Development of Alkali-Promoted Ruthenium as a Novel Catalyst for Ammonia Synthesis

ATSUMU OZAKI

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama, 227, Japan

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There are two different approaches, synthetic and analytic, for developing a new catalyst. Some catalysts in homogeneous systems have been derived by ingenious combinations of stoichiometric reactions. This type of approach may be called the synthetic way. Catalyst development in heterogeneous systems, on the other hand, has originated mostly from unexpected findings. The poor activity or selectivity found with a certain material can be improved by analyzing the nature of active catalyst. We find a good example of this in the development of a cracking catalyst starting from natural clay. This type of approach may be called the analytic way.

The ammonia synthesis reaction was first found in 1905 on an iron dispersion at 1000 °C and atmospheric pressure, but the yield of ammonia was very low because of thermodynamic limitations. High-pressure operation was thus adopted for subsequent studies, and osmium was found to have excellent activity at 550 °C and 100 atm. Since osmium was too expensive and had too small a production, exploratory work for commercially more acceptable catalysts was carried out at BASF. This work led in 1910 to the discovery of the famous catalyst $Fe-Al_2O_3-K_2O$, which is essentially the catalyst used in the present industrial process.

After 1920, a tremendous number of studies into the nature of the catalyst were made, giving rise to progress in the characterization of the catalyst surface as well as in the kinetic theory of heterogeneous catalysis. The famous method of surface area determination was born in those studies, and the rate-determining step of ammonia synthesis was proved to be chemisorption of dinitrogen.[1]

Isotopic Studies of Ammonia Synthesis

The first work on ammonia synthesis by the present author was to confirm the rate-determining step in terms of a deuterium isotope effect. Unexpectedly it was found that the rate of ammonia synthesis is 3 to 4 times faster with D_2 than with H_2.[2] However, no isotope effect was found in the rate constant, in conformity with the rate-determining chemisorption of dinitrogen. The inverse isotope effect was reasonably accounted for by the relative abundance of adsorbed species formed from the product ammonia under the steady state of reaction. Because of the larger zero point energy difference in ammonia than in adsorbed species and molecular hydrogen, the equilibrium for the dissociative adsorption of ammonia,

$$NH_3(ND_3) \rightarrow N + {}^3/_2H_2(D_2) \text{ or } NH(ND) + H_2(D_2)$$
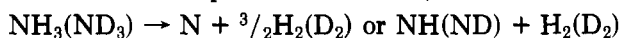
Atsumu Ozaki was born in Nagoya, Japan, in 1920. He received his B.E. degree from Tokyo Institute of Technology and his D.Sc. from Hokkaido University. He has subsequently been a faculty member of Tokyo Institute of Technology, where he is now Professor of Catalytic Chemistry. He served as Director of the Research Laboratory of Resources Utilization of the Institute from 1970 to 1973.

Table I
Effects of Potash Addition on Adsorbed Species and Rate of Equilibration on Iron

catalyst	adsorbed species	ref	effect of H_2 on rate of equilibration	ref
Fe	N	2	no	5
$Fe-Al_2O_3$	N	3	negative	6
$Fe-K_2O$			positive	7
$Fe-Al_2O_3-K_2O$	NH	1	positive	4, 8

is farther on the right-hand side for NH_3 than for ND_3, thus resulting in a larger amount of adsorbed species (N or NH) for the H_2 system. Since the adsorbed species occupies some part of the catalyst surface on which the rate-determining chemisorption of dinitrogen should take place, the relative abundance of adsorbed species gives rise to the observed slower rate with H_2 than with D_2.

The above analysis of the isotope effect suggested a procedure to identify the adsorbed species during reaction on the basis of the extent of isotope effect as well as of the reaction order with respect to hydrogen. In brief, the adsorbed species of N gives rise to an isotope effect larger than NH as estimated from the calculated values of the ratio of adsorption constants for the H_2 and D_2 systems. Thus, identity of the adsorbed species, N or NH, may be given by the observed isotope effect on the adsorption constant. A series of isotope effect studies made on differently promoted iron catalysts gave results as summarized in Table I.[3] It appears that the addition of potash to iron catalyst gives rise to the change of adsorbed species from N to NH.

