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Activation of Nitrogen by Alkali Metal-Promoted Transition Metal

VIII. Reactivity of Sorbed Nitrogen on Ru-K/Al_2O_3 Catalyst

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A considerable amount of nitrogen is absorbed by Ru–K/Al_2O_3 while nitrogen is hardly adsorbed by Ru/Al_2O_3 or K/Al_2O_3. Although the absorbed nitrogen can be converted to ammonia by hydrogen treatment above about 270°C, the rate of hydrogenation is much slower than the rate of ammonia synthesis on the catalyst. The isotopic mixing between the sorbed and gaseous nitrogen also becomes detectable above about 270°C, while the isotopic equilibration of nitrogen takes place readily at 250°C. There can be at least three different species of sorbed nitrogen, the absorbed one being predominant in amount and much less reactive.

INTRODUCTION

It has been reported that the potassium-promoted ruthenium is remarkably effective as a catalyst for the activation of nitrogen (*1*, *2*). The ruthenium metal supported on alumina is consistently promoted by the addition of potassium (*1*). An intense ir band of sorbed nitrogen has been found at 2020 cm^{-1} on Ru–K/Al_2O_3, while no analogous band was found on Ru/Al_2O_3 and K/Al_2O_3 (*3*). Since a considerable amount of nitrogen was found to be absorbed by the Ru–K/Al_2O_3, the nature of absorbed nitrogen has been examined in terms of its reactivity in hydrogenation to form ammonia as well as in isotopic mixing with gaseous nitrogen. The present paper deals with the nature of sorbed nitrogen.

EXPERIMENTAL METHODS

Catalysts. Ru/Al_2O_3 (2% wt) was obtained from Japan Engelhard Ltd. and subjected to pretreatment with hydrogen at increasing temperatures up to 400°C for 43 hr. Potassium was added on the treated Ru/Al_2O_3 at room temperature and distributed among the catalyst bed in circulating helium at increasing temperatures up to 400°C for 60 hr. Four catalysts different in potassium content (1–4% wt) were used. K/Al_2O_3 (4.7% wt) was analogously prepared using the alumina support for the Ru/Al_2O_3. Other catalysts reported previously and used for reference in the present study were Ru–K (K, 0.24% wt) (*1*), 0.5% wt Ru–K/Al_2O_3 (K, 0.5% wt) (*1*) and 5% wt Ru–K/active carbon (AC) (K, 19.1% wt) (*4*). The BET area of 0.5 and 2% Ru/Al_2O_3 was 94 m^2/g.

Apparatus and procedures. The apparatus was a closed circulating system with a total volume of 85 cm^3 including catalyst vessel, connected to a manometer, a gas burette and a quadrupole type mass spec-

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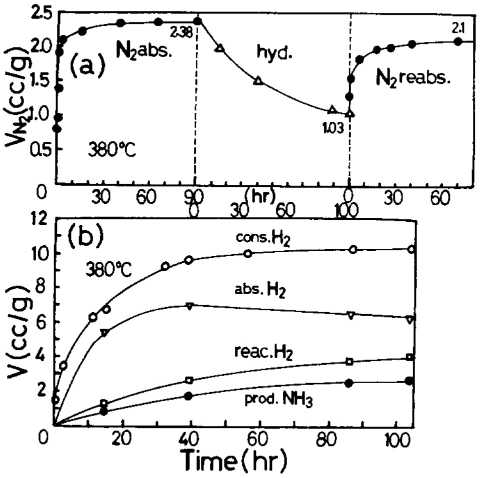

FIG. 1a. Time course of nitrogen uptake followed by hydrogenation and second uptake on Ru–K/Al_2O_3 at 380°C. (b). Time course of hydrogen consumption during the hydrogenation run shown in (a).

trometer which permitted continuous analyses of the circulating gas.

