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On the rate-determining step and the role of potassium in the catalytic synthesis of ammonia

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The simple concept of a single rate-determining step, the dissociation of N_2(a), in ammonia synthesis is inconsistent with experimental results. It is proposed that three reaction steps,

$$N_2(a) \rightarrow 2N(a) \quad (1)$$

$$N(a) + H(a) \rightarrow NH(a) \quad (2)$$

$$NH_3(a) \rightarrow NH_3(g) \quad (3)$$

are dominant in determining the rate of synthesis. Under industrial conditions reactions (2) and (3) are more important than (1). The role of K^+ as promoter in these reactions is discussed, especially as an "anchor" for adsorbed oxygen.

Keywords: Ammonia; synthesis; nitrogen; rate-determining step; potassium promotion

1. Introduction

It is a truth universally acknowledged, that the dissociation of molecular nitrogen, must be the rate-determining step in the catalytic synthesis of ammonia. From the work of Emmett and Brunauer [1] some 60 years ago, where they showed that the overall rate of nitrogen adsorption on an industrial catalyst is of the same order as the rate of ammonia synthesis, to the modern surface science, reviewed by Ertl [2], a self-consistent mechanism of ammonia synthesis has been assembled. It was uncertain from the early results whether the hydrogenation steps involved dissociatively adsorbed nitrogen, N(a), or molecular nitrogen, N_2(a), but modern surface chemistry has shown conclusively that the hydrogenation of N(a) is the principal route. Further, kinetic modelling by Stoltz and Norskov [3], using the surface science data together with the assumption that reaction (1) is rate-controlling, gave a very good fit of calculated rates of ammonia synthesis with the rates

$$N_2(a) \rightarrow 2N(a) \tag{1}$$

observed under industrial conditions.

Nevertheless some features of the reaction are still not fully understood, especially those relating to precursor states of adsorbed nitrogen and the mechanism of promoter action. The early view of alumina as a physical or structural promoter and potash (in whatever form the potassium is present) as a chemical or electronic promoter has been shown to be too simple [4].

2. Problems of the orthodox view

There are various experimental results which do not fit well into the orthodox mechanism, especially in its application to industrial synthesis conditions.

1. Johnson and Roberts [5] showed in 1979 that nitrogen dissociated readily on a polycrystalline iron surface at 80 K. On Fe(111), the most active iron crystal face present in the catalyst, the sticking coefficient for nitrogen in reaction 1 is 4×10^{-6} at 683 K, with an activation energy of only ca. 42 kJ mol^{-1} [6]. The activation energy for reaction (2), given by Ertl [6] as about 117 kJ mol^{-1}, is the highest value of any of the

$$N(a) + H(a) = NH(a) \tag{2}$$

reaction steps in ammonia synthesis. Ertl [2] states: "It is, however, quite apparent that the nature of the rate-limiting step would switch from dissociative nitrogen adsorption to hydrogenation of the adsorbed atomic nitrogen species if the temperature were lowered sufficiently because of these differences in activation energy". A sufficient increase in reaction pressure would bring about the same effect.

2. Emmett and Brunauer [1] found that the rates of ammonia synthesis on their catalysts were of the same order of magnitude as the nitrogen chemisorption rates. Later groups of workers have confirmed these results but none has tested this relation at pressures above 1 bar. Some of the most careful work was by Scholten et al. [8], who followed nitrogen adsorption gravimetrically during ammonia synthesis at 1 bar. In the range 210°–295 ° C ammonia synthesis and nitrogen chemisorption rates were equal to within experimental error. However, at both 165° and 65°C, "the ammonia synthesis rate was lowered by a factor of about 30 compared with that expected from the chemisorption run at the same temperature and nitrogen pressure" [8]. The most likely explanation is that of Ertl above, relating to the activation energies of reactions (1) and (2). On this basis, the experimental results were used in a simple calculation to assess the

relevance of rate control by reaction (2) under industrial conditions. The ratio, ϕ, of the rates of reactions (1) and (2) is given by the expression:

