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Ammonia Synthesis Catalyzed by Uranium Nitride

II. The Transient Behavior

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An explanation is offered for the transient increase in activity of U_2N_3 catalyst for the ammonia synthesis. This is believed to be due to the absorption of interstitial nitrogen into the U_2N_3 lattice at the higher temperatures and this nitrogen becomes frozen in at lower temperatures. It diffuses to the surface at working temperatures and being in an active atomic form this interacts rapidly with hydrogen in the synthesis mixture to produce ammonia.

INTRODUCTION

In the preceding paper (*1*) reference was made to the fact that uranium sesquinitride exhibited unusual behavior when used as a catalyst for the ammonia synthesis. Unsteady state phenomena have been important in the investigation of adsorption and desorption processes, but they have not been systematically studied in catalytic reactions. Miscellaneous transient effects have been reported by others for the hydrogenation of benzene and the dissociation of cyclohexane on platinized aluminium, and for the oxidation of ethylene to ethylene oxide on silver (*3*, *4*). In the present work, however, an elucidation of the transient behavior has been necessary for an understanding of the overall catalysis by U_2N_3.

EXPERIMENTAL

The apparatus and various analytical procedures have been described, and a full description of the chemical and physical nature of the two catalysts used will be found in the preceding paper (*1*). Except where otherwise stated, the total pressure was 30 atm and the reaction mixture was the stoichiometric mixture flowing at a rate of 4.15 liter (STP)/hr.

RESULTS AND DISCUSSION

Preliminary results showed that the catalyst behavior was a sensitive function of its immediately previous history and that a change in the operating conditions (temperature, pressure, gas composition, but not necessarily space velocity) normally gave rise to significant transient effects. These effects were found to be reproducible and were conveniently studied by carrying out the following cycle of cooling and heating operations (the synthesis mixture usually being kept flowing throughout):

(i) holding the catalyst at a high temperature, T_1 (usually chosen as 525°C);

(ii) allowing the temperature to drop from T_1 to a lower value, T_2; T_2 was usually 100°C—it took about 3 hr for the catalyst to cool from 525° to 100°C;

(iii) raising the temperature from T_2 to T_3 (mostly 375°C, occasionally 443°C), where $T_2 < T_3 < T_1$.

The heating rate between T_2 and T_3 was the same each time, the Variac in the reactor furnace circuit simply being set at the same output. The time of heating between 100° and 375°C was 1 hr. The temperature rose linearly in the first stages of the heating, after which the rate slowly decreased until

375°C was reached. There was an initial overshoot of about 1°C before the temperature remained constant.

During the heating period between T_2 and T_3 and afterwards when T_3 had been reached, the rate of formation of ammonia rose rapidly through a maximum before decreasing slowly (sometimes so slowly that it took as long as 10 days) to the time steady state value as obtained from the Arrhenius plots previously constructed (*1*). If an activity–time plot showing no maximum but only a steady rise to the final steady state value is taken as "normal," then the difference between this and the peak curves can be regarded as "excess" ammonia. The rate of production of excess ammonia was found to depend on the following factors, all other conditions being maintained constant:

(i) The higher the value of T_1, the greater the peak (Fig. 1).

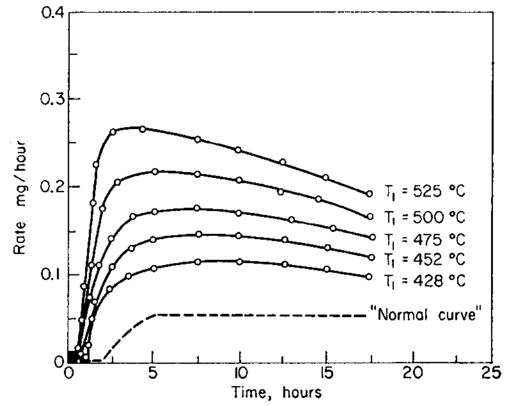

FIG. 1. Rate as function of T_1.

(ii) The longer the time at T_1, the greater the peak, the upper limit being for the case corresponding to the attainment of steady state at T_1 (Fig. 2). This is subject to the condition that the temperature as well as the instantaneous rate of ammonia production immediately prior to increasing the temperature to T_1 should always be the same.

