^2 \quad (8)$$

which was evaluated from Eq. (7).

This method is somewhat different from those used by Nielsen *et al.* (9) and Guacci *et al.* (2). No variation with temperature was involved in our optimization, since the activation energy might vary with temperature (4, 12, 15). Also in the function F each experiment is given the same weight irrespective of the value of the conversion.

Experimental Results

Figure 3 gives the optimum values of k, α, and w of four catalysts. The values of ln k_1 for each single experiment as calculated from Eq. (7) at the optimum values of α and w illustrate the scatter due to experimental
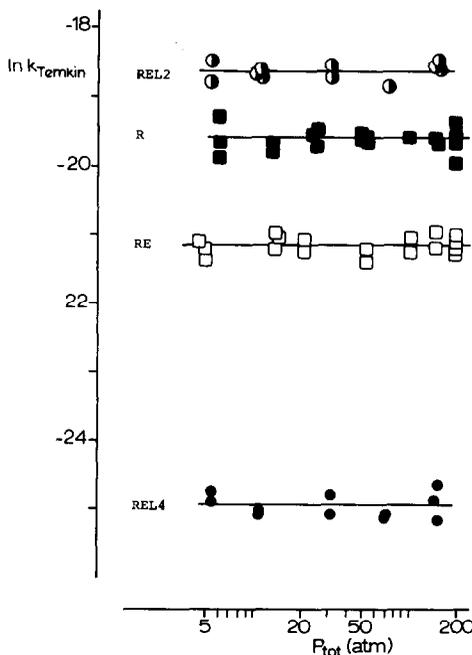
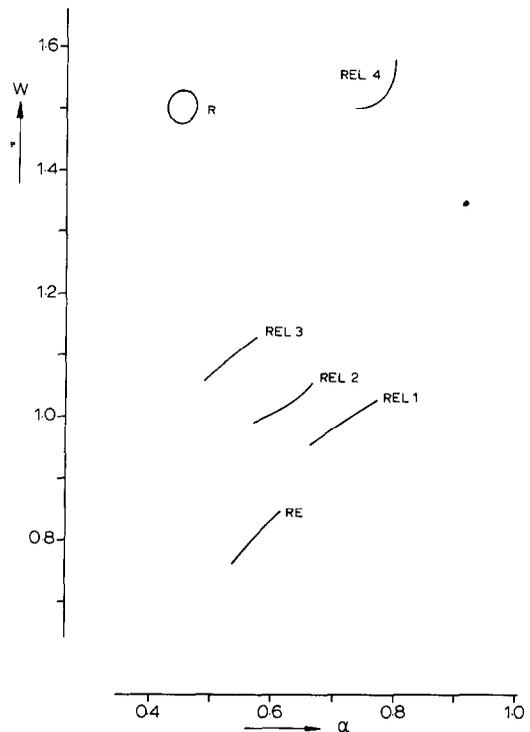

Fig. 4. Optimum values of α and w. The minimum of the function given by Eq. (8) lies in the indicated regions because, due to the scatter in the experimental results, it cannot be determined as a single point in the α–w plane.

errors. The mean deviation in ln k_1 is not more than 3%.

Figure 4 shows the combinations of α and w for each catalyst for which the function F reaches its minimum within the accuracy of the experimental measurements. α varies somewhat from one catalyst to another, in agreement with the results mentioned above (2, 9). Accepting this variation it is seen that there is a distinct increase of w as the catalyst is loaded with a larger amount of K.

The activities of catalysts with different values of α and w cannot be compared directly on the basis of their reaction rate constants because of their different dimensions. Therefore reaction rates (mole $NH_3/g \cdot cat/s$) have been calculated from rate Eq. (5) at concentration levels of 1 and 10% NH_3. The results are plotted in Fig. 5

Fig. 3. Some examples of the pressure dependence of k_{Temkin} at the optimum values of α and w; ■ R: $T =$ 721 K, $\alpha = 0.69$, $w = 1.30$; □ RE: $T = 618$ K, $\alpha = 0.48$. $w = 0.71$; ◐ REL2: $T = 674$ K, $\alpha = 0.65$, $w = 1.05$; ● REL4: $T = 674$ K, $\alpha = 0.79$, $w = 1.55$.

as a function of the total pressure (5–200 atm, 400°C). The dotted lines are interpolated from the calculations at 350 and 450°C as mentioned above.