$$\phi = [N_2] \cdot f(\theta) \cdot (A_1/A_2) \cdot \exp(-(E_1 - E_2)/RT)$$

where $f(\theta)$ is a function of the surface coverages of the various adsorbed species, and the other symbols are conventional. From the experiments of Scholten et al. [8], $\phi = 1$ for $[N_2] = 0.25$ bar at some temperature in the range 440–480 K, so, with the values of $E_1 = 42$ kJ mol^{-1} and $E_2 = 117$ kJ mol^{-1} given by Ertl [6], the range of possible values of $f(\theta) \cdot (A_1/A_2)$ could be calculated. With the assumption that $f(\theta)$ is approximately constant (probably valid for the low accuracy of this calculation), these values of $f(\theta) \cdot (A_1/A_2)$ were then used in the same expression to calculate temperatures at which $\phi \sim 1$ under industrial conditions (e.g. total pressure 250 bar, $[N_2] = 62.5$ bar). This indicated that reaction (2) should be significant in rate control under industrial pressures at temperatures of 300°–450°C and below. However, as Scholten et al. [8] used a singly-promoted (Al) catalyst their results are not necessarily applicable in detail to conventional doubly-promoted catalysts (see below).

3. For nitrogen dissociation to be the rate-determining step, the steady-state coverage of N(a) (and indeed those of NH(a), etc.) on the catalyst during ammonia synthesis would be expected to be low. This was observed [6] in experiments with a Fe(111) surface at total pressures below 1 bar for $p(H_2) > 50$ Torr. However, various studies with industrial catalysts at or above atmospheric pressure indicate a high coverage of reactive N(a) exists under these conditions. A transient-kinetic analysis [7] of the synthesis reaction over a commercial catalyst indicated that N(a) was the most abundant reactive intermediate, with coverages in the range 0.1–0.7 under reaction conditions. These are in broad agreement with the earlier *in situ* values of 0.44–0.54 at 1 bar reported by Scholten et al. [8]. High coverages of N(a) are also predicted in calculations for industrial synthesis conditions based on surface science data. Stoltze and Norskov [3] estimate N(a) coverage to be ca. 0.75 in the presence of ammonia, and Waugh and co-workers [9,10], with two different models, calculate N(a) coverages of 0.84 and 0.98 for synthesis at 720 K and 108 bar.

4. Recent TPD experiments by Vandervell and Waugh [11] on industrial catalysts which had been synthesising ammonia gave two nitrogen desorption peaks, one at 120 K (corresponding to molecular nitrogen on clean Fe) and one at 800–820 K (corresponding to adsorbed atomic nitrogen). There was no peak from any higher-energy precursor molecular state, e.g., the potassium-promoted state proposed [2] as the reactant in the rate-determining step. Nwalor et al. [7], from the results of steady state isotopic transient experiments, also concluded that nitrogen was not present in significant amounts as N_2(a) on the surface of the working catalyst.

5. The stoichiometric number of rate-determining step in ammonia synthesis over an iron catalyst was found to be 2 both near [17,18] and far [19] from

equilibrium. Boudart and Djega-Mariadassou [20] point out that this is compatible with reaction (2) being rate-determining but not with reaction (1).

6. It has been proposed [2,4,6,21] that the Fe(111) surface is dominant in industrial ammonia synthesis catalysts and UHV data for this surface has been used successfully in modelling ammonia synthesis [3,9,10]. Nevertheless the hydrogen desorption spectrum from a *working* industrial ammonia synthesis catalyst [11] indicated that no extensive reconstruction to the Fe(111) surface had occurred. Also, temperature cycling during ammonia synthesis at 30 bar and especially at 90 bar gave a marked hysteresis in rate. Richard and Vanderspurt [22] attributed this effect to "reversible reconstruction of the catalyst surface on a time scale of hours ... [this] reconstruction is inhibited at higher total pressure".