The number of surface ruthenium atoms was estimated for Ru and Ru/Al_2O_3 by chemisorption of hydrogen at room temperature after Dalla Betta (*5*) which was determined by extrapolation of linear part of isotherm above 50 Torr to zero pressure. Prior to the hydrogen adsorption measurement, the catalyst was evacuated at 400°C for 2 hr. The amounts of hydrogen chemisorption were 0.28 cm^3/g on Ru and 0.42 cm^3/g on 2% wt Ru/Al_2O_3. As for the nitrogen uptake experiment on potassium-promoted catalysts, nitrogen was introduced after a brief evacuation at the uptake temperature only to remove helium used to distribute potassium. For the isotopic mixing experiment, the enriched nitrogen (^{15}N; 31.4%) stored in one part of the circulating system was mixed with $^{14}N_2$ on the catalyst without changing the total pressure of nitrogen as made previously (*4*) and the time course of isotopic composition in gas phase was followed. The hydrogenation of absorbed nitrogen was carried out after a brief evacuation of nitrogen at the reaction temperature using 400 to 500 Torr of circulating hydrogen and removing ammonia by a liquid nitrogen trap. The amount of ammonia in the trap was intermittently determined. The rates of ammonia synthesis and isotopic equilibration were determined in the same manner as previously made (*2*).

RESULTS AND DISCUSSION

1. Nitrogen Absorption by Ru–K/Al_2O_3

The time course of nitrogen uptake followed by hydrogenation and second uptake on 2% wt Ru–K/Al_2O_3 (K, 1.5% wt) at 380°C is shown in Fig. 1a. It is seen that the substantial part of uptake is made in the initial 5 hr, while a very slow uptake continues even after 90 hr. On the other hand no detectable uptake of nitrogen was observed on 0.5% wt Ru/Al_2O_3 at 350°C for 21 hr and also on K/Al_2O_3 at 300°C for 20 hr. Thus the uptake is characteristic of the Ru–K/Al_2O_3. Moreover the amount of uptake, 2.3 cm^3/g, is remarkably large compared to the amount of hydrogen chemisorption, 0.42 cm^3/g, on the Ru/Al_2O_3. In other words the uptake, in atoms, is 5.5 times as large as the number of surface ruthenium atoms and is comparable with the total number of ruthenium atoms in the catalyst. Another similar experiment on 2% Ru–K/Al_2O_3 (K, 2.2%) gave an uptake of 3.5 cm^3/g at 350°C for 96 hr, which corresponds (in N atoms) to 1.6 times the total ruthenium. In view of the large amount, the nitrogen uptake cannot be a simple adsorption and seems to be absorption or corrosive chemisorption in nature. In a separate experiment of desorption, only a few percent of the uptake was found to be readily desorbed at 300°C.

2. Hydrogenation of Absorbed Nitrogen on Ru–K/Al_2O_3

The time course of hydrogen consumption during the hydrogenation run shown in Fig. 1a is separately shown in Fig. 1b together with the amount of ammonia produced. It is obvious that the hydrogen consumption is in large excess of that needed to form ammonia, disclosing a hydrogen uptake which can be estimated by subtracting the consumption for ammonia from the total consumption. The hydrogen uptake thus estimated increases with time to a plateau as shown in Fig. 1b. It is to be noted that the plateau value (7.0 cm^3/g) is as large as 3.2 times the total ruthenium in atom basis, while it might be caused by spillover (*6*).

The rate of hydrogenation is very slow as is clear from Fig. 1a and is much slower than the initial rate of nitrogen uptake, demonstrating a high stability of absorbed nitrogen. The effect of temperature on the stability was examined separately. The 2% Ru–K/Al_2O_3 (K, 1.5%) catalyst was treated with nitrogen at 380°C for 90 hr to give 2.3 cm^3/g of nitrogen uptake. The absorbed nitrogen was treated with circulating hydrogen at temperatures for 100 hr. As shown in Fig. 2, the conversion to ammonia is detectable above 200°C and increases with temperature. An analogous result was obtained by temperature programmed hydrogenation of absorbed nitrogen on Ru–K/Al_2O_3 (K, 3.5%) where the nitrogen uptake was made at 300°C for 17 hr and the rate of temperature increase was 5°C/min. The formation of ammonia as detected by a thermal conductivity cell was appreciable above 250°C and increased with temperature. Summarizing, all the results described above are consistent in showing the high stability of absorbed nitrogen.

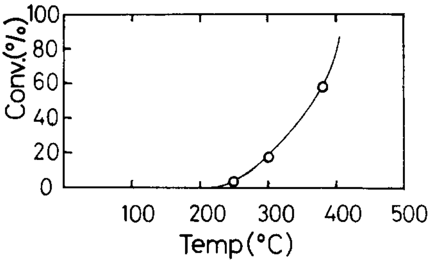

FIG. 2. Effect of temperature on conversion of absorbed nitrogen to ammonia on Ru–K/Al_2O_3 (100 hr at each temperature).

