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Mechanism and Kinetics of Ammonia Decomposition on Iron

The kinetics of ammonia decomposition on iron were studied quite frequently in the past, mainly in order to obtain insight into the mechanism of the ammonia synthesis reaction (*1–6*). Thus the derivation of the famous Temkin rate law (*7*) for ammonia synthesis was essentially based on Winter's results (*1*) on the decomposition reaction. In a series of recent investigations in our laboratory using well-defined Fe single crystal surfaces and surface spectroscopic techniques the nature of the surface species could be identified and the mechanism of the decomposition reaction can accordingly be formulated as (*8–15*):

$$NH_3 \overset{(1)}{\rightleftharpoons} NH_{3,ad} \xrightarrow{(2)} NH_{2,ad} + H_{ad} \xrightarrow{(3)} NH_{ad} + 2\,H_{ad} \xrightarrow{(4)} N_s + 3\,H_{ad}$$

$$2\,H_{ad} \xrightarrow{(5)} H_2$$

$$2\,N_s \xrightarrow{(6)} N_2$$

The following derivation of kinetic expressions holds for situations far away from the equilibrium of the overall reaction, i.e., at vanishingly small partial pressures of H_2 and N_2. Under these conditions it was found (*8*, *16*) that the recombination reaction (5) is much faster than the reaction of H_{ad} with any of the N-containing surface intermediates. For this reason the reverse reactions of steps (2)–(4) can be neglected.

N_s denotes the "surface nitride" species, whose structural, energetic, and electronic properties have been investigated in detail (*12–14*). If the P_{NH_3}/P_{H_2} ratio is high enough the formation of bulk nitrides (γ'-nitride = Fe_4N and ϵ-nitride) below the surface nitride layer is thermodynamically allowed and was verified experimentally (*15*). Under nonstationary conditions it was found that reaction steps (1)–(5) proceed much faster and at lower temperatures than the desorption of nitrogen (step (6) = decomposition of the surface nitride). The latter step was found to follow first order kinetics with respect to $[N_s]$ (instead of second order as one would have expected). This effect is ascribed to the decomposition of the "surface nitride" whose rate is not determined by surface collisions of randomly distributed N-atoms (*13*). Its activation energy was found to vary between 51 and 58 kcal/mole (1 kcal/mole = 4.18 kJ/mole) at various single crystal planes (*13*, *14*) and corresponds also with the activation energy for decomposition of Fe_4N (*15*). Decomposition of ϵ-nitride proceeds with a considerably lower activation energy of about 27 kcal/mole (*15*). The overall reaction rate under steady-state conditions may be formulated as the rate of N_2 production which is given by the rate of decomposition of the "surface nitride":

$$r_{\text{stat.}} = \frac{d[N_2]}{dt} = k_6[N_s]. \qquad (1)$$

According to the above formulated sequence of reaction steps the steady-state coverage of N_s may be evaluated and rate Eq. (1) transforms into

$$r_{\text{stat.}} = \frac{\dfrac{k_1 k_2 p_{NH_3}}{(k_{-1} + k_2)}}{1 + \dfrac{k_1 k_2 p_{NH_3}}{k_6(k_{-1} + k_2)}}. \qquad (2)$$

Two limiting cases may now be considered:

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(i) At low temperatures (i.e., k_6 small) and/or high NH_3 pressures $k_1k_2p_{NH_3}/k_6(k_{-1} + k_2) \gg 1$ and Eq. (2) simply becomes

$$r \approx k_6. \tag{3}$$

This means that desorption of N_2 (= decomposition of the surface nitride) is rate limiting and the surface is saturated with N_s (i.e., the atomic nitrogen species. The adsorption energy of molecularly held N_2 is <10 kcal/mole (*12*) so that saturation with this species will never be reached above room temperature). It is predicted that the reaction kinetics will follow zero order with respect to the NH_3 pressure and to exhibit an energy equal to that for decomposition of the "surface nitride" (≈50 kcal/mole).