(iii) The longer the time at the low temperature T_2, or the slower the rate of cooling to T_2, the smaller the peak (Fig. 3).

(iv) For the same cooling time, higher values of T_2 reduced the peak.

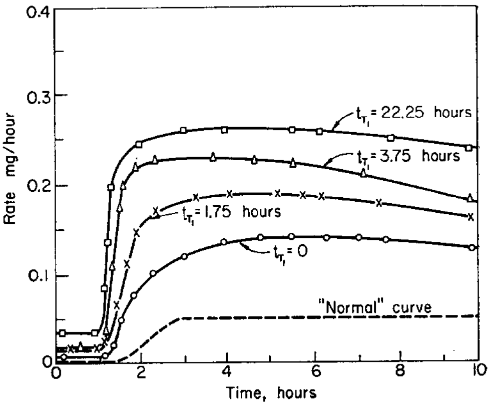

FIG. 2. Rate as function of time of pretreatment at T_1.

(v) The higher T_3, the faster the rate of production of excess ammonia.

(vi) If the rate of heating between T_2 and T_3 was increased, the initial rate of ammonia formation was enhanced, although the total amount of excess ammonia produced was independent of the rate of heating.

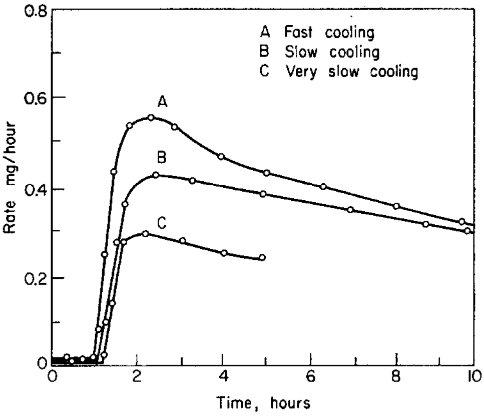

FIG. 3. Rate as function of cooling time between T_1 and T_2.

(vii) The composition of the gas stream at (a) T_1 and (b) during the heating period between T_2 and T_3, affected the surge in activity. Higher nitrogen compositions at (a) (Fig. 4) and lower at (b) increased the rate and amount of excess ammonia formation. These particular experiments provide a strong clue to understanding the overall transient behavior. In fact, the results suggest that the only apparently consistent interpretation of each step in the cycle of

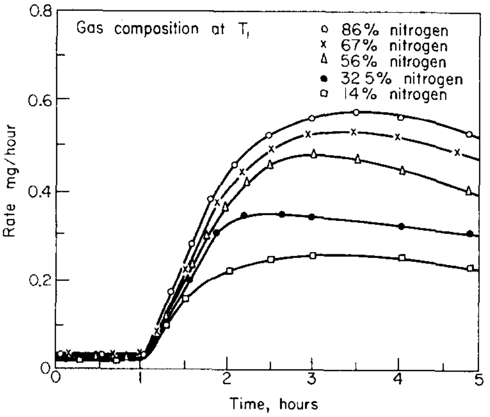

FIG. 4. Rate as function of gas composition during pretreatment at T_1.

operations is (a) increased nitrogen uptake by the catalyst at T_1; (b) freezing in of this species on cooling from T_1 to T_2; (c) removal of this nitrogen, which is evidently very reactive, in heating to T_3.

On the assumption that nitrogen is adsorbed atomically in a close-packed monolayer and ignoring the presence of the oxide, at complete coverage catalyst N2 would be able to accommodate 9.1×10^{20} nitrogen atoms—this would represent maximum adsorption. If the nitrogen is adsorbed ionically and if, as is highly probable, not all of the surface is available but only a small fraction of it (20% say), then the number would be 0.38×10^{20}. Since the adsorbed nitrogen is probably partly but not fully ionized (*5*), it might be expected that the true value will tend towards the lower of these two extremes. In a set of experiments on the same catalyst it was found (for $T_1 = 525°$; $T_2 = 100°$; $T_3 = 375°$, synthesis mixture throughout) that the total amount of excess ammonia produced was equivalent to 7.3×10^{20} nitrogen atoms. It thus seems reasonable to suggest that the nitrogen atom participating in the formation of excess ammonia cannot be held only on the surface but must come from the catalyst itself, and almost certainly from only the first few subsurface layers. Since the U_2N_3 phase is a defect structure possessing a large number of vacancies and having a wide nonstoichiometric range, this seems a quite tenable conclusion. The unfilled sites can readily be occupied by nitrogen, presumably by the diffusion of a vacancy to the surface, where there is already chemisorbed nitrogen. The fact that uranium exhibits a variable valency would facilitate this process, and so there probably exists a situation loosely analogous to some metal–oxygen systems (*1*).