At low pressures the activities of R and RE are about equal, while at high pressures R is much more active than RE, which agrees with remarks in the literature (4, 10) that K has a promoter effect especially at high pressures. The reloaded catalysts REL1, REL2 and REL3, however, show a relatively high activity also at lower pressures, as compared to R. REL4, on the other hand, has a very low activity at low pressures, but is as active as the other K-containing catalysts at higher pressures.

From the plots at 1 and 10% NH₃ (Fig. 5) it can be seen that, as at increasing NH₃-level in the reactor the reaction rate decreases according to Eq. (5), this decrease is much less for catalysts containing more

K. Apparently the promoter-effect of K is not necessarily operative only at high pressures, but seems to depend on the way the catalyst is loaded with K. Moreover, the promoter-effect tends to increase with increasing NH₃ concentration.

The relatively low activities of REL4 at low pressures might be due to the large amount of K making the Fe surface inaccessible for nitrogen at these low pressures.

DISCUSSION

Figure 1 is in agreement with the results presented by most authors, as mentioned in the Introduction, showing that for "doubly" promoted catalysts $w = 1.5$ and for "singly" promoted catalysts $w = 1.0$. This pronounced promoter effect is often described as a change of the electron donor-acceptor properties of the Fe surface by K (see e.g. (16)). This would be expected to
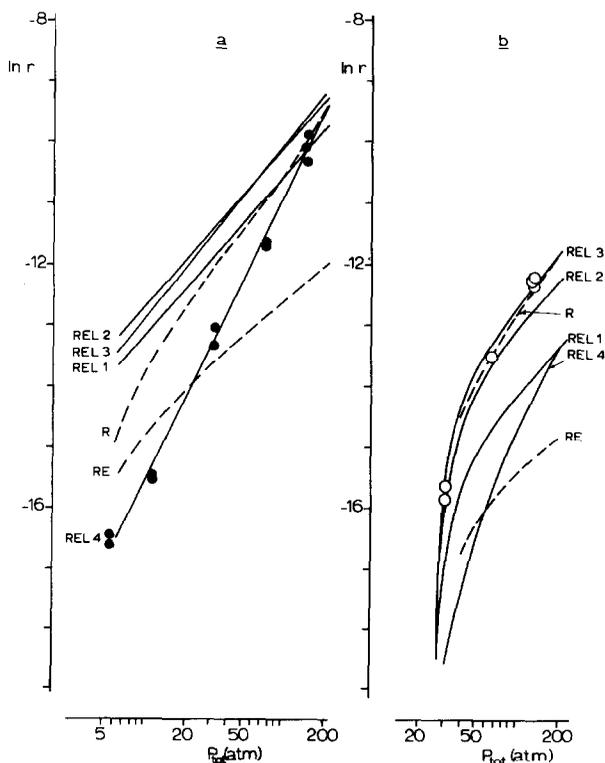

FIG. 5. Calculated reaction rates at 400°C. (a) At 1% NH₃; (b) at 10% NH₃ (this value represents the equilibrium state at $P = 26$ atm). The points represent reaction rates recalculated from experimental values to constant ammonia concentration. ●, REL4; ○, REL3.

lead, however, to a significant change in activation energy over the whole temperature range on going from a singly to a doubly promoted catalyst, which is not observed, as shown in Fig. 2. Similar results have been obtained for all catalysts investigated. It is also questionable whether K *compounds* exert such an influence (*17*).

Recently Ertl *et al.* (*18*) have found that *metallic* K on a Fe(100) single crystal surface increases tremendously the rate of N-chemisorption at 430 K and at pressures $<10^{-4}$ Torr. This phenomenon is also ascribed to the transfer of electronic charge from K to the Fe surface. It is doubtful whether this mechanism also accounts for the promoter-effect under synthesis conditions, since K is also a promoter in the prereactor of large scale NH_3 plants (*19*). Under those conditions K will certainly be present in ionic form, either due to traces of H_2O (or O_2), or due to the formation of KNH_2 (*5*).