7. Potassium promotion still raises difficulties of interpretation. If nitrogen dissociation is the rate-determining step then the promoter action must apply to this reaction step. Ertl [2] has shown that K^0 on iron crystal surfaces accelerates nitrogen dissociation by electron donation, sometimes by factors much greater than those achieved by the potassium promotion of ammonia synthesis catalysts. Further, the rate of ammonia synthesis at ca. one bar is little affected by potassium addition to a singly-promoted (alumina) catalyst [12,13].

There is, however, much evidence [4,14,15] that there is no K^0, free or adsorbed, on industrial ammonia synthesis catalysts. The iron phases in these catalysts are not normally fully reduced and the potassium species on the iron metal surface is (KO). It remains possible that strongly adsorbed, metallic potassium, undetected by *ex situ* methods, could be formed under highly reducing synthesis conditions and then act as promoter. Even so, the lack of sensitivity of the promoted catalysts to extremes of reduction (see below) argues against significant promotion by $K^0(a)$. Paal et al. [16] found the promotional effect of potassium on the rate of nitrogen dissociation on a polycrystalline iron surface to be decreased by the co-adsorption of oxygen. This was attributed to site blockage by oxygen, but, when all the potassium is present as K^+, electron donation must be negligible. Indeed electron donation from an argon atom is more facile than from a potassium cation (ionisation energies: Ar, 1521 kJ mol^{-1}; K^+, 3069 kJ mol^{-1}). Similar considerations apply to (KO)(a) species.

8. In experiments with catalysts of different potassium content, Altenburg et al. [12] found that in synthesis over 5–200 bar pressure the reaction order in H_2 (in a modified Temkin rate equation) increased from 0.7 to 1.5 with increasing potassium content. This result indicates that a common mechanism with the same rate-determining step was not applicable to these catalysts.

9. Rubidium or caesium can replace potassium in synthesis catalysts but there is disagreement over the relative efficiencies of the alkali promoters. In work with precipitated catalysts at 100 bar, Bosch et al. [23] found the Cs-promoted catalyst to be the most effective, with an activity of ca. 20% higher than that of the K-promoted catalysts. The Rb-promoted catalyst, even though ca. 7.4 times

more active than the catalyst without alkali, was ca. 10% less active than the K-promoted catalysts. In contrast, fused catalysts made with Rb or Cs show much lower activities than conventional fused, K-promoted catalysts [24]. If alkali promotion is critically dependent on electron donation from M^0 then both Rb^0 and Cs^0 would be expected to be much more effective promoters than K^0. Clearly this is not the case.

Calculations by van Ommen et al. [15] showed that potassium hydroxide was the only bulk potassium compound stable under industrial ammonia synthesis conditions. Similar calculations [25] for caesium compounds show that water levels of less than 1 ppb would be needed for metallic caesium to be the stable bulk phase. However, the various suboxides of Rb and Cs, which should be effective electron donors, may well be formed at the ppm levels of water of conventional synthesis conditions. This is further evidence that it is improbable that electron donation is the mechanism of potassium promotion of ammonia synthesis. This casts further doubt on the identification of reaction (1) as the single, rate-determining step.

10. C_7 sites, i.e. Fe atoms coordinated to 7 other Fe atoms, are believed [4] to be the most active iron atoms for ammonia synthesis. It is not apparent that nitrogen dissociation is necessarily faster on C_7 than on other sites, especially as these highly coordinated sites are less effective in adsorbing carbon monoxide.

3. The rate-determining step?

Boudart and Tamaru [26] have given a rigorous operational definition of the rate-determining step, if such exists, for one-way and two-way catalytic cycles. This requires an accurate determination of the true rate equation (in contrast to empirical or semi-empirical rate equations) but as there is unresolved disagreement over kinetic modelling of the synthesis reaction [3,9,10] Boudart and Tamaru's approach is difficult to use unambiguously for ammonia synthesis.

A modified, less rigorous approach is the following: by use of all the data available (both kinetic and other), examine the probable effect on the overall reaction rate of an order of magnitude increase in the rate constant of a reaction step. If this probable effect is a large, even proportional, increase in overall rate, then the step in question is the rate-determining step or one of the rate-determining steps. This approach, like Boudart and Tamaru's definition, is in accord with the general, intuitive understanding of what is meant by "rate-determining step".