In view of the above results, the effect of potash addition was further examined with the isotopic equilibration of dinitrogen. Since the dinitrogen molecule should undergo dissociation in the isotopic equilibration, the catalytic activity for equilibration seems to be relevant to ammonia synthesis, the rate of which is determined by chemisorption or dissociation of dinitrogen. Although the rate of equilibration on promoted iron catalyst was known to be enhanced by the presence of hydrogen,[4] it was found that the enhancement by hydrogen does not take place on pure iron[5] or

(1) For further reading on the kinetics and mechanism of ammonia synthesis, see (a) P. H. Emmett, Ed., "Catalysis", Vol. III, Academic Press, New York, 1955, pp 171, 265. (b) A. Nielsen, "An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia", 3rd ed., Giellerups, Copenhagen, 1968; (c) A. Nielsen, *Catal. Rev.*, **4**, 1 (1970); (d) A. Ozaki and K. Aika in "A Treatise on Dinitrogen Fixation", Hardy, Bottomley, and Burns, Eds., Wiley, New York 1979, pp 169; (e) M. I. Temkin, *Adv. Catal.*, **28**, 250 (1979).

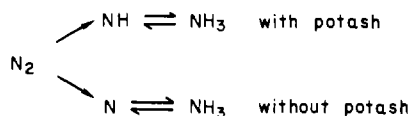(2) A. Ozaki, H. S. Taylor, and M. Boudart, *Proc. Ry. Soc. London, Ser. A*, **258**, 47 (1960).

(3) (a) K. Aika and A. Ozaki, *J. Catal.*, **13**, 232 (1969); (b) K. Aika and A. Ozaki, *ibid.*, **19**, 350 (1970).

(4) G. G. Joris and H. S. Taylor, *J. Chem. Phys.*, **7**, 893 (1939).

(5) (a) Y. Morikawa and A. Ozaki, *J. Catal.*, **12**, 145 (1968); (b) Schulz and H. Schaefer, *Z. Phys. Chem.*, **64**, 333 (1939).

on Fe–Al₂O₃[6] at around 300 °C. Those results are summarized in Table I. The enhancement by hydrogen appears to be induced by the addition of potash to iron.[7,8] An analogous result was reported by Chesnokova et al. for the rate of dinitrogen chemisorption on iron catalysts.[9] That is, the rate is enhanced by the presence of hydrogen only on potash-promoted iron catalysts.

In this way it was found that the potash promoter is responsible for the hydrogen-enhanced activation of dinitrogen on iron. The hydrogen-enhanced equilibration may imply that the dissociation of dinitrogen is promoted by way of an interaction with hydrogen atom, giving NH directly. This can be the reason why the adsorbed species on iron changes from N to NH on addition of potash, as illustrated by

$$N_2 \; \begin{matrix} \nearrow NH \rightleftharpoons NH_3 & \text{with potash} \\ \\ \searrow N \rightleftharpoons NH_3 & \text{without potash} \end{matrix}$$

Note, however, that the rate of isotopic equilibration divided by the iron surface area is three to four times higher on Fe–K₂O–Al₂O₃ than on pure iron, even in the absence of hydrogen.[8] Since the role of Al₂O₃ is to increase the iron surface area, it appears that the effect of potash on iron is 2-fold, i.e., the increase of specific activity per iron and the induction of hydrogen effect.

Role of Potash Promoter

It became clear that the potash promoter brings about a significant change in the surface property of iron. Some suggestions have been made for the role of potash promoter in iron catalysts. They include (1) neutralization of acidic properties associated with the other indispensable promoter, Al₂O₃, giving rise to enhanced desorption of ammonia from the catalyst surface;[10] (2) electronic effects on iron as demonstrated by a marked increase in heat of adsorption of carbon monoxide[11,12] and also by significant decrease in work function of iron[13] on addition of potash. In fact it had previously been demonstrated that cathodic polarization applied on an iron catalyst under its working condition causes a significant increase in its ammonia synthesis activity[14] and that the ammonia synthesis activity of iron increases with decrease in work function caused by the addition of potash promoter.[13] These results indicated that a higher electron density in iron is favorable for ammonia synthesis activity, attaching more importance on the second suggestion.