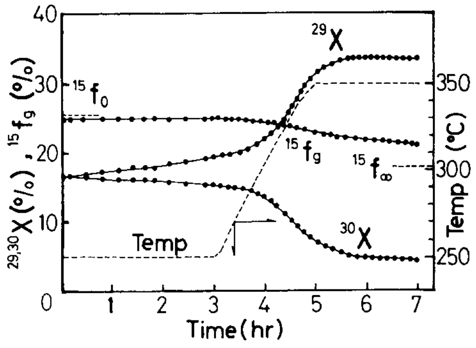

FIG. 3. Time course of exchange reaction between sorbed ^{14}N and gaseous ^{15}N on Ru–K/Al_2O_3 (242 Torr, 250–350°C).

3. *Isotopic Mixing between Sorbed and Gaseous Nitrogen*

In view of the high stability of absorbed nitrogen against hydrogen and desorption, it is of interest to examine the rate of displacement with isotopic nitrogen. Figure 3 illustrates the time course of exchange reaction between sorbed ^{14}N and gaseous ^{15}N on 2% Ru–K/Al_2O_3 (K, 2.2%), first at 250°C and later at increasing temperatures where the nitrogen was sorbed at 350°C for 96 hr to give 3.5 cm^3/g of uptake and the total pressure of gaseous $^{14}N_2$–$^{15}N_2$ mixture was 242 Torr. The $^{15}f_g$ denotes the atomic fraction of ^{15}N and the ^{29}X and ^{30}X denote the mole fraction of $^{14}N^{15}N$ and $^{15}N_2$, respectively, in gas phase. At 250°C the value of $^{15}f_g$ changes little with time, indicating that the rate of displacement is negligibly small, while the isotopic equilibration of gaseous nitrogen proceeds at an appreciable rate (2.1×10^{17} molecules/min g) as demonstrated by increase of ^{29}X as well as decrease of ^{30}X. It is clear that only a small part of sorbed nitrogen can be involved in the pathway of isotopic equilibration. In this respect it is to be noted that the initial value of $^{15}f_g$ (24.8%) is slightly

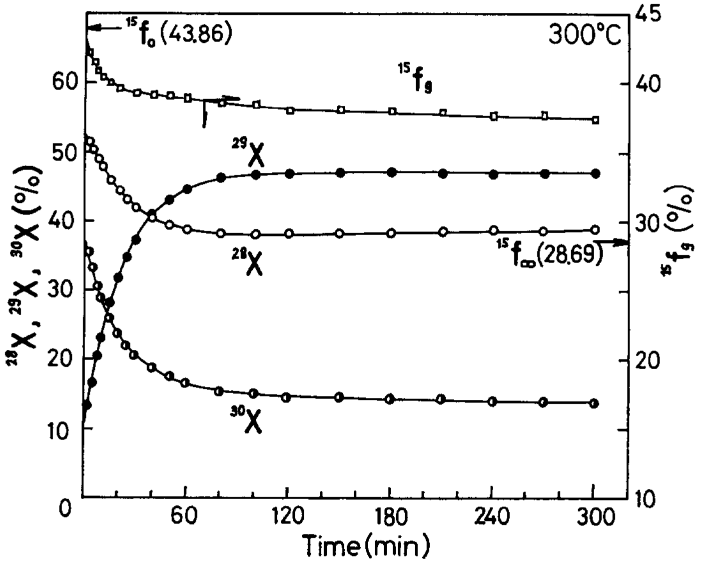

Fig. 4. Time course of isotopic displacement of sorbed nitrogen on Ru–K/AC (150 Torr, 300°C).

smaller than ${}^{15}f_0 = 25.7\%$, the ${}^{15}f_g$ value of gas mixture. Since the difference 0.9% is beyond the error limit of 0.1%, it is suggested that a small part of sorbed nitrogen undergoes a rapid displacement. This would be reasonable since the sorbed nitrogen should involve labile adsorbed species in addition to absorbed one.