It is now possible to examine closely the significance of the various experimental results given earlier.

The effect of different values of T_1. Since it was found for higher values of T_1 that the rate and the amount of excess ammonia formed increased, it would appear that the further nitridation of U_2N_3 is favored by higher temperature. While it was once thought that this reaction might be endothermic (*6*) there is now little doubt that the process is exothermic (*7*, *8*, *9*). The only possible explanation for the observation made in this work would thus appear to be that under the usual experimental conditions (relatively high nitrogen pressures and low temperatures) the U_2N_3 catalyst is unable to attain true equilibrium. The situation would then be analogous to that of the nonequilibrium region of the usual adsorption isobar, which has been satisfactorily explained (*10*, *11*), and which is well illustrated by the chemisorption of nitrogen on tungsten powder (*12*) and, more significantly, the high pressure adsorption/absorption of nitrogen on iron (*13*).

In this case, the temperature range (375–525°C) in which nearly all this work has been conducted must lie in the nonequilibrium section in the absorption part of the isobar. Bauer (*14*) has made similar qualitative observations, and has emphasized that long reaction times are necessary for full equilibrium to be reached in the uranium-nitrogen system at 700°C, despite the use of a very fine powder. He has stressed, too, that between 375° and 525°C "only a surface reaction can be expected" (*14*), a conclusion which has also been suggested above. In addition, Mallett and Gerds (*15*) have found that, at temperatures of 550°C and a little higher, the surface product of the direct nitridation of massive uranium is richer in nitrogen than the region nearer the interior.

It can be seen from an isobar that while one adsorption (incorporation) type is in the nonequilibrium range, the "previous" type (which is not necessarily a precursor) is probably still present, decreasing with temperature in the usual way. If work is being carried out in a nonequilibrium region, it might then be expected to find some evidence of the occurrence of the exothermic species. This is indeed the case here, as seen, for example, in Fig. 5 (where the catalyst reached steady state at 452°C before being cooled to 100°C). Clearly there is present on the surface a nitrogen species which becomes activated with increased temperature; the size of the peak in all cases suggests that this species covers only a small fraction of the surface.

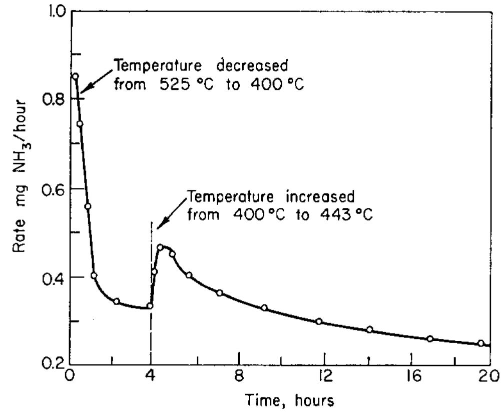

FIG. 5. Effect of temperature change on rate of ammonia formation.

Some of the results of this work can be analyzed in terms of the theory of absolute reaction rates. Since we are here concerned with the formation of excess ammonia, the reaction is between hydrogen from the gas phase (A) and nitrogen from the catalyst (B). The system is thus reduced to the case of a bimolecular reaction, $A + B + S_2 \rightleftarrows (A\text{–}B\text{–}S_2) \rightarrow$ products, where S_2 is a dual site on the surface. Considering only the equilibrium between the initial and activated states, it can be shown that $V = d(NH_3)/dt = kC_B$, since only C_B the concentration of nitrogen from the catalyst is allowed to vary (by varying T_1 in the present instance), all other factors being maintained constant.