If the above suggestion is valid, the activity should be increased effectively by using a more electropositive substance as the promoter. Since the electropositivity

Table II
Ammonia Synthesis Activities of Metals on Active Carbon Promoted by Metallic Potassium[a]

6B	7B	8-1	8-2	8-3
Mo 0.6		Fe 0.72	Co 0.40	Ni 0.04
		Ru 22.4	Rh 0.52	Pd nil
	Re 0.36	Os 5.6	Ir 0.68	Pt 0.008

[a] Activity is given by mL of NH₃ STP/(h g) at 300 °C, 600 torr of 3H₂/N₂ gas, flow rate 4.5 L/h. Metal and potassium loadings are 5.0 wt and 25 wt % of carbon.

of potassium is considerably decreased by being combined with oxygen, metallic potassium should be much more electropositive than potash. Indeed the ammonia synthesis activity of pure iron was found to be increased by 5- to 8-fold on adsorption of potassium vapor, depending on temperature.[7] This would be a chemical verification of above hypothesis which led to the discovery of a new catalyst system promoted by metallic potassium.[7,15] It is clear that the role of the potash promoter is electronic in nature. Additional support for the electronic promotion can be found in a recent paper by Ertl et al.[16] who showed that preadsorbed potassium increases remarkably the rate of nitrogen chemisorption.

New Catalyst System

It was supposed earlier that the direct addition of metallic potassium would not be very effective because the added potassium would decrease the effective area of the catalyst metal. If the metallic potassium is added to the catalyst metal supported on an electric conductor, such as carbon, the electron donation might be made through the support, thus realizing an effective promotion of the catalyst metal. In fact, an analogous catalyst, Ni–C–Na, was known for ethylene polymerization, suggesting that the interaction between Ni and Na can be effectively made on carbon support. In order to test the above idea, transition metals supported on active carbon (prepared by impregnation followed by reduction with hydrogen) were examined for ammonia synthesis activity after adsorption of potassium vapor. The relative values at 300 °C are given in Table II.[15a,17] It is clear that the iron family metals are most active, with ruthenium standing out.

The above result is in contrast with the classical result by Mittasch et al.[18] that ruthenium is less active than iron. Later studies indicated that the discrepancy is likely caused by the difference in reaction conditions. The classical result was obtained under elevated pressure (100 atm) and high temperature (550 °C), while the above experiments were made at low pressure and temperature.

In this way, subsequent studies were made primarily on ruthenium catalysts. Figure 1 shows the effect of alkali metals on the rate of ammonia synthesis on Ru/carbon.[15] The activity increases with increase in the electropositivity as well as the added amount of the alkali metal, in conformity with the concept that the ruthenium metal is activated by electron donation from metallic alkali. In addition, as expected from the

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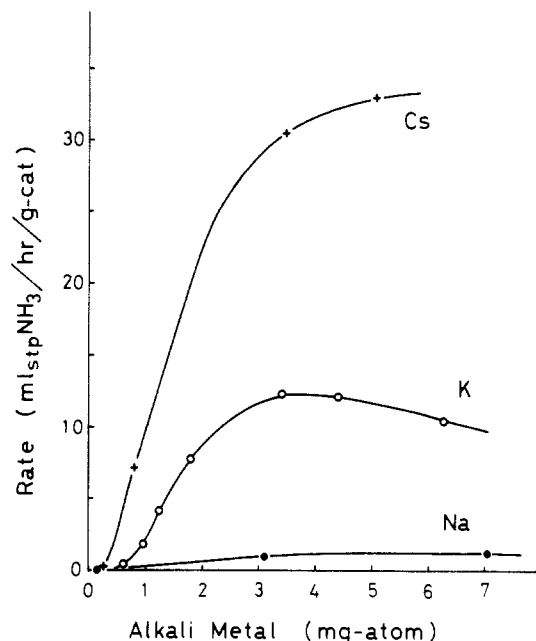(18) A. Mittasch, *Adv. Catal.*, 2, 81 (1950).

Figure 1. Rates of ammonia synthesis on Ru/C promoted by metallic alkali as functions of alkali content at 290 °C and 600 torr. Reprinted with permission from ref 15b. Copyright 1972, Academic Press.
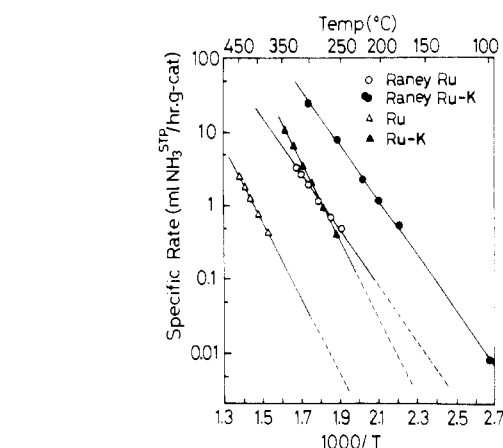

