

## Ammonia Synthesis Activity of a Raney Ruthenium Catalyst

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A Raney ruthenium catalyst prepared from a Ru/Al ( $\frac{1}{3}$ ) alloy exhibits a high activity for ammonia synthesis. The apparent activation energy of ammonia synthesis is lower on the Raney catalyst than on pure ruthenium by 5 kcal/mol. The specific activity with respect to the number of surface ruthenium atoms determined by chemisorption of hydrogen as well as carbon monoxide is three times higher on the Raney catalyst at 300°C, and the addition of metallic potassium brings about a further 12-fold increase in the activity, retaining the lower activation energy. The higher specific activity of the Raney catalyst discloses a promoter effect of aluminum.

### INTRODUCTION

It has been shown that effectiveness of ruthenium catalysts in the activation of the nitrogen molecule (1-4) is remarkably promoted by the addition of metallic potassium which has been interpreted in terms of electron donation by potassium to ruthenium (1). It is accordingly suggested that analogous promotion may be expected with electropositive metals other than the alkali metals. In this respect aluminum is an electropositive metal which can form an alloy with ruthenium. Moreover the alloy should give a well-dispersed ruthenium catalyst on treatment with sodium hydroxide. Thus it is of interest to study the catalytic activity of Raney ruthenium in the ammonia synthesis reaction, on which there is no known report.

### EXPERIMENTAL

The Ru-Al alloy was prepared at National Research Institute for Metals (Tokyo) by an arc-melting method in an

argon atmosphere from briquettes of component metals (99.9% Ru and 99.998% Al) with a ruthenium content of 50 wt% (Ru/Al = 1/3). The X-ray diffraction of the alloy gave peaks at  $2\theta = 23.9, 43.7$  and  $44.6^\circ$  which correspond to  $\text{RuAl}_2$  instead of  $\text{RuAl}_3$ . The alloy was leached according to the so-called W-1 method of Raney nickel preparation (5); i.e., 80 ml of distilled water and 20 g of sodium hydroxide were placed in a 300-ml beaker. To this solution, cooled by an ice bath, 4 g of the alloy powder was added in small portions with stirring. The suspension was digested at 115°C for 7 hr with stirring. The product was washed with water until no alkali was detected and then stored in water. Since it was highly pyrophoric, the catalyst powder was transferred to the reaction vessel as a water suspension and dried *in situ*, followed by treatment with hydrogen (600 Torr) at 300°C for 3 hr. The specific BET surface area was found to be as high as 30.7 m<sup>2</sup>/g. The amount of residual aluminum was about 10 wt% of the Raney catalyst as

estimated from the amount of hydrogen evolved during the leaching treatment. The X-ray diffraction of the Raney catalyst gave broad peaks which can be assigned to ruthenium metal when the sample was protected from air by immersing it to decalin.

Pure ruthenium catalyst was prepared from  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  by reduction with circulating hydrogen at increasing temperatures from 130 to 450°C (24 hr at 450°C). Ru- $\text{Al}_2\text{O}_3$  (1.0 wt% Ru) was obtained from Japan Engelhardt Ltd. and was treated with circulating hydrogen at increasing temperatures up to 450°C (24 hr at 400°C).

The addition of potassium metal was performed in circulating helium by treating the ruthenium catalyst with potassium vapor at 300°C for 30 hr. The amount of potassium incorporated into the catalyst was determined by an acid titration of water extract of the catalyst.

The measurements of rate of ammonia synthesis were carried out in a conventional circulating system with a liquid nitrogen trap using a stoichiometric mixture (600 Torr) (1), where the stationary formation of ammonia was confirmed for the trapped product. The adsorption of hydrogen and of carbon monoxide was carried out in this apparatus.

## RESULTS

### *Catalytic Properties of Raney Ruthenium*

The Raney ruthenium without added potassium was found to be highly active in the synthesis of ammonia. A considerable amount of synthesis gas (8.0 ml/g) was sorbed in the initial period of the first run (300°C) before the stationary formation of ammonia, in contrast to the case of pure ruthenium on which ammonia appeared without a time lag. Although no analysis of the sorbed gas was made, an enrichment of nitrogen or hydrogen could have taken place. Thus the synthesis gas was replaced with the stoichiometric mixture after a

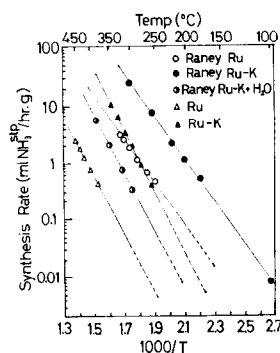


FIG. 1. Arrhenius plots of ammonia synthesis rate over ruthenium catalysts under 600 Torr of total pressure.

stationary state was attained. Thereafter the rate of volume decrease was in agreement with the rate of formation of ammonia in the trap.