We can apply this approach to reaction (1). For synthesis at low pressure (below ca. 1 bar) the accumulated experimental results show clearly that an order of magnitude increase in the rate constant of reaction (1) would give a correspondingly large increase in the rate of ammonia synthesis. There is no controversy here. At somewhat higher pressures, 1–10 bar, the Fe surface has a high coverage of reacting N(a). An order of magnitude increase in the rate constant of reaction (1) would now give an increase, but much less than proportional in N(a) coverage and so in the rate of ammonia synthesis. Thus the rates of some subsequent step or steps also influence the overall rate. Even so, Nwalor et al. [7] showed that reaction (1) was far from quasi-equilibrium at synthesis pressures of 2–4 bar, so none of the subsequent reactions can be regarded as *the* rate-determining step.

No comparable work with ^{15}N appears to have been done at industrial synthesis pressures, 100–300 bar. Nevertheless the N(a) coverages on Fe must be high, so the influence of an order of magnitude increase in k_1 would probably have little effect on synthesis rate. Reaction (1) may be unexpectedly facile at high pressures: under industrial synthesis conditions the specific gravity of the reactant gas is ca. 0.05. Low-energy precursor states to N_2 dissociation of low adsorption energy, insignificant at low pressures or even low temperatures, could be important.

Application of the criteria to reaction (2) gives the inverse of the pattern for reaction (1): reaction (2) is of increasing importance in controlling overall synthesis rate as the synthesis pressure is increased. At low conversions (i.e. conditions at the reactor inlet) increases in the rate constants of subsequent reaction steps seem unlikely to influence overall reaction rates. However, near-equilibrium the partial pressure of ammonia in a converter can be 10 bar or higher. Temperature-programmed desorption of ammonia from Fe(111) is modified by potassium, with a decrease in ammonia adsorption energy [27]. Strongin and Somorjai [4] suggest that a promoter action of potassium is that of lowering the concentration of ammonia on the Fe surface, thus making more sites available for dissociative nitrogen chemisorption and so enhancing the overall rate of ammonia synthesis. If this is the case then reaction (3) also controls the overall rate.

$$NH_3(a) = NH_3(g) \tag{3}$$

Thus there is considerable evidence that, under various synthesis conditions, reactions (1), (2) and (3) all control the rate of ammonia synthesis. Only at low pressures can a single rate-determining step, reaction (1), be identified and for higher pressures this assumption is invalid. Under industrial conditions reactions (2) and (3) are more important than reaction (1) in controlling the synthesis rate. The success of the Stoltze and Norskov [3] model in fitting industrial data, despite the philosophically unsound premise that reaction (1) is the rate-determining step, may be seen as another example of the ease with which many kinetic equations can be fitted to a given set of kinetic results.

4. Role of the potassium promoter

This analysis of the rate-determining steps in ammonia synthesis leads to a different interpretation of the role of the potassium promoter. The small or negligible promotion effect at synthesis pressures of 1 bar or below, where reaction (1) is the rate-determining step, is seen to be in agreement with the analysis above that K^+ of KO(a) is unlikely to promote nitrogen dissociation. In contrast, KO(a) can plausibly promote both reactions (2) and (3), so accounting for the increased promotion effect of potassium at high pressures when reactions (2) and/or (3) become rate controlling.

