

# ON THE ROLE OF ALKALI METALS IN AMMONIA SYNTHESIS

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Bowker et al. [1] recently predicted rates of ammonia synthesis at industrially relevant temperatures and pressures. They used a compilation of detailed kinetics of adsorption and desorption of nitrogen, hydrogen and ammonia, based on the potential energy diagram for low coverage of nitrogen [2]. Agreement with known activities could only be achieved by assuming that, under these conditions, the dissociative adsorption of  $N_2$  is activated and, therefore, the potential well for adsorbed N and H atoms should be raised. In their concluding remarks they put forward the necessity of quantifying their calculations for iron catalysts containing potassium. This (again) draws attention to the role of K in the mechanism of the synthesis reaction.

In a previous communication from this laboratory, Altenburg et al. [3] reported kinetic measurements for the  $N_2+H_2$  reaction over doubly promoted commercial catalysts with K-contents ranging from 0.55 to 3.8 wt%. We showed that in a temperature range from 620 to 720 K and at pressures from 0.5 to 20 MPa the reaction rate of doubly promoted Fe catalysts can be expressed as

$$r = k \cdot f_{N_2} \cdot \left( \frac{f_{H_2}^w}{f_{NH_3}} \right)^{2a} \cdot \left\{ 1 - \frac{f_{NH_3}^2}{f_{H_2}^3 \cdot f_{N_2} \cdot K} \right\} \quad (1)$$

where  $k$  = reaction rate constant

$f_i$  = fugacity of species  $i$

$w$  = order in hydrogen

$a$  = constant

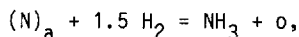
$K$  = equilibrium constant of synthesis reaction

$a$  and  $w$  were found to be a function of catalyst formulation only, whereas  $k$  was a function of temperature only. This rate equation was found to give the best fit for all the catalyst formulations examined.

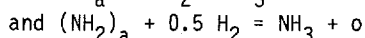
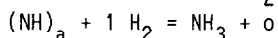
For catalysts with a very low K-content the order in hydrogen was found to be 0.5 and this order increased with increasing K-content. On a catalyst with

optimum formulation it was found to be 1.5. These apparent orders can be derived from the hydrogenation equilibria of the predominant N-containing species on the surface, assuming the chemisorption and/or dissociation of  $N_2$  to be the rate determining step.

Were the following equilibrium established (a = adsorbed state, o = vacancy):



the resulting order in  $H_2$  would amount to 1.5. Analogously the steps



lead to apparent orders of 1 and 0.5 respectively. Altenburg et al. gave a full derivation of the equations.

From these results, we concluded that a low K-content would favour the rapid formation of  $(NH_2)_a$  species, whereas higher K-contents would favour  $(NH)_a$  and  $(N)_a$  species. We tried to explain these findings by the speculation that alumina OH-groups play an important role in the hydrogenation of  $(N)_a$  species through their ability to form H-bridges, but only at low K-contents. At higher potassium loads, the nature of these OH-groups was thought to be changed by the alkaline nature of K, making them less effective for conversion of  $(N)_a$  to  $(NH)_a$  (apparent order in  $H_2 = 1$ ) or even to  $(NH_2)_a$  (order = 0.5).

However, we were not able to prove the presence of predominantly hydrogenated N species in catalysts with low K-content, nor the presence of mainly  $(N)_a$  in catalysts with higher K-content. Among others, Ertl [4] was able to detect with ESCA under UHV conditions the presence of  $(N)_a$  and  $(NH)_a$  species on pure iron crystallites. On the other hand, it was not possible to reduce our commercial triply promoted catalysts completely; ESCA pictures of our samples always revealed the presence of considerable amounts of  $Fe^{2+}$ . Also, the presence of OH-groups could not be confirmed either.

Recently, Roberts et al. [5] showed by electron spectroscopy that N chemisorbed on a Zn(0001) surface was hydrogenated by hydroxyl species. Although this system is quite different from that used in ammonia synthesis, this spectroscopic evidence for the formation of  $(NH)_a$  and  $(NH_2)_a$  groups by hydroxylic species in our opinion has important implications for the mechanism of the ammonia formation and specifically for the hypothesis mentioned above.