When the temperature is increased from 250 to 350°C at a constant rate of 0.83°C/min, detectable change in ${}^{15}f_g$ is observed above 270°C in addition to increase in the rate of isotopic equilibration. At 350°C the isotopic equilibration approaches an equilibrium, while the displacement is still far from equilibrium as demonstrated by the departure from ${}^{15}f_\infty = 17.9\%$, the value expected for the complete mixing with sorbed nitrogen. The extent of displacement as defined by

$$({}^{15}f_0 - {}^{15}f_g)/({}^{15}f_0 - {}^{15}f_\infty),$$

is 54% at 7 hr. Thus the displacement is much slower than the isotopic equilibration, although it is faster than the hydrogenation in which 57% conversion was attained at 380°C for 100 hr. At 355°C on 2% Ru–K/Al_2O_3 (K, 1.5%) the rate of equilibration (R) and the initial rate of displacement (V) (*4*) were determined as follows:

$$R = 1.9 \times 10^{19} \text{ molecules/min g},$$

$$V = 1.8 \times 10^{17} \text{ molecules/min g};$$

R is two orders of magnitude larger than V. These results of isotopic experiment again demonstrate the low reactivity of absorbed nitrogen.

4. Reactivity of Sorbed Nitrogen on Ru–K/AC

It was previously reported (*4*) that all the adsorbed nitrogen on Ru–K supported by active carbon (AC) is displaceable by the gas phase nitrogen within 2 hr at 300°C, apparently in conflict with the present results. It would be required to examine the possible cause of discrepancy. In the previous work the adsorption of nitrogen was carried out at 250°C for 1 hr and at 300°C for 20 hr on 5% wt Ru–K/AC (K, 7%) to give 1.53 cm^3/g of nitrogen uptake. Obviously the time of nitrogen uptake was shorter in the previous work. Thus the sorption process was reexamined on 5% Ru–K/AC (K, 19%) giving more time at 300°C. It was found that a rapid initial uptake is finished within a few hours and followed by a slow uptake which does not stop even after 160 hr. The average rate in the later period was 0.025 $cm^3/hr\ g$, which is much larger than that in Fig. 1a and thus the total uptake for 166 hr was as much as 8.73 cm^3/g. Figure 4 illustrates the time course of isotopic displacement of the sorbed nitrogen under 150 Torr at 300°C. The initial rapid displacement is followed by a slow process, while the extent of displacement is 39% at 2 hr and 42% at 5 hr, being far from equilibrium as is the case with $Ru–K/Al_2O_3$. After the displacement run the sorbed nitrogen was hydrogenated at 300°C for 96 hr, giving 8.2 cm^3/g of ammonia, or 47% conversion again as in the case with $Ru–K/Al_2O_3$.

Thus the apparent discrepancy first results from the difference in the time of nitrogen uptake. The later slow uptake is likely to give the less reactive species so that the shorter the time of uptake, the larger the extent of displacement readily attained. In fact in the previous work (*4*) the displacement was complete within 2 hr at 300°C. The faster attainment of equilibrium, however, not only results from the shorter uptake time, but also possibly from the higher activity of Ru–K/AC as observed in the isotopic equilibration as well as in the nitrogen uptake. This difference in activity would be related to the higher ability of carbon to hold potassium which gives rise to the higher content of potassium.

5. *Nature of Sorbed Nitrogen*

There can be at least three types of sorbed nitrogen, i.e., (a) adsorbed nitrogen, atomic or molecular, on ruthenium surface, (b) bound nitrogen on potassium (*7*), (c) corrosively chemisorbed nitrogen in the bulk of ruthenium (*2*). The slow uptake, slow displacement and slow hydrogenation are likely to be caused by type (c) and a larger amount of potassium on carbon would increase type (b), while at least some part of type (a) should be involved in the pathway of ammonia synthesis as well as of isotopic equilibration.

The previous infrared work (*3*) on $Ru–K/Al_2O_3$ was planned to detect type (b) nitrogen. An intense ir band was found unexpectedly at 2020 cm^{-1} which can be assigned to a dinitrogen species. It has been shown that the band appears slowly on nitrogen chemisorption at above 200°C and disappears slowly on hydrogen treatment at above 260°C giving ammonia. Such slow changes are strikingly in agreement with the behavior of type (c) nitrogen as described above. Although the 2020 cm^{-1} band has been ascribed to a "chemisorbed" species, the chemisorption is very likely a corrosive one so that the dinitrogen species are located in the bulk solid. A further work on the nature of $Ru–K–N_2$ system has been made and a preliminary result is reported separately (*8*).

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