By taking the rates over the first half-hour after 375°C (T_3) had been reached (Fig. 1), it is shown that, for catalyst N1, C_B varies exponentially with the inverse of T_1°K, i.e., $C_B = A \exp(\gamma/T_1)$ (Fig. 6). Catalyst N2 shows the same behavior. It is tempting to associate γ with the heat of incorporation of nitrogen or perhaps the heat of formation of a lattice vacancy at the surface. However, it must be remembered that the nitridation reaction is occurring in a nonequilibrium region, so that normal thermodynamic relationships are not applicable. The fact that further reaction occurs with increasing temperature is the result of kinetic, not thermodynamic, factors. Hence the above expression must be regarded as purely empirical, and to it no theoretical significance can be attached. There is a twofold difference in the value of γ for each catalyst ($\gamma_{N1} = -3.17$, $\gamma_{N2} = -1.58$); this is probably due to the greater degree of oxygen contamination in N1 thanin N2.

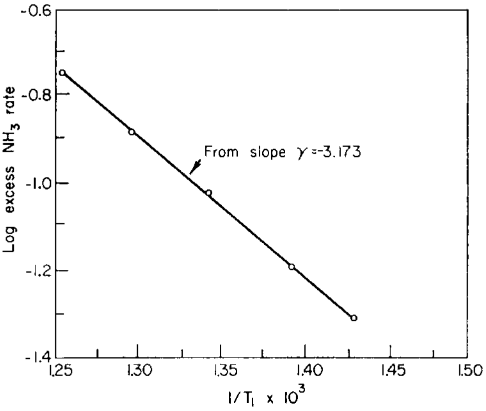

FIG. 6. Derivation of relationship between C_B and $1/T_1$ for catalyst N1.

The effect of different cooling rates between T_1 and T_2. If the rate with which "equilibrium" in the catalyst and between the catalyst and the reacting gases is established were infinitely rapid the state at the temperature T_1 would be of no importance; the catalyst would possess the properties corresponding to complete equilibrium at any temperature. But if all processes leading to equilibrium were infinitely slow, cooling would lead to the solid having exactly the same properties after cooling as it had at T_1, and the real situation would normally lie somewhere between these two extremes, with the final state being nearer to the state at T_1 for faster rates of cooling.

The results shown in Fig. 3 (for catalyst N1) are fully consistent with the above. Curve 1 (obtained for rapid cooling) shows a considerably greater peak than curve 2 (slow cooling), and curve 3 (very slow cooling).

The variation with time at T_1. For the conditions employed in this set of experiments over catalyst N1, the rate of formation of excess ammonia varies directly as the concentration of active nitrogen in the catalyst (as above), which itself is some function of the time that the catalyst is held at temperature T_1. Following Evans (*16*), it is found that the data obtained from Fig. 2 are best fitted by a logarithmic equation of the form $C_B = b \log (t_{T_1} + 2)$, where t_{T_1} is the time of nitridation at T_1 and b is a constant (see Fig. 7).

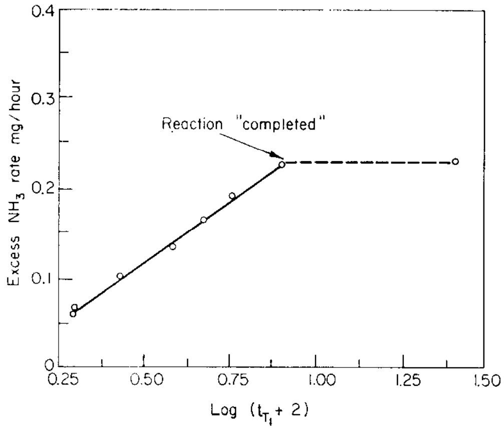

FIG. 7. Proof that $C_B = b \log (t_{T_1} + 2)$.

The dependence on gas composition at T_1. Once again $V = d(NH_3)/dt = kC_B$. Here C_B is varied as a function of P_{N_2} and P_{H_2}, and, using the data of Fig. 4 for catalyst N1, it is found that, at $T_1 = 525°C$, the concentration of active nitrogen in the catalyst varies with the gas composition according to the equation

$$C_B = 0.120 P_{N_2}^{0.49} P_{H_2}^{-0.01}$$

Since the nitrogen index is almost exactly 0.5 it may be inferred that the active nitrogen is atomic.