The steady rate of ammonia formation was determined at temperatures from 250 to 350°C, and is shown in Fig. 1 as an Arrhenius plot together with the results obtained with pure ruthenium with and without potassium. It is clear that the Raney ruthenium is as active as Ru-K which is much more active than pure ruthenium on a gram-catalyst basis. It should be noted that the apparent activation energy is decreased from 24 kcal/mol on pure ruthenium to 19 kcal/mol on Raney ruthenium.

After the above experiments metallic potassium was added to the Raney ruthenium catalyst. The amount of added potassium, determined after the synthesis runs, was found to be 0.97 mmol/g. The steady rate of ammonia formation was determined at temperatures from 100 to 300°C and is shown in Fig. 1. The addition of potassium causes an approximately 10-fold promotion of activity, holding the low activation energy of 19 kcal/mol while the total surface area was found to be decreased to one-third of its original value. It is remarkable in an ammonia synthesis reaction that the straight Arrhenius plot extends to as low as 100°C, covering three orders of magnitude of variation in the

reaction rate. Since the large difference in the reaction rate should give rise to a large difference in the ammonia concentration in the effluent stream from the reactor, the above result reveals that the rate of ammonia formation is independent of ammonia pressure (below 6 Torr).

The Raney ruthenium with added potassium was then treated with 18 Torr of water vapor at 70°C for 3 hr until no pressure increase was observed, followed by reduction with hydrogen at 300°C for 11 hr and evacuation at 300°C for 2 hr. The specific surface area of the catalyst was decreased to 0.77 m<sup>2</sup>/g by the above treatments. In Fig. 1, although the rate of ammonia formation after the treatment is slower than that on the original catalyst as expected from the lower surface area, it should be noted that the water-treated catalyst is still much more active than the pure ruthenium catalyst in spite of the nearly equal specific area. It should also be noted that the apparent activation energy reverts to the 24 kcal/mol observed on pure ruthenium.

#### *The Number of Surface Ruthenium Sites*

Although Raney ruthenium is much more active than pure ruthenium, the activity should be compared in terms of the specific rate per surface ruthenium site to examine the effect of aluminum. The number of surface ruthenium sites was estimated by chemisorption of hydrogen (6) as well as carbon monoxide at 0°C. The isotherms on the Raney ruthenium without potassium and on pure ruthenium as shown in Fig. 2.

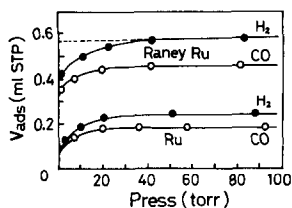


FIG. 2. Chemisorption of hydrogen and carbon monoxide on Raney ruthenium (0.166 g) and pure ruthenium (1.12 g) at 0°C.

TABLE 1  
Amount of Chemisorption of Hydrogen and Carbon Monoxide at 0°C

	Catalyst	
	Pure Ru	Raney Ru
BET area (m <sup>2</sup> /g)	1.0	30.7
H <sub>2</sub> (ml/g)	0.20	3.43
CO (ml/g)	0.16	2.65

Since the adsorption increases little above 20 Torr in each case, the amount of chemisorption is determined by extrapolation of the linear part above 20 Torr. The results are given in Table 1 together with BET surface areas. Assuming atomic adsorption of hydrogen on ruthenium atoms, the BET area divided by the number of hydrogen atoms chemisorbed on pure ruthenium gives a cross-sectional area for the exposed ruthenium atom of 9.4 Å<sup>2</sup>/atom, which is close to an averaged value of 8.9 Å<sup>2</sup>/atom for the (001) and (100) planes of ruthenium. It is accordingly concluded that the amount of chemisorption obtained with the present method can be regarded as a measure of surface ruthenium atoms.

The amount of chemisorption of carbon monoxide on pure ruthenium is nearly equal to that of hydrogen, indicating a stoichiometry of one CO for two Ru atoms. Although the amount of chemisorption of carbon monoxide is less than that of hydrogen, it is to be noted that the ratio CO(a)/H<sub>2</sub>(a) on Raney ruthenium (0.77) is close to the value on pure ruthenium (0.80), indicating that both gases are adsorbed on the ruthenium part of the Raney ruthenium surface. Thus the ruthenium part of the Raney ruthenium may be estimated to be 17.5 m<sup>2</sup>/g or 57% of the total surface, using the value of 9.4 Å<sup>2</sup>/atom mentioned above.