Figure 2. Arrhenius plots of ammonia synthesis rate on ruthenium catalysts under 600 torr. Reprinted with permission from ref 28. Copyright 1978, Academic Press.

rate-determining dissociation of dinitrogen in ammonia synthesis, the Ru–K/carbon was found to give a high activity for the isotopic equilibration of dinitrogen.[19]

It is remarkable that the Ru/carbon (thoroughly reduced with hydrogen) has no activity before the addition of alkali metal, either for ammonia synthesis or for isotopic equilibration[19] (Figure 1). The lack of activity was observed even at 400 °C, at which pure ruthenium exhibits a definite activity. It appeared that the intrinsic activity of ruthenium is lost by being supported on carbon. The lack of activity was found with all other carbon-supported metals, including iron, which were known to give some activity for ammonia synthesis when they are unsupported. These results suggest an inhibitory effect of carbon ascribable to its electron-accepting property. In fact, it was later demonstrated by Mössbauer spectroscopy that iron atoms intercalated into graphite lattice carry some positive charge even after reduction treatments.[20] The situation seems to be reversed on addition of alkali metal, resulting in the remarkable gain in activity as observed. Potassium metal added to the active carbon alone gives no activity for dinitrogen,[15] but exhibits a high activity for H_2–D_2 exchange.[21]

It was known that transition-metal chlorides are intercalated into layered lattice of graphite.[22] Ichikawa et al. reported ammonia synthesis activities of the intercalated compounds promoted by metallic potassium.[23] Volpin et al. showed that on reduction of these compounds, transition metals remain intercalated as metal atoms, giving no activity, whereas they are activated for ammonia synthesis by addition of metallic potassium.[24]

Although the Ru–K/carbon catalyst is found to be more active than an Fe–K_2O–Al_2O_3 catalyst at around 300 °C and atmospheric pressure,[15a] the relative efficiency is reversed under high pressure. Because of an inhibitory effect of hydrogen, the rate of ammonia formation on Ru–K/carbon levels off above about 30 atm at 350 °C.[25] Even on pure ruthenium, the kinetics of ammonia synthesis have a negative order with respect to hydrogen.[26] Thus, the superiority of the ruthenium catalyst, particularly at lower temperatures, is limited to lower pressures.

Another problem to be considered for the catalyst promoted by metallic potassium would be a possible loss of potassium due to vaporization during use. In this respect carbon is a good support since it has a large capacity for holding metallic potassium. As much as 20 wt % of potassium can be retained on the active carbon surface at 400 °C. It is natural that the requirement for purity of synthesis gas is more severe with the catalyst promoted by metallic potassium than that by potash because of the high reactivity of potassium with oxygen compounds.

Different Types of Ruthenium Catalysts

The remarkable promotion by metallic potassium was also found for ammonia synthesis activity of pure ruthenium powder[27] and of Raney ruthenium,[28] as shown in Figure 2. The Raney catalyst (90 wt % Ru) was prepared by leaching a Ru–Al alloy with sodium hydroxide so that it had a high specific surface area of 30 m^2/g as compared with 1–2 m^2/g for the ruthenium powder. The high surface area is admittedly due to fine structure maintained by the alloy. Hence, the higher activity of Raney Ru relative to pure Ru is partly traced back to the difference in surface area, while the specific activity per surface ruthenium is 3.3 times as high on Raney Ru at 300 °C. Thus the Raney Ru–K appears to be doubly promoted by K and Al, resulting in a very high activity to give steady formation of ammonia even at 100 °C.