In the light of recent developments discussed above it is now relevant to add some additional experimental results and to discuss some recent observations which may contribute to the quite speculative hypothesis which we previously put forward. If the presence of potassium influences the nature of OH-groups, the other elements of the 1A group would influence those OH-groups in a different way because of their different charge/radius ratio  $z/r$ . To test this idea, a series of catalysts was prepared in which the K was replaced by other group 1A elements but with the same molar percentages.

A singly promoted catalyst (3 wt%  $Al_2O_3$ ) was prepared by coprecipitation from an aqueous solution of 2 molar  $Fe(NO_3)_3$  and 0.1 molar  $Al(NO_3)_3$  with ammonia. This

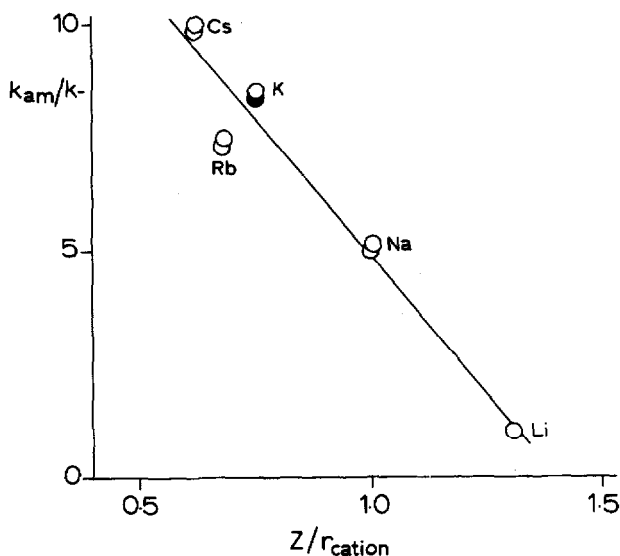


FIGURE 1 The activity of alkali promoted iron catalysts at 10 MPa and 673 K as a function of charge/radius of the alkali metal. Reaction rate constants were calculated from equation 1 with the values  $a = 0.5$  and  $w = 1.5$ .  $k_{AM}$  = reaction rate constant of the doubly promoted catalysts,  $k_-$  = reaction rate constant of the reference singly promoted catalyst with 3 wt%  $Al_2O_3$ . ○ impregnated from a carbonate solution, ● impregnated from a KOH solution.

product was suspended in a solution of alkali carbonate, and in the case of potassium also in a solution of KOH. After drying at 110°C the product was pressed, crushed and the fraction with diameter 0.3-0.6 mm was used for activity measurements, catalyst reduction and activity measurements are described previously [3].

The activity of the K-containing precipitation catalysts was comparable with the commercial doubly promoted one reported previously, no matter in which stage of the preparation, or in which form (KOH,  $K_2CO_3$ , this work) the potassium was added [3]. Thus, the catalyst activity is governed mainly by its chemical composition, not by the preparation method, in agreement with the findings of Dmitrenko [6] for molten iron catalysts.

The activity of the promoted catalysts was compared with that of the unpromoted one, the results of these measurements being given in Figure 1. It can be seen that the influence of the alkali additives decreases with  $z/r$  of the alkali metal. This is in agreement with the mechanism proposed earlier, which is based on how the promoter may influence the surface OH-groups. If  $z/r$  of the alkali metal is small the formation of NH and/or  $NH_2$  is apparently prevented, possibly by the formation of H-bridges between the OH-groups already present on the surface and hydroxyl-groups of the alkali hydroxide. At high  $z/r$  ratios, as for Li and Na, the electron density on the oxygen atom in the surface OH group is lower, so that H-bridge formation will

be less favourable. This means that N-H (and/or  $\text{NH}_2$ ) group formation can take place, thus decreasing the promotor effect. For reasons of comparison the reaction rate constants in Figure 1 are calculated with the value of  $w = 1.5$  which applies to doubly promoted catalysts. In fact, the kinetic behaviour of Li-containing catalysts is best described by equation 1 with the value  $w = 0.5$ , typical of singly promoted catalysts.

We agree with the idea of Bowker et al. [1] of paying more attention to the behaviour of commercial catalysts, but we also suggest the application of modern surface techniques in order to study the degree of hydrogenation of N-species as a function of catalyst formulation.

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