In Fig. 4 the optimum values of α and w for all catalysts at 400°C are presented. The values of $w < 1.0$ for catalyst RE are not surprising, bearing in mind the suggestion of Ozaki *et al.* (*8*) that NH_2-groups might also be present on the surface so that the equilibrium:

$$NH_2(a) + 0.5\ H_2(g) \rightleftarrows NH_3(a) \qquad (9)$$
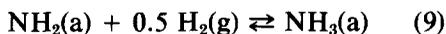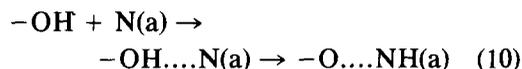
also plays a role. When this is the only equilibrium to be taken into account w would be 0.5

Since the value of w is associated with the form in which N is chemisorbed, we will discuss the surface structure of promoted Fe catalysts to some extent. Small amounts of promoters already cover a great part of the highly heterogeneous surface (*6, 9, 10, 13*). This picture is supported by our ESCA measurements which show that a well-reduced Fe catalyst contains oxidized Fe even ten layers below the outer surface. It is also known that it is hardly possible to prepare a "clean" oxygen-free Fe surface unless extreme precau-
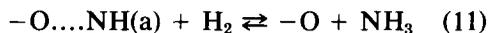
tions are used (*20, 21*). Thus the catalyst surface consists of small metallic Fe and oxidic domains (*9*), probably of at most a few nm in diameter.

Infrared studies demonstrate that hydroxylic groups are present on reduced MoO_3/Al_2O_3 catalysts (*22*) and on reduced Fe/MgO catalysts (*23*). Although no direct evidence is available, it seems reasonable to assume that on Fe/Al_2O_3 catalysts OH-groups are also present, which is not inconsistent with available literature data (see for instance (*24, 25*)). Due to the large charge/radius ratio (z/R) of the Al-ions, the OH-groups are highly polarized and are therefore able to form H-bonds. This is clearly reflected by the crystal structure of hydroxides of cations with a large z/R ratio (*26*).
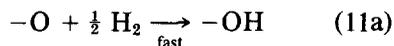
Accordingly, we suggest that, retaining the adsorption and/or dissociation of N_2 molecules as the rate-determining step, the presence of NH or NH_2 groups on singly promoted catalysts can be explained by a fast reaction of dissociatively adsorbed N on the metallic parts with these strongly polarized hydroxylic groups on the neighboring oxidic parts of the surface. This can be represented schematically by

$$-OH + N(a) \rightarrow$$
$$-OH....N(a) \rightarrow -O....NH(a) \quad (10)$$

and

$$-O....NH(a) + H_2 \rightleftarrows -O + NH_3 \quad (11)$$

followed by

$$-O + \tfrac{1}{2}\ H_2 \xrightarrow[\text{fast}]{} -OH \qquad (11a)$$

NH_2-groups can be formed analogously from NH-groups, depending on the effective polarizing power of the ions in the catalyst. Thus for catalysts containing acidic OH-groups, the resulting value of w in the modified Temkin rate expression (Eq. (5)) will range from 1.0 down to 0.5, depending on the ratio of NH- and NH_2-groups. This is supported by the observations that NH- or NH_2-groups are also

present on catalysts supported on oxides with cations with a large z/R ratio (23–25), where the influence of these oxides will be even stronger than when they are only present in a few wt% as promoters.

The OH-groups in KOH, on the other hand, behave quite differently. At least above 180°C they show spherical symmetry and are therefore not able to form H-bridges (26). On a catalyst loaded with K the nature of the OH-groups will thus be changed. Either a reaction between the acidic OH-groups and KOH such as

$$-OH + KOH \rightarrow H_2O + -OK \quad (12)$$

can occur or KOH is adsorbed on the metallic parts of the surface so that the adsorbed nitrogen is screened from the acidic OH-groups on the oxidic parts of the catalyst surface. In both cases reaction (10) cannot occur under synthesis conditions and the metal surface is covered by N-atoms only, to an extent which depends on the amount of K present. This results in a higher order in H_2, up to the maximum value for w of 1.5 for doubly promoted catalysts with optimum K-content. The promoter-effect is thus merely an increase of NH_3 formation rate by an increase of the order in H_2, which is most pronounced at higher pressures (4, 27).