The promotion by potassium was found to be more extensive for the isotopic equilibration of dinitrogen

(19) K. Urabe, K. Aika, and A. Ozaki, *J. Catal.*, **32**, 108 (1974).
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(22) R. C. Croft, *Q. Rev., Chem. Soc.*, **14**, 1 (1960).
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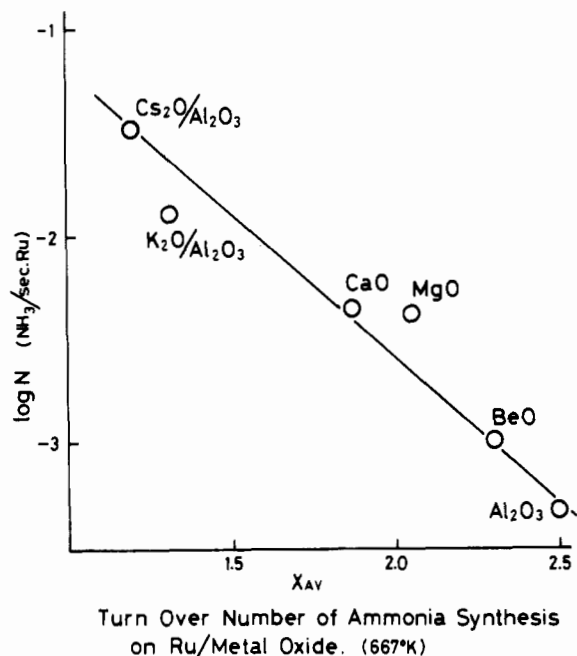(28) K. Urabe, T. Yoshioka, and A. Ozaki, *J. Catal.*, **54**, 52 (1978).

Figure 3. Specific rates of ammonia synthesis per surface ruthenium on metal oxide supported ruthenium as a function of electronegativity of metal oxide.

Figure 4. Infrared spectra of dinitrogen absorbed at different temperatures by Ru–K/Al$_2$O$_3$: (—) 200 °C; (- - -) 230 °C; (····) 250 °C; (—····) 350–380 °C. Reprinted with permission from ref 34. Copyright 1976, Academic Press.

(about 500-fold at 400 °C) than for ammonia synthesis on Ru or Ru/Al$_2$O$_3$. The difference in the extent of promotion is caused by the presence of hydrogen in ammonia synthesis. In other words, the promotion by potassium is reduced to some extent by partial occupation of the active surface by hydrogen.[29] This undesirable effect of hydrogen was unexpected from the studies on iron catalysts, and this is probably a unique feature of ruthenium catalysts.

Another catalyst starting from K$_4$Ru(CN)$_6$ was examined.[30] The complex was supported on alumina and reduced by hydrogen at temperatures up to 450 °C. The stoichiometry of hydrogen reduction to form methane and ammonia disclosed that the number of CN ligands hydrogenated per complex molecule reaches 4.7, which is much larger than the value expected for a reduction of Ru(II) to Ru(0), suggesting a reduction of K(I) to K(0). In fact the reduction of KCN by H$_2$ is not impossible thermodynamically when the products are removed continuously. It was confirmed that the reduced catalyst generated hydrogen on addition of water vapor. It can be estimated that a Ru–K or Ru–K–Al system is formed on hydrogen reduction of K$_4$Ru(CN)$_6$/Al$_2$O$_3$, although the catalytic activity of the product was not very high, presumably due to loss of potassium during reduction.

The effect of oxide support on the ammonia synthesis activity of ruthenium was examined.[31] Figure 3 gives the specific rates of ammonia synthesis per surface ruthenium on different supports as a function of averaged electronegativity of the oxide support which is estimated as the geometric mean of Pauling's value for elements. The values for Cs$_2$O and K$_2$O are assumed for Cs$_2$O/Al$_2$O$_3$ and K$_2$O/Al$_2$O$_3$, respectively. There is a definite tendency that the more basic the support, the
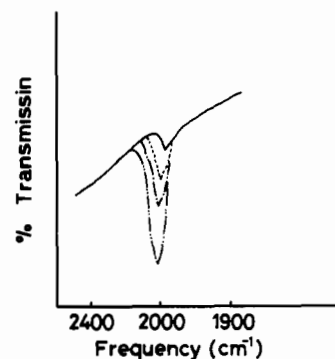
higher the activity, in conformity with the activation by electron donation. It is thus suggested that the same principle underlies in the activations by metallic alkali and basic oxide.