(ii) If the temperature is high enough (i.e., k_6 large) and/or the NH_3 pressure small $k_1k_2p_{NH_3}/k_6(k_{-1} + k_2) \ll 1$ the delivery of NH_3 from the gas phase will become rate-limiting and accordingly

$$r \approx \frac{k_1k_2p_{NH_3}}{(k_{-1} + k_2)}. \tag{4}$$

The qualitative behavior will now be dependent on the relative magnitudes of k_2 (= dissociation of $NH_{3,ad}$) and k_{-1} (desorption of ammonia). Löffler and Schmidt (*2*) assumed that $k_{-1} \gg k_2$, leading to decomposition of $NH_{3,ad}$ from a well-estblished adsorption–desorption equilibrium. (This assumption leads to the conclusion that the adsorption energy of NH_3 is about 39 kcal/mole which would indeed be too large by a factor of about 3 if compared with actual experimental values (*9, 10*).)

Recent measurements, however, indicated that a NH_3 molecule striking an Fe surface at elevated temperatures has a much higher probability for being dissociated than to desorb (*10, 16*) so that indeed $k_2 \gg k_{-1}$. We thus arrive at

$$r \approx k_1 \cdot p_{NH_3} \tag{5}$$

where k_1 is equivalent to the sticking coefficient of NH_3 on a clean Fe surface which is practically independent of temperature. It is thus predicted that in this case the activation energy will tend to zero and that the kinetics will follow a first-order law with respect to p_{NH_3}.

In the intermediate range between these two limiting cases it is of course expected that the activation energy gradually decreases from about 50 kcal/mole to zero, whereas simultaneously the reaction order increases from 0 to 1.

In order to check the predictions concerning the activation energy, experiments were performed within a UHV system with a polycrystalline Fe wire (total surface area 8 cm²) at a constant NH_3 pressure of 5.10^{-6} Torr. The surface was cleaned by repeated oxidation–reduction cycles until the concentration of impurities as monitored by Auger spectroscopy was below about 1% of a monolayer. The reaction kinetics were studied under flow conditions with a high pumping speed, so that the partial pressures of H_2 and N_2 were always kept very small and the reverse reaction could be neglected. The partial pressures were recorded by means of a quadrupole mass spectrometer.

Figure 1 shows an Arrhenius plot for the rate of N_2 production betwen 580 and 830 K. In order to achieve stationary conditions the segregation equilibrium between N_s and dissolved nitrogen atoms was always established. The highest temperature (860 K) corresponds just to the $\alpha \rightarrow \gamma$ transformation point of α-Fe saturated with N. γ-Fe exhibits a much higher solubility for nitrogen so that under the present conditions of very low pressures no reliable steady-state data for the rate of decomposition were obtained above this temperature.

Figure 1 shows the predicted behavior. The activation energy has a value of 45 ± 5 kcal/mole up to about 640 K, then decreases continuously until it becomes about 5 kcal/mole above 710 K. Around 850 K the reaction rate becomes nearly temperature-independent (i.e., $E^* \approx 0$).

The discussed mechanism and kinetics are also in agreement with literature data. The investigations by Mittasch *et al.* (*3*) at

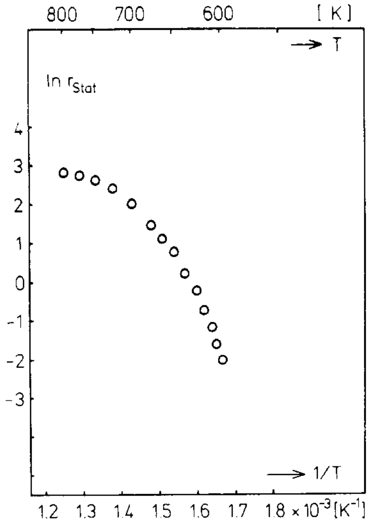

FIG. 1. Arrhenius plot for the rate of ammonia decomposition at a clean polycrystalline Fe wire at $p_{NH_3} = 5 \times 10^{-6}$ Torr.

630 K revealed zero-order kinetics, and nitride decomposition was proposed to be rate-determining. Kunsmann (*4*) determined an activation energy of 51 kcal/mole at low temperatures which decreased to about 20 kcal/mole above 800 K. Winter (*1*) reported zero-order kinetics and an activation energy of 51 kcal/mole.

According to Eq. (2) the transition region from high to low activation energy should be shifted to higher temperatures with increasing NH_3 pressures. That is the reason why Löffler and Schmidt (*2*) determined an activation energy of 49.6 kcal/mole (and zero-order kinetics) up to $T \approx 1000$ K for $p_{NH_3} > 0.05$ Torr. Logan *et al.* (*5*) derived a somewhat smaller value of 39 kcal/mole for the activation energy but also suggested that desorption of nitrogen is rate-limiting.

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