O. V. KRYLOV

1960

SovietRxiv

Abstract

Full Text

O. V. KRYLOV

ON ONE CASE OF HOMOGENEOUS CONTINUATION OF A HETEROGENEOUS CATALYTIC REACTION

(Presented by Academician P. A. Rebinder, 21 X 1959)

The decomposition of hydrazine is an example of an exothermic reaction that proceeds readily on a number of catalysts at low temperatures with a low activation energy. We have studied (¹) the decomposition of hydrazine on a number of catalysts: metallic ones (Pt, pure Fe and Fe promoted with alkali), semiconducting ones (Ge, GaAs, Ga_2Se_3, Ga_2Te_3, $GaAs \cdot Ga_2Se_3$, $3GaAs \cdot Ga_2Se_3$, V_2O_5), salt-like ones (CuBr), acidic ones (aluminosilicate, quartz), and basic ones (CaO). We proposed that the decomposition of hydrazine on metallic and semiconducting catalysts proceeds by a chain or radical mechanism. After approximate thermochemical calculations, analogous to the calculations of N. N. Semenov (²) and V. V. Voevodskii (³), the hypothesis (¹) was advanced that the hydrazine molecule is cleaved on the surface at the N—N bond:

$$N_2H_4 + L \to NH_2 - L + (NH_2\cdot)_{\mathrm{ads}}. \qquad (1)$$

The notation adopted by us is analogous to that of Semenov—Voevodskii: L is a free radical on the catalyst surface; $(A\cdot)_{ads}$, for example $(NH_2\cdot)_{ads}$, is a radical formed as the result of one of the acts of the catalytic reaction, i.e., a particle not bound by a strong bond to the catalyst surface; A—L, for example NH_2—L, are particles that have entered into a strong (two-electron) bond with the catalyst. Reaction (1) is followed by a surface chain reaction:

$$N_2H_4 + (NH_2\cdot)_{\mathrm{ads}} \to NH_3 + (N_2H_3\cdot)_{\mathrm{ads}},$$

$$(N_2H_3\cdot)_{\mathrm{ads}} + N_2H_4 \to 2NH_3 + N_2 + (H\cdot)_{\mathrm{ads}},$$

$$(H\cdot)_{\mathrm{ads}} + N_2H_4 \to (NH_2\cdot)_{\mathrm{ads}} + NH_3.$$

At high surface coverages, radical reactions are possible:

$$NH_2 - L + (NH_2\cdot)_{\mathrm{ads}} \to N_2H_4 + L,$$

Fig. 1. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on an iron catalyst: 1 –120°; 2 –230°

Figure 1: Fig. 1. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on an iron catalyst: 1 –120°; 2 –230°

$$\mathrm{NH_2 - L + (H\cdot)_{ads} \rightarrow NH_3 + L},$$

$$\mathrm{NH_2 - L + (N_2H_3\cdot)_{ads} \rightarrow NH_3 + N_2 + H_2 + L}.$$

On acidic and basic catalysts the reaction proceeds by an ionic or molecular (^{4}) mechanism.

Indirect arguments in favor of a chain mechanism for hydrazine decomposition are: a) very high values of the pre-exponential factor in the Arrhenius equation; b) the presence of charged forms on the surface, detected from measurements of the electron work function (up to 0.2 V) during the reaction; c) the existence in some cases of an induction period; d) high stoichiometric coefficients in the decomposition of hydrazine on semiconductors and metals, indicating the multistage character of the reaction. A more direct proof of the chain scheme could be furnished by testing the possibility of the reaction proceeding in the bulk at temperatures at which the radicals ($\mathrm{NH_2\cdot}$), ($\mathrm{N_2H_3\cdot}$), ($\mathrm{H\cdot}$) are no longer retained on the surface of the adsorption forces. To check the transition into the bulk, we used the method of differential calorimetry of Bogoyavlenskaya and Kovalskii (5). The reaction was carried out in a vessel made of molybdenum glass, analogous to that used by Butyagin and Margolis (6). A differential thermocouple was introduced into the reactor. One junction of the thermocouple was located in the catalyst, the other in the gas phase. The sensitivity of the galvanometer, which recorded the relative heating according to the differential thermocouple, was 0.05° per division. The temperature was maintained by a Strelkov-type thermostat with an accuracy of $±$0.01°. In view of the low vapor pressure of hydrazine at room temperature, the initial pressures of N_2H_4 during the reaction were small (1-8 mm).

Fig. 1. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on an iron catalyst: 1 –120°; 2 –230°.

Below are given some typical curves of the change in galvanometer readings on the catalysts we studied. The following catalysts were studied: iron; ammonia catalyst KATZ-55, i.e., iron promoted with alkali; ZnO; $3GaAs \cdot Ga_2Se_3$; CaO, and an aluminosilicate cracking catalyst.

Fig. 2. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on ammonia catalyst KATZ-55 (27.3 FeO; 3.94 Al_2O_3;

Fig. 2. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on ammonia catalyst KATZ-55 (27.3 FeO; 3.94 Al2O3; 1.82 K2O; reduced H2): 1 –175°, 2 –250°

Figure 2: Fig. 2. Change in the relative heating of the catalyst during the decomposition reaction of hydrazine on ammonia catalyst KATZ-55 (27.3 FeO; 3.94 Al2O3; 1.82 K2O; reduced H2): 1 –175°, 2 –250°

Fig. 3. Decomposition of hydrazine on an aluminosilicate catalyst at 240°C: 1 –kinetic curve, 2–curve of relative heating

Figure 3: Fig. 3. Decomposition of hydrazine on an aluminosilicate catalyst at 240°C: 1–kinetic curve, 2–curve of relative heating

1.82 K_2O; reduced H_2): 1 –175°, 2 –250°.

When inert gas (krypton) was introduced into the apparatus with the catalyst, the following was observed: a) an initial short-term cooling of the central junction of the thermocouple, which was outside the catalyst, and b) a subsequent decrease in the temperature difference Δt due to the thermal conductivity of the gas. When hydrazine vapor was introduced, the initial change in the temperature difference was still greater, since to the cooling of the central junction due to the introduction of cold gas there was added the heating of the junction located in the catalyst, owing to the heat of adsorption or the heat of the surface reaction that had begun. At subsequent moments in time, the change in Δt was not the same on different catalysts.