Dinitrogen Complex Formed in Ru–K Catalyst under Working Conditions

It was found as described above that the addition of potassium to pure ruthenium brings about a remarkable promotion, which was unexpected because the added potassium was expected to occupy the ruthenium surface. The high activity thus attained was found to be very stable during repeated runs at temperatures up to 380 °C, suggesting a strong interaction between Ru and K.[27] An explanation for the high stability was a stable compound formed between Ru and K in which the ruthenium atoms assume an anionic nature, because it was known that gold reacts with cesium to give a semiconducting compound.[32] Since the electronegativity of ruthenium is close to that of gold, an analogous compound, Cs–Ru, was considered and examined for its reality in terms of electric resistance of ruthenium film. If the compound is formed, the resistance of film should increase significantly on addition of cesium vapor. However we failed to observe any increase in the resistance.[33]

On the other hand, a strong infrared absorption band was found at 2020 cm^{-1} (1997 cm^{-1} for ^{15}N$_2$) on Ru–K/Al$_2$O$_3$ treated with dinitrogen at above 200 °C as shown in Figure 4.[34] The observed frequency as well as the isotope shift indicates a dinitrogen species held by the catalyst. When sodium is used in place of potassium, the band shifts to 2026 cm^{-1}, in contrast to the absorption by NaN$_3$ at 2128 cm^{-1}. This rules out the possibility of azide form of nitrogen, and in fact azides are known to decompose at this temperature. The corresponding absorption band for Ru–N bond is found at 520 cm^{-1} with Ru–K/KBr.[35]

The observed species is quite different from those species hitherto reported on metal surfaces which are readily desorbed by evacuation at room temperature and give absorption bands at higher wave numbers. It is unique in giving ammonia on hydrogen treatment,

(29) K. Urabe and A. Ozaki, *J. Catal.*, **42**, 197 (1976).
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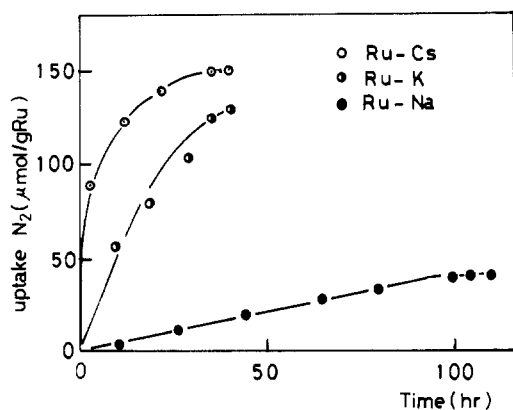(35) M. Ohkita, K. Urabe, and A. Ozaki, *J. Catal.*, **52**, 432 (1978).

Figure 5. Time courses of dinitrogen uptake by ruthenium powder in the presence of alkali metal vapor at 350 °C and 300 torr.

but the rate of conversion to ammonia is much slower than the rate of ammonia synthesis on the catalyst. Thus it cannot be the reaction intermediate of the ammonia synthesis. Subsequent studies on the nitrogen uptake discloses that significant amounts of nitrogen are absorbed by the $Ru-K/Al_2O_3$, attaining a value of N_2/total Ru ratio of 0.8 for 96 h at 350 °C. Moreover, the absorbed nitrogen is quite stable even in the presence of hydrogen. Although the hydrogenation of absorbed nitrogen to give ammonia is detectable above 200 °C, the rate of conversion is very slow, giving 60% conversion for 100 h at 380 °C.[36] Thus, the hydrogenation of absorbed nitrogen is just as slow as the decay of 2020 cm^{-1} band by hydrogen treatment. It is very likely that the infrared absorption is caused by an absorbed dinitrogen.

Since the above experiments were made on supported ruthenium, the absorption of nitrogen was examined with unsupported ruthenium powder in the presence of potassium vapor. Although the specific surface area of the powder was as small as 0.9 m^2/g, show uptake of dinitrogen was found, with the rate of uptake decreasing with time. The uptake under 210 torr was 40, 55, and 67 μmol/g of Ru for the initial 10 h at 250, 350, and 450 °C, respectively.[33] Although the effect of temperature on the rate of uptake is rather small, larger differences are observed by changing alkali metal as shown in Figure 5.[37] The rate of uptake increases in the order Cs > K > Na, as is the case with the rate of ammonia synthesis shown in Figure 1.

