

NOTE

A Reinterpretation of the Mechanism of the Heterogeneous Catalytic Synthesis of Ammonia

The Haber synthesis of ammonia is one of the most important catalytic processes. The mechanistic interpretation of the Temkin kinetic (1) equation of ammonia synthesis was based on the assumption that the rate of the overall process is limited by the chemisorption of nitrogen and that neither hydrogen or ammonia influences the rate of nitrogen adsorption; nitrogen chemisorption leads to the formation of surface nitrides (2). This interpretation followed largely from the observation that only metals which strongly chemisorb nitrogen as atoms are active in ammonia synthesis; on the other hand, transition metals which usually adsorb and activate hydrogen are not always active. The metal to nitride bond is not, however, so weak as was previously supposed and while it is easily hydrolyzed to ammonia (3), as evidenced by many titanium complexes in the homogeneous synthesis of ammonia (4, 5), it is not easily reduced by hydrogen. Moreover, the rate of nitrogen adsorption depends on the extent of the pre-adsorption of hydrogen (6) and an isotopic hydrogen effect was detected on the rate of ammonia synthesis (7, 8). This is not predictable by the original mechanistic scheme. Recent investigations (9) in both homogeneous and heterogeneous phases of the hydrogenation of unsaturated hydrocarbons have shown that hydrogen activation by coordination or chemisorption plays a more important role than the coordination or chemisorption of the olefins. Possibly, even in the case of ammonia synthesis, the role of hydrogen chemisorption may be more important than previously supposed al-

though the metals that are very active in the hydrogenation of hydrocarbons (such as group VIII noble metals) are not so useful in ammonia synthesis even if they adsorb both hydrogen and nitrogen (10).

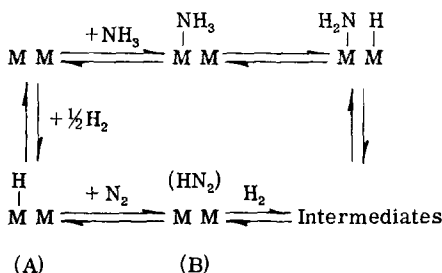
The specificity of the catalysts for ammonia synthesis may be then closely related with a specific nitrogen adsorption which facilitates further reduction by hydrogen.

A recent report (11) on the nature of nitrogen chemisorption on metals, which are active in ammonia synthesis, has shown that three types of surface adsorption must be considered on a clean surface: physical adsorption, weak and strong chemisorption. When an investigation was performed on iron both in the case of a clean surface and on a surface covered with pre-adsorbed hydrogen or nitrogen, some important conclusions were derived. With strongly chemisorbed nitrogen there is no specific influence in the suppression of hydrogen adsorption but at the same time (at 273°K), there is no formation of ammonia (although ammonia is formed at the temperature of the catalytic process) (12). By contrast, when hydrogen is pre-adsorbed there is no nitrogen adsorption at 273°K, showing that the increase of the rate of nitrogen adsorption, found by other authors (6) under the conditions of catalytic reaction, must be due to a new specific combination of both hydrogen and nitrogen adsorption.

It follows that weak or strong chemisorption of nitrogen on clean surfaces should not be considered to be the first step in the catalytic process which must require

a new specific nitrogen chemisorption probably on previously hydrogenated centers, this could explain why ammonia synthesis is *not* a facile reaction (13). Our assumption implies that hydrogen is involved in this step. However, we prefer, to a dissociative adsorption of nitrogen on previously hydrogenated centers (8), the formation of a dehydrodiimide (N_2H) surface complex in which the adsorbed nitrogen is practically undissociated (14, 15). This proposal is consistent with the fact that, although the presence of hydrogen increases the rate of nitrogen adsorption, there is *no* kinetic isotope effect in this process (6).

We propose the following mechanism in which the nitrogen adsorption takes place on special surface sites (M M) with the assistance of a hydridic center:



We assume that the rate determining step in the reaction is the reduction of the half-hydrogenated surface nitrogen complex (B) while the other steps are at equilibrium. The dissociative adsorption of hydrogen can be expressed by applying the Langmuir isotherm to the adsorption equilibria:

$$\theta_A = \frac{\sqrt{b_H t_{H_2}}}{1 + \sqrt{b_H P_{H_2}} + b_{NH_3} P_{NH_3} (1 + K_A / \sqrt{b_H t_{H_2}})}$$

θ_A being the coverage of the centers by hydrogen, b_H and b_{NH_3} the equilibrium adsorption constants of hydrogen and ammonia, respectively; K_A is the equilibrium constant of the surface dissociation of ammonia. In such an interpretation it is implied that any metal atom of the surface centers can bind a hydrogen atom or an

ammonia molecule by coordinative chemisorption.