Figure 1 shows the change in temperature difference during the decomposition reaction of N_2H_4 on a pure iron catalyst (obtained by reduction of Fe_3O_4, containing 0.2% Al_2O_3) at an initial vapor pressure

hydrazine 7 mm. The initial deflection of the galvanometer pointer in the negative direction (cooling of the central junction) occurred over 5-10 sec and, because of the small scale, is not shown in Fig. 1. After this there is a relative heating of the central layer and a subsequent equalization of the temperature. We see no other explanation for the relative heating of the central junction except the emergence of the decomposition reaction of N_2H_4 into the volume, since the other causes—cooling upon admission, nonuniformity of the temperature field in the reactor, heating of the catalyst owing to the heat of adsorption and the heat of the surface reaction—shift Δt in the other direction. The subsequent decrease in Δt is due to a decrease in the reaction rate and to equalization of the temperature between the catalyst and the volume of the vessel. It is seen from Fig. 1 that at the high temperature (230°) the effect is expressed much more strongly than at the low temperature.

Fig. 3. Decomposition of hydrazine on an aluminosilicate catalyst at 240°C: 1–kinetic curve, 2–curve of relative heating

Fig. 4. Decomposition of hydrazine on semiconductor catalysts. 1, 2—on ZnO at 290°: 1—kinetics, 2—relative heating; 3—on $3GaAs \cdot Ga_2Se_3$ at 100° (relative heating)

Figure 4: Fig. 4. Decomposition of hydrazine on semiconductor catalysts. 1, 2 —on ZnO at 290°: 1—kinetics, 2—relative heating; 3—on $3GaAs \cdot Ga_2Se_3$ at 100° (relative heating)

Such a picture was not observed (see Fig. 2) when the reaction was carried out on the ammonia catalyst KAT3-55 (iron promoted with alkali). After the initial heating of the catalyst caused by adsorption and the surface reaction, the absolute value $|\Delta t|$ continuously decreased owing to the drop in the reaction rate and the equalization of temperature. Let us recall [1] that the character of hydrazine decomposition on these two catalysts also differed: on pure iron the decomposition proceeded according to the equation $3N_2H_4 \rightarrow N_2 + 4NH_3$; on iron promoted with alkali, according to the equation $2N_2H_4 \rightarrow N_2 + H_2 + 2NH_3$.

On the alkaline CaO catalyst, emergence into the volume likewise was not observed, and the decomposition of hydrazine proceeded according to the reaction $N_2H_4 \rightarrow N_2 + 2H_2$.

Figure 3 gives the kinetic curve and the heating curve for the decomposition of N_2H_4 on an aluminosilicate cracking catalyst (initial vapor pressure of N_2H_4, 5 mm). A very large heating of the catalyst is observed owing to adsorption of hydrazine on it, followed by a continuous decrease of $|\Delta t|$ to a certain constant value.

The results of experiments on semiconductors were similar to the results of experiments with the iron catalyst. Figure 4 gives curves of the change in Δt during the decomposition of hydrazine on catalyst $3\ GaAs \cdot Ga_2Se_3$ (pressure

hydrazine 8 mm, temperature 175°) and on zinc oxide (3 mm and 290°). At lower temperatures (145° in the case of $3GaAs \cdot Ga_2Se_3$ and 240° in the case of ZnO) no increase in Δt after the initial drop was observed. Evidently, at these low temperatures the bulk stage of the reaction is practically absent. From Fig. 4 it is seen that on these catalysts the increase in Δt after the initial drop is small, and on zinc oxide the curve does not even cross the abscissa axis. After a series of experiments this increase disappears altogether, and the reaction rate decreases substantially.

Fig. 4. Decomposition of hydrazine on semiconductor catalysts.
1, 2—on ZnO at 290°: 1—kinetics, 2—relative heating;
3—on $3GaAs \cdot Ga_2Se_3$ at 100° (relative heating)

The data obtained constitute evidence in support of the previously made [1] assumption of a radical-chain mechanism for the decomposition of hydrazine

---

[1] O. V. Krylov, V. M. Frolov, E. A. Fokina, Yu. N. Rufov, VIII Mendeleev Congress on Pure and Applied Chemistry, Collection: *Physical Chemistry*, 1959, p. 172.

on metallic and semiconductor catalysts. On the investigated catalysts of the oxidation-reduction type—metals and semiconductors (with the exception of the iron catalyst promoted with alkali)—the reaction was observed to pass from the surface into the bulk; conversely, on catalysts of the acid-base type (CaO, aluminosilicate) no passage into the bulk was observed. In the author' s opinion, the method for detecting the bulk continuation of a heterogeneous reaction may be proposed as one of the criteria for assigning a catalytic reaction to the oxidation-reduction (as distinct from the acid-base) class.

The author considers it his duty to express gratitude to Corresponding Member of the Academy of Sciences of the USSR S. Z. Roginsky for valuable advice and to M. Ya. Kushnerev for friendly assistance in the experiment.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
8 X 1959

CITED LITERATURE

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.