#### *Specific Activity per Surface Ruthenium*

On the basis of above value of surface ruthenium area, the specific rates of ammonia formation per surface ruthenium are

TABLE 2  
Specific Activity of Surface Ruthenium Atoms at  
300°C and 600 Torr

Catalyst	Activity (molecules of NH <sub>3</sub> /site·sec)
Ru	$2.4 \times 10^{-5}$
Raney Ru	$8.1 \times 10^{-5}$
Raney Ru-K	$101 \times 10^{-5}$

evaluated for 300°C and given in Table 2. The specific rate on pure ruthenium at 300°C is estimated from Fig. 1. The specific rate on the Raney Ru-K is based on the ruthenium area before potassium addition, since the determination of ruthenium area is disturbed by the chemisorption of hydrogen on potassium. Thus the estimated value for Raney Ru-K would be too small in view of the decrease in BET area on addition of potassium. It is clear that the specific activity of ruthenium is about threefold larger on the Raney ruthenium, and at least 40-fold larger on the Raney Ru-K.

#### DISCUSSION

The increased specific activity of Raney ruthenium is associated with the presence of residual aluminum. It is generally accepted that the aluminum in a Raney alloy is oxidized to form alumina hydrate during leaching treatment. In this respect the catalytic behavior of Ru-Al<sub>2</sub>O<sub>3</sub> would be of interest. Ammonia synthesis on Ru-Al<sub>2</sub>O<sub>3</sub> is characterized by a low apparent activation energy, 14 kcal/mol, which is increased to 23 kcal/mol on addition of potassium, as reported previously (1) and reconfirmed in the present study, while the activation energy on the Raney ruthenium, 19 kcal/mol, changes little on addition of potassium. Thus Raney ruthenium is different in its behavior from Ru-Al<sub>2</sub>O<sub>3</sub>, suggesting that the residual aluminum remains, at least partly, as the alloy. In-

deed the presence of metallic aluminum has been accepted in the case of Raney nickel (7), although it could not be detected by X-ray diffraction of Raney ruthenium. The enhanced activity of Raney ruthenium seems to be caused by the presence of metallic aluminum, possibly because of its electropositive nature.

It should be noted that the activation energy of Raney Ru-K is increased to the value for pure ruthenium after water vapor treatment at 70°C, suggesting that the Raney alloy is completely decomposed by the treatment. Since Raney ruthenium is prepared by leaching with an aqueous solution of sodium hydroxide at 115°C, a simple treatment with water at 70°C should not give rise to further decomposition of the alloy. The suggested decomposition of alloy must be caused by the presence of potassium, which must be transformed to potassium hydroxide by the reaction with water. The added potassium might be dissolved into the alloy giving rise to enhanced decomposition of alloy in the water vapor treatment. The remarkable decrease in surface area during the treatment also suggests a disintegration of the Raney alloy structure, which results in sintering of ruthenium. Since the water-treated catalyst is still more active than pure ruthenium, the potash formed by the treatment seems to be able to promote the activity of ruthenium.

The amount of potassium found in Raney Ru-K catalysts after the runs amounts to approximately 1 mmol/10 mmol of ruthenium. Although the present results give no information about the disposition of potassium in the catalyst, our recent results have demonstrated that both potassium and dinitrogen are incorporated into bulk ruthenium, forming a compound which is reported separately (9). An analogous incorporation of potassium likely takes place on the Raney catalyst.

Another point to be discussed is the low

activation energy observed on the Raney Ru-K catalyst. It has been suggested that promotion through electron donation is caused by a reduction of activation energy (8), while the apparent values observed so far on potassium-promoted ruthenium catalysts are mostly in the range of 23-27 kcal/mol and not much different from the value of 24 kcal/mol for pure ruthenium. The observed low value of 19 kcal/mol on the Raney Ru-K catalyst is of interest in this respect. The rather high apparent activation energy on potassium-promoted ruthenium has been ascribed at least partly to a strong competitive chemisorption of hydrogen as demonstrated by retarding effect of hydrogen on the rate of isotopic equilibration of nitrogen (4). The role of aluminum in reducing the activation energy will be the subject of future study.

In summation it may be concluded that the high activity of Raney ruthenium is caused first by a remarkable increase in surface area which is stable at temperatures as high as 400°C, and second by electronic

promotion, both of which are realized as results of alloying with aluminum.

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