Moreover, the previous equation takes into account the ammonia dissociation (16). However, at high hydrogen pressure, as in ammonia synthesis conditions, such an equation can be approximated as follows:

$$\theta_A = \frac{\sqrt{b_H P_{H_2}}}{1 + \sqrt{b_H P_{H_2}} + b_{NH_3} P_{NH_3}}$$

Consequently, it follows that chemisorption of ammonia poisons the catalytic process, as has been found in the case of the hydrogenation of other unsaturated substrates (17). The adsorption of nitrogen on the hydrogenated centers can be described by means of the following equation:

$$\frac{\theta_B}{P_{N_2} \theta_A} = K,$$

K being the equilibrium constant. The rate of the overall process is given by:

$$r = k P_{H_2} \theta_B,$$

where

$$\theta_B = K P_{N_2} \theta_A = \frac{K P_{N_2} \sqrt{b_H P_{H_2}}}{1 + \sqrt{b_H P_{H_2}} + b_{NH_3} P_{NH_3}}$$

It follows:

$$r = \frac{k K P_{H_2} \sqrt{b_H P_{H_2}} \cdot P_{N_2}}{1 + \sqrt{b_H P_{H_2}} + b_{NH_3} P_{NH_3}}$$

To a first approximation, taking the chemisorption of ammonia on iron to be stronger than hydrogen chemisorption and neglecting the unity, this equation can be rewritten as follows:

$$r \simeq \frac{k K \sqrt{t_H}}{b_{NH_3}} \cdot \frac{P_{H_2} \sqrt{P_{H_2}} P_{N_2}}{P_{NH_3}} \simeq k_{eff} \cdot \frac{P_{H_2}^{3/2} P_{N_2}}{P_{NH_3}}$$

This equation is similar to the experimental Temkin equation for the direct reaction,

$$r = k_{eff} P_{N_2} \left(\frac{P_{H_2}^3}{P_{NH_3}^2} \right)^\alpha$$

It is known that the measurements of the rates over a wide range of conditions and

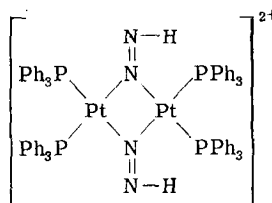
of catalysts (17, 18) can be represented by this equation with α being approximately 0.5. The discrepancies found from this simple value (7) can be explained probably by the inadequacy of the approximation which considers ammonia chemisorption to be much stronger than hydrogen and by the reaction rate as being determined only by one step.

The novelty of the above proposed mechanism consists in the formation of specific N_2H surface complexes on topologically special sites. On the other side, the existence of such species was evidenced indirectly by the work of Ozaki, Taylor, and Boudart (7) and more recently confirmed by Logan and Philp (8) who pointed out that their results were consistent with the presence on the surface of a considerable amount of a hydrogenated nitrogen species rather than of chemisorbed nitrogen atoms.

The assumption of N_2H groups rather than NH (which must additionally exist on the surface being formed in the following steps that lead to ammonia) is mainly based on the recent mass-spectrometric studies of Schmidt (19) and on the analogies with the known chemistry of nitrogen transition metal complexes.

The nitrogen complexes show a nitrogen coordination which, on the basis of infrared spectroscopy (20), is very similar to the weak nitrogen adsorption on the surface of some metals of group VIII (10). The coordinated nitrogen is not reduced to ammonia even by very strong reducing agents (21) or even when one or more hydridic hydrogens are bound to the same transition metal atom (22, 23).

This indicates that the simple coordination to one metal does not imply an "activation" of nitrogen. However, it has been found that nitrogen can bridge two metal atoms (24) (which can be also different) (25) and, although not yet definitely isolated, also with one hydrogenated metal to form a binuclear metal complex of the N_2H species (20). The geometry of a dehydrodiimide-bridged binuclear platinum complex has been discussed (26):



This complex forms nitrogen and platinum hydrides on thermal decomposition and may be reduced, with strong reducing agents, to platinum hydrides and ammonia.

It is of interest that similar N_2H -bridged species between iron (nitrogenase) and molybdenum (reductase) have been proposed to explain the biological nitrogen fixation (20, 27). The fact that in this case ammonia synthesis is an easy reaction is probably due to the specific topology of the enzyme, which facilitates the formation of the bridging species, and to the very low potential of the hydrogenating enzyme (27). Also in this case the step-wise reduction of the N_2H group to ammonia is kinetically important. On the other hand, the introduction of poisoning agents such as carbon monoxide or tertiary nitrogen species (20) hinders nitrogen reduction, particularly the nitrogenase part of the enzyme, confirming that specific nitrogen coordination on iron can be inhibited, as we have supposed in the case of heterogeneous catalysis.

ACKNOWLEDGMENT

Support from Italian C.N.R. and from N.A.T.O. are gratefully acknowledged.

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Received June 18, 1968