Mechanism of Ammonia Decomposition on Tungsten; NH_3 and ND_3 Isotope Effect

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Dedicated to Prof. Schwab on his 80th birthday

Light and heavy ammonia were decomposed on a clean tungsten foil at 973–1123 K and at $p_{NH_3, ND_3} \approx 0.2$ Torr. The nitrogen uptake and the kinetics of the formation of nitride layers were examined during the course of the reaction. The amount of nitrogen chemisorbed (or the thickness of the nitride layers formed) at higher pressures was found to be appreciably larger from NH_3 than from ND_3. Addition of hydrogen had no effect on the thickness of the nitride layer nor on the rate of ammonia decomposition. These facts support the concept of a dynamic balance between two consecutive rate determining steps: supply of chemisorbed nitrogen from ammonia into the surface and consumption of the chemisorbed nitrogen through its desorption from the surface to form nitrogen molecules.

Introduction

The decomposition of ammonia on tungsten has already frequently been studied, but its reaction mechanism has so far not been completely understood. Hinshelwood and Burk [1] reported that the reaction is of zero-order, the initial rate being independent of the pressures of ammonia, hydrogen and nitrogen, although the rate depends upon ammonia pressure in the later stage of the reaction. Zero-order kinetics would be expected if the catalysts were fully covered by some species whose decomposition is rate determining. On the other hand Frankenburger and Holder [2] found that ammonia adsorbed on tungsten leads easily to the release of hydrogen. Even at 523 K, a temperature which is considerably lower than the usual reaction temperature, more than one hydrogen molecule is desorbed per adsorbed ammonia molecule without any nitrogen desorption. Consequently one possibility would be that the tungsten surface becomes saturated with nitrogen atoms during the decomposition, and nitrogen desorption being the rate-determining step.

Jungers and Taylor, as well as Barrer [3], on the other hand, observed the occurrence of a kinetic isotope effect in the reaction, namely that at around 1000 K, NH_3 decomposes 1.6 times faster than ND_3, which seems to exclude a mechanism in which nitrogen desorption from a saturated layer is rate-determining. Rather it looked as if some hydrogen containing species on the surface is playing an important role for the decomposition reaction. Actually, Dawson and Hansen [4], and Peng and Dawson [5] suggested that some surface species, such as $W_2N_2H_2$ and W_2N_3H as well as W_2N would participate in the rate-determining step.

One of the authors [6] previously studied the decomposition of ammonia on tungsten powder by measuring adsorption during the course of the reaction. He found that at 773–873 K almost no hydrogen is adsorbed on the catalyst surface, whereas the uptake of a considerable amount of nitrogen, which corresponds to multilayer formation, was observed. In the absence of gaseous ammonia the surface nitride layers decomposed, producing nitrogen molecules at the same rate as in the presence of gaseous ammonia. As the thickness of the layer increased, the rate of surface nitride formation decreased and the rate of desorption of nitrogen, i.e., the rate of decomposition of surface nitride increased rapidly. Accordingly a reaction mechanism of "dynamic balance" between two consecutive rate determining steps was proposed: supply of N atoms from ammonia into the surface nitride, and its consumption by desorption as N_2. In this mechanism, the kinetic isotope effect in the decomposition rate of ammonia should correspond to a difference in the thickness of the nitride layers. This latter effect has so far, however, never been examined experimentally.

In the present work the uptake of nitrogen under steady-state conditions was directly measured by using flash desorption and Auger electron spectroscopy (AES) in an ultrahigh vacuum reaction

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chamber. The proposed reaction mechanism will be able to explain all the kinetic data including the previously observed isotope effect as well as the absence of hydrogen containing species in the surface under reaction conditions.

Experimental

Polycrystalline tungsten foil (99.95%, Japan Lamp Industrial Co. Ltd.) with a geometric surface area of 8.8 cm^2 was used as a sample. The number of W atoms at the surface was estimated to be 1.22×10^{16} from saturation coverage of nitrogen and ammonia adsorption, the atomic ratio of N to surface W being 1:2 $\left(\mathrm{W}{\diagup}^{\mathrm{N}}{\diagdown}\mathrm{W}\right)$ and 1:1 (W—N), respectively [7]. The sample was heated resistively by DC and the temperature was measured using a Pt/Pt-Rh (13%) thermocouple and an optical pyrometer. A clean surface was obtained by O_2 treatment to remove carbon followed by heating at 2000 K in vacuo. The cleanliness of the sample was checked by AES.

All the experiments were carried out in a stainless steel ultrahigh vacuum apparatus (base pressure 2×10^{-10} Torr) equipped with an Auger electron spectrometer and a mass-filter.

In a lower pressure range ($P_{NH_3, ND_3} = 10^{-8}$ to 10^{-5} Torr), ammonia decomposition was studied in a flow system. The decomposition rates were followed by the mass filter; the reaction rate was calculated from the drop in N_2 partial pressure, when the sample was cooled down from the reaction temperature to room temperature to stop the reaction on the catalyst surface. The amount of nitrogen uptake, Θ_N, was estimated by AES (peak-to-peak height of differentiated spectrum) as far as Θ_N did not exceed 2 ($\Theta_N = 2$ is defined here by full coverage with NH_3), which had been calibrated by flash desorption.

At higher pressures ($P_{NH_3, ND_3} \sim 0.2$ Torr), the reaction was performed in a closed system. After a certain time interval of the reaction, the sample was cooled down to room temperature to stop the reaction. Then the system was evacuated to high vacuum by a turbomolecular pump and flash desorption was performed. From the time integral of the desorption spectrum the total amount of nitrogen uptake or the thickness of surface nitride was estimated.