The variation with T_3. The experimental procedure was such that $V = k \exp (-\epsilon_0)/RT_3$. Data for catalyst N1 are plotted in Fig. 8, from which it is found that ϵ_0, the apparent activation energy, has a

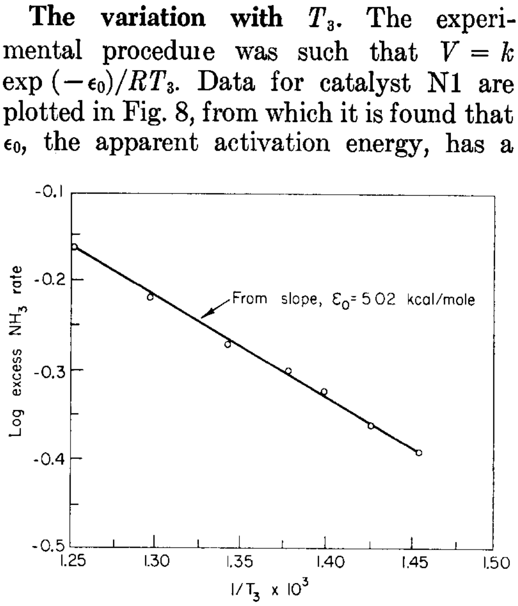

FIG. 8. Apparent activation energy ϵ_0 for excess ammonia formation.

value of 5.02 kcal/mole. This is an extremely low value, a little more than that for the steady state ammonia synthesis over the same catalyst, and so this provides some measure of the greater rate with which the transient reaction occurs.

The effect of gas composition during the denitriding period. In these experiments over catalyst N2 it was not possible to obtain activity–time curves for the "normal" synthesis of ammonia. In order to obtain values of the rate of formation of excess ammonia it was necessary to take the rates during the early stages of the heating-up period while the temperature was still rising to T_3. This is in contrast to all the previous data, where the rates were taken only once T_3 was reached.

Figure 9 shows how the results were obtained. It can be seen that the rates were taken over a temperature range and thus the data are not for isothermal conditions. However, since the heating rate was the same in each case and also the rate was taken over the same time interval (and hence temperature range), it can be shown that this is still a valid procedure.

On the grounds of simple kinetics we may write

$$d(\mathrm{NH_3})/dt \Big|_{T_a}^{T_b} = k_3 P_{\mathrm{N_2}}{}^{x} P_{\mathrm{H_2}}{}^{y}$$

where $T_a - T_b$ is the temperature interval over which the data are taken (in practice, 18°C). Three sets of data were obtained, the resulting rate equations being:

$$\text{(i)}\quad d(\mathrm{NH_3})/dt = 0.16\, P_{\mathrm{N_2}}{}^{-0.11}\, P_{\mathrm{H_2}}{}^{0.48}$$

$$\text{(ii)}\quad d(\mathrm{NH_3})/dt = 0.14\, P_{\mathrm{N_2}}{}^{-0.05}\, P_{\mathrm{H_2}}{}^{0.55}$$

$$\text{(iii)}\quad d(\mathrm{NH_3})/dt = 0.11\, P_{\mathrm{N_2}}{}^{-0.07}\, P_{\mathrm{H_2}}{}^{0.52}$$

It will be seen that gaseous nitrogen retards the denitridation reaction. It may also be inferred that since the rate is pressure-sensitive, the controlling step takes place at the solid–gas interface (*17*). In addition, since the hydrogen exponent is very nearly 0.5, a dissociated hydrogen species is probably active in the controlling step.

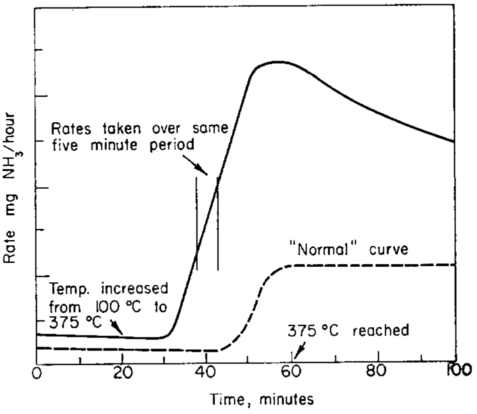

FIG. 9. Procedure adopted for obtaining rate data before constant temperature reached.