Working industrial catalysts are not fully reduced [14]. The effect of residual surface oxygen on reaction (2) can be predicted from Kishi and Roberts' [28] work: the N(1s) binding energy was shifted ca. 1.0 eV to a higher binding energy by co-adsorbed oxygen, indicating a weakening of the Fe-N bond. An analogous "loosening of the surface nitrogen bond" as a result of sulphur adsorption has also been reported [29]. (The XPS N(1s) peaks of nitrogen adsorbed on industrial catalysts were too broad for a comparable shift to be detected [14]). Thus partial coverage of O(a) should increase the rate of reaction (2) by weakening the Fe-N bond. This has now been observed directly by Vandervell and Waugh [30] over both unsupported polycrystalline iron and industrial synthesis catalysts. Oxygen addition at low levels to a working catalyst gave initially a rise of several times in ammonia synthesis rate (i.e., comparable with that given by potash promotion under industrial conditions), followed by de-activation as extensive oxidation took place. A similar transitory increase in rate was seen when the supply of oxygen was stopped and the synthesis gas re-reduced the catalyst. On both oxidation and reduction cycles, maximum activity was found with partially-oxidised catalysts. This pattern of activity would be expected from the direct promotion of reaction (2) by O(a), although O(a)-promoted reconstruction of the iron surface may also contribute. The coverage of O(a) on Fe in a working catalyst is typically 1–2% whereas KO(a) coverage is typically 40% [14]. Thus a promoter role for K^+ could be that of "anchor" for O(a), greatly increasing the coverage of O(a). Recent work on potassium promotion also supports this interpretation of the promoter action. Tornqvist and Chen [31] studied ammonia synthesis at 3.5 bar over polycrystalline iron foils close to the steady state. Oxygen was always seen associated with potassium at the iron surface after ammonia synthesis rate measurements. The maximum promotion effect on the rate was 3 × only, at $\theta_K \sim 0.12$. The synthesis rate fell to zero for $\theta_K > 0.25$, corresponding to K(a) with 4 O(a) or N(a).

The promotions of reaction (3) by KO(a), observed experimentally [4], can be interpreted as the displacement of a weak base by a strong base.

Two further points can be made. The activities of promoted catalysts are not dependent on the degree of reduction beyond that normally employed. The rates of ammonia synthesis in plants using a liquid nitrogen wash in the recycle loop, which reduces residual water to an extremely low level, are no higher than those observed in more conventional plants in which ammonia is removed by refrigeration [24]. This is in accord with the role of K^+ as an "anchor" for O(a). The relative effectiveness of alkali metal cations as O(a) "anchors" must depend on the details of the surface chemistry. Although there is no a priori reason to expect Rb^+ and Cs^+ to be more effective than K^+, any alkali cation, provided that the catalyst activation procedure gives MO(a) species on the metallic iron surface, should function as an "anchor" for O(a).

5. Some general conclusions

There is strong evidence that the ammonia synthesis reaction under industrial conditions cannot be described kinetically in terms of a single rate-determining step. This is not surprising for an optimised industrial catalyst and process. The result of the successful development of catalyst and process, whether purely empirical or based on catalytic science, is typically the elimination of the rate-determining step, i.e. the removal of the process bottleneck. When, to take the Boudart and Tamaru definition [26], the rate constants of several process steps appear in the rate equation then improvements in more than one reaction step is required for significant increases in overall rate.

There has been much discussion, e.g. [32], of a "pressure gap" between UHV and industrial catalytic conditions, and the relations between data obtained under these very different conditions. The discussion above shows that the "pressure gap" in ammonia synthesis, across which promoter action and the kinetic pattern change, is smaller, between < 1 and > 100 bar. As a consequence, some extrapolations to industrial conditions from conventional catalytic experiments at ~ 1 bar have been misleading. The use of separate reaction step parameters obtained from UHV experiments has avoided this problem, but the extent and consequences of partial surface oxidation were underestimated. There is a pattern emerging [33] that the most active state of many metal catalysts, even in hydrogenation reactions, is one of partial surface oxidation. Perhaps the conclusion to be drawn is no more than commonplace: UHV, single crystal and conventional catalytic experiments are all needed to understand industrial catalytic processes.

Carbon-supported ruthenium catalysts can be active catalysts for ammonia synthesis [34], but alkali promotion is essential for significant synthesis activity. The model proposed here for potassium promotion of iron catalysts may also be qualitatively applicable to these ruthenium catalysts. Rhenium catalysts [35] have high intrinsic activities for ammonia synthesis but under practical conditions the rates are low, limited by reaction (3).

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However, it should not be assumed that they necessarily agree with all the points made in this paper.

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