Results and Discussion

The rate of ammonia decomposition and the amount of nitrogen uptake during the course of the reaction were measured simultaneously in a flow system at 1073 K and in 10^{-8}—10^{-5} Torr of ammonia. The results of the rate measurements are given in Figure 1. The reaction order of nitrogen production was found to be 0.8 with respect to ammonia and not of zero-order in this range of pressure. Practically no hydrogen is adsorbed on the surface. The decomposition rate of NH_3 was 1.2 times larger than that of ND_3. However, the difference between Θ_N during the course of NH_3 and ND_3 decomposition was not appreciable in the AES measurements. In Fig. 2 the relation between nitrogen coverage and the rate of gaseous nitrogen formation is given in a semilogarithmic scale. When the ammonia pressure was increased from 10^{-7} to 10^{-5} Torr, Θ_N was correspondingly increased from 1.0 to 1.5. As can be seen from Fig. 2 in this pressure range the curve is so steep that a difference of 20% in the reaction rate corresponds to a change

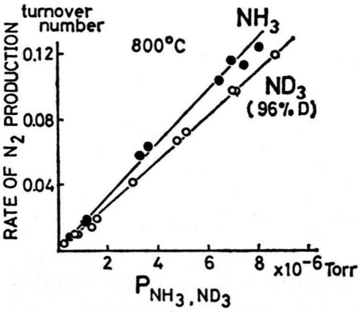

Fig. 1. NH_3 and ND_3 decomposition rates at 1073 K plotted against the pressure of ammonia. ● NH_3, ○ ND_3 (96% D) (turnover number = 1 means the formation of $\frac{1}{2}$ N_2 molecule from every surface W atom per second).

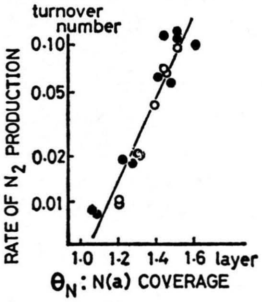

Fig. 2. Rates of gaseous nitrogen formation on tungsten at 1073 K under 10^{-7}—10^{-5} Torr of ammonia, plotted against nitrogen coverage Θ_N on W ($\Theta_N = 1$; N/W (surface = 1/2). ● NH_3, ○ ND_3 (96% D).

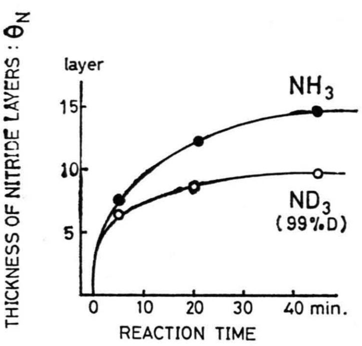

Fig. 3. Thickness of nitride layers formed during NH_3 and ND_3 decomposition on W ($\Theta_N = 1$; N/W (surface) $= 1/2$). $P_{NH_3, ND_3} = 0.21$ Torr, 1023 K. ● NH_3, ○ ND_3 (99% D).

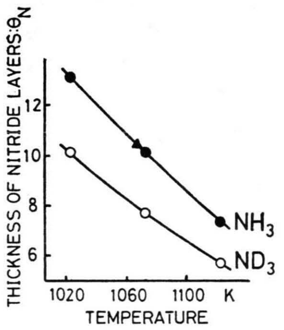

Fig. 4. Temperature dependence of the thickness of nitride layers formed in 15 minutes of NH_3 and ND_3 decomposition on W. $P_{NH_3, ND_3} = 0.23$ Torr, 1023—1123 K. ● NH_3, ○ ND_3 (99% D), ▲ NH_3 (0.23 Torr + H_2 (0.20 Torr).

of only 0.03 in Θ_N, which is within the experimental error.

The formation of nitride layers was also studied at an ammonia pressure of 0.2 Torr. In this case thicker layers were formed and the difference between Θ_N formed from NH_3 and ND_3 becomes detectable. Figure 3 shows the nitride formation during the course of NH_3 and ND_3 decomposition at 1023 K in 0.21 Torr of ammonia in a closed system.

Θ_N was measured at suitable times by the flash desorption method. At the beginning of the decomposition, the nitride formation proceeded rapidly and thick nitride layers were formed, and then gradually the rate slowed down, the thickness approaching a saturation value. In the steady-state of the reaction the thickness of the nitride formed from NH_3 is definitely larger than that from ND_3 as shown in Figure 3.

The thickness of nitride in the steady-state of ammonia decomposition in the temperature range 1023—1123 K under 0.23 Torr of ammonia is given in Figure 4. The steady-state is almost attained in 15 minutes and the thickness of the surface nitride was measured. At higher temperatures the nitride layer becomes thinner because the temperature dependence of N_2 desorption rate is larger than that of nitride formation. The difference between the thicknesses of nitride layers formed from NH_3 and from ND_3 was also observed at higher temperatures.

When a mixture of H_2 (0.20 Torr) and NH_3 (0.23 Torr) was used as a reaction gas at 1073 K, the thickness of the nitride layer was the same as that obtained when using only NH_3, as shown by the triangles in Fig. 4, practically no hydrogen being adsorbed during the reaction. No effect of the presence of hydrogen on the nitride formation as well as ammonia decomposition was observed.

The present experimental results obtained with a clean tungsten surface support the reaction mechanism of "dynamic balance", which one of the authors proposed previously on the basis of results obtained with tungsten powder, although the turnover number per surface W atom was smaller in the previous study than in the present case, presumably because of the unavoidable surface contamination of tungsten powder in the conventional reaction vessel used previously. The kinetic behavior of adsorbed species and the adsorption during the course of the reaction have been studied in connection with the reaction mechanism, too. These results will be published elsewhere in detail.

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Our own experiments on adsorption of NH_3 and N_2 on W indicated that the amount of N atoms adsorbed from NH_3 at saturation is almost twice as much as that from N_2.