If it is true that the nature of the OH-groups on iron catalysts is influenced by the charge/radius ratio of the promoting cation(s), as proposed above, an analogous behavior is expected when comparing the activities of catalysts promoted with alkali metals ranging from Cs to Li. In fact, we have observed in recent experiments that catalysts promoted with Li, which has the highest charge/radius ratio of the alkali metals, act as singly promoted catalysts with $w = 1$, indicating the presence of NH-groups. This will be the result of a less pronounced influence of the acidic OH-groups of Al_2O_3 due to the higher polarizing effect of Li as compared to that of K. The complete results will be presented separately. Some additional ESCA experiments

will be performed in order to try to substantiate the proposed mechanism.

REFERENCES

1. Temkin, M., and Pyzhev, V., *Acta Physicochim. USSR* 12, 327 (1940).
2. Guacci, U., Praina, F., Buzzi Ferraris, G., and Barrisone, R., *Ind. Eng. Chem., Proc. Des. Dev.* 16, 166 (1977).
3. Temkin, M., *Zhur. Fiz. Khim.* 24, 1312 (1950).
4. Bokhoven, C., van Heerden, C., Westrik, R., and Zwietering, P., in "Catalysis III" (P. H. Emmett, Ed.). Reinhold, New York, 1955.
5. Van Ommen, J. S., Bolink, W. F., Prasad, J., and Mars, P., *J. Catal.* 38, 120 (1975).
6. Nielsen, A., in "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia," 3rd Ed. Julius Gjellerups Forlag, Copenhagen, 1968.
7. Frankenburg, W., in "Catalysis III" (P. H. Emmett, Ed.). Reinhold, New York, 1955.
8. Ozaki, A., Taylor, H. S., and Boudart, M., *Proc. Royal Soc. London* A258, 47 (1960).
9. Nielsen, A., Kjaer, J., and Hansen, B., *J. Catal.* 3, 68 (1964).
10. Brunauer, S., and Emmett, P. H., *J. Amer. Soc.* 62, 1732 (1940).
11. Kubota, H., and Shindo, M., *Chem. Eng. (Japan)* 23, 242 (1959).
12. Ozaki, A., Aika, K., and Morikawa, Y., *Proc. Internat. Congr. Catalysis, 5th* (Florida 1972), p. 1251. North Holland/American Elsevier, 1973.
13. Love, K. S., and Brunauer, S., *J. Amer. Chem. Soc.* 64, 745 (1942).
14. Gillespie, L. J., and Beattie, J. A., *Phys. Rev.* 36, 743 (1930).
15. Love, K. S., and Emmett, P. H., *J. Amer. Chem. Soc.* 63, 3297 (1941).
16. Jones, A., and McNicol, B. D., *J. Catal.* 47, 384 (1977).
17. Ugo, R., Proc. Internat. Congr. Catalysis, 5th (Florida 1972), p. 1262. North Holland/American Elsevier, 1973.
18. Ertl, G., Weiss, M., and Lee, S. B., *Chem. Phys. Lett.* 60, 391 (1979).

19. Mars, P., private communications.

20. Almquist, G. A., *J. Amer. Chem. Soc.* **48**, 2822 (1926).

21. Bozso, F., Ertl, G., Grunze, M., and Weiss, M., *J. Catal.* **49**, 18 (1977).

22. Fransen, T., *Thesis,* Twente University of Technology, The Netherlands, 1979.

23. Brill, R., Jirti, P., and Schulz, G., *Z. Phys. Chem. Neue Folge* **64**, 215 (1969).

24. Oh-Kita, M., Aika, K., Urabe, K., and Ozaki, A., *J. Catal.* **44**, 460 (1976).

25. Nakata, T., and Matsushita, S., *J. Phys. Chem.* **72**, 458 (1968).

26. Wells, A. F., "Structural Inorganic Chemistry," 4th ed. p. 516. Oxford, 1975.

27. Larson, A. T., and Brooks, A. P., *Ind. Eng. Chem.* **18**, 1305 (1926).