The interaction of hydrogen with the catalyst. Additional formation was obtained by following the interaction of the catalyst with hydrogen during the heating-up period (Fig. 10). The total pressure was held constant at 30 atm, using argon as diluent, the partial pressure of the hydrogen being allowed to vary. The results were used to derive the following equation:

$$d(\mathrm{NH_3})/dt = 0.79\, P_{\mathrm{H_2}}{}^{0.52}$$

This kinetic expression, which has the same hydrogen index as found in the immediately preceding section, can be consistent either with an hydrogenation step involving hydrogen atoms or with the dissociative chemisorption of hydrogen being rate-controlling. The second alternative seems unlikely since the chemisorption of hydrogen is generally considered to occur rapidly. If an hydrogenation step controls the rate and since the active nitrogen species is already on the surface, it may be inferred that an hydrogenation step is the second slowest step in the normal ammonia synthesis. This is in agreement with Tamaru's recent work (*18*).

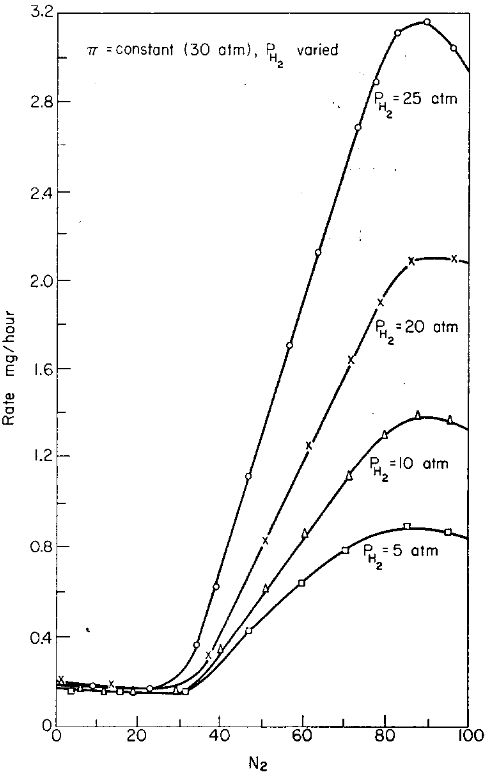

FIG. 10. Reduction of catalyst N2 by hydrogen-argon mixtures.

In conclusion, it will be instructive to describe the transient behavior by reference to the hypothetical isobar for nitrogen uptake by uranium sesquinitride shown in Fig. 11. The further nitridation of the catalyst occurs at T_1 (point A on the isobar). In cooling to T_2 the amount of Type 1 adsorption increases (assuming that T_2 lies to the right of point B, the maximum in the Type 1 isobar). At the same time some of the Type 2 species will be lost, although very slowly, and so the amount of nitrogen held by the catalyst at T_2 is drawn as a little more than that at T_1 (A). (Strictly speaking, this is valid only if pure nitrogen were present; since there is hydrogen also present, and this during the cooling process would certainly tend to remove some of the surface nitrogen, this scheme is somewhat oversimplified.) In heating to T_3, Type 1 nitrogen is lost rapidly, but even after this is used up (D) there is still considerably more nitrogen in the catalyst than required by the isobar (corresponding to the amount DE).

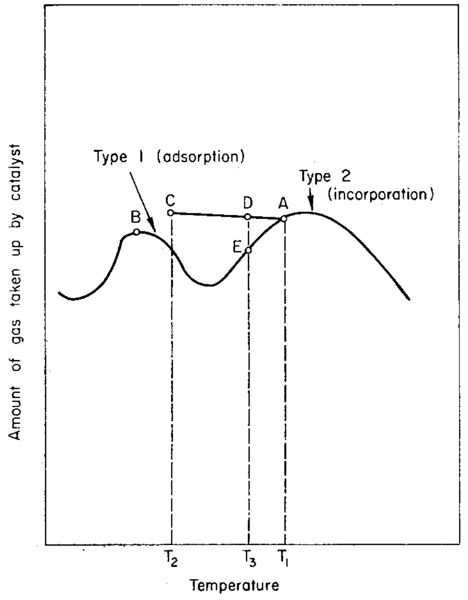

FIG. 11. Hypothetical isobar for nitrogen uptake by U_2N_3 catalyst.

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