A significant finding is that the total amount of uptake exceeds by far the number of surface ruthenium atoms, attaining a factor of 9 on a molar basis, in conformity with an absorption or a corrosive chemisorption of dinitrogen. In fact it is confirmed that the incorporated nitrogen does not come off on evacuation at the temperature of uptake.[33]

Since little uptake of dinitrogen was observed on the ruthenium powder in the absence of potassium, the potassium should play some role in the absorption. Thus the amount of potassium held by the ruthenium powder was determined after the dinitrogen–potassium treatment. Although the potassium content is 600 μmol/g of Ru after uptake at 350 °C for 40 h, it decreases with the time of evacuation at 350 °C to a stable
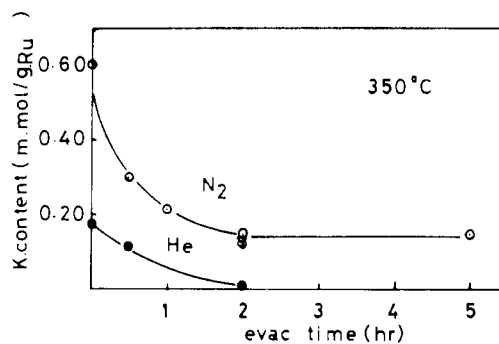

Figure 6. Variation of potassium content of ruthenium powder after potassium treatment in dinitrogen or helium with evacuation time at 350 °C. Reprinted with permission from ref 33. Copyright 1979, Academic Press.

value of about 150 μmol/g of Ru after 2 h of evacuation, as shown in Figure 6. Since analogous experiments carried out in helium give rise to much a lesser potassium content which decreases to a negligible value on evacuation as shown also in Figure 6, it is likely that nitrogen acts as a "binder" between Ru and K and is responsible for the stably bound potassium.

If nitrogen is chemically involved in producing the stable potassium, there may be a stoichiometric relation between potassium and nitrogen. Indeed, the molar ratios of dinitrogen uptake to the stable potassium content are found within a range of 1.0 ± 0.2 irrespective of the temperature and the time of potassium addition.[33] It is accordingly suggested that potassium and dinitrogen are cooperatively incorporated into the bulk of ruthenium metal.

If this is the case, there must be another stoichiometric relation between N_2 and Ru. This information is unavailable from the ruthenium powder, because the particle size of ruthenium is too large to give a full incorporation. However, it was noted previously that the slow uptake of dinitrogen by supported ruthenium attains an N_2/Ru value of 0.8 on $Ru-K/Al_2O_3$. More recently on $Ru-K/MgO$ it attained 1.0.[31] It is reasonable that the large N_2/Ru value is realized because of the small particles of ruthenium dispersed on the support. In this way a ternary complex of the formula $(KN_2Ru)_n$ was suggested.[33] In fact, an analogous dinitrogen compound of cobalt, $KN_2Co(PMe_3)_3$, is known.[38] The real active surface appears to be formed on the complex in which ruthenium assumes an anionic character. Further addition of potassium on this surface results in an increase in the activity.[33]

There might be another possibility that potassium and dinitrogen form a 1:1 complex on the ruthenium surface. The identity of the complex should be examined further.

Additional Evidence for the Dinitrogen Complex

The behavior of the absorbed dinitrogen and the IR-active species is identical with respect to their development on dinitrogen treatment as well as their decay on hydrogen treatment, giving support for the dinitrogen species being involved in the complex. It was found further that on introduction of oxygen at about 150 °C, the 2020-cm^{-1} band decays rather rapidly, giving

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(37) A. Ohya, K. Aika, and A. Ozaki, *Nihon Kagaku Kaishi*, 1468 (1979).

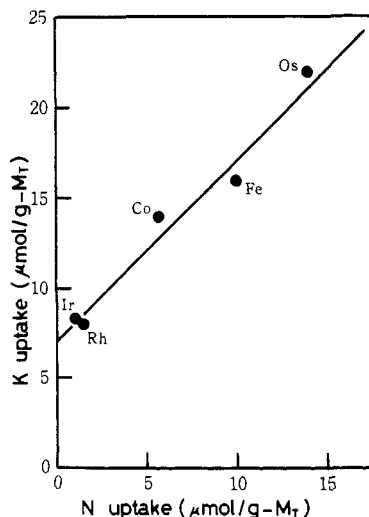(38) R. Hammer, H. F. Klein, P. Friedrich, and G. Huttner, *Angew. Chem., Int. Ed. Engl.*, 16 485 (1977).

Figure 7. Potassium uptake by transition metals (M_T) as a function of dinitrogen uptake.

a new band at 2160 cm^{-1} (2125 cm^{-1} for $^{15}N_2$) which is ascribable to an adsorbed nitrous oxide.[39] Thus the fate of incorporated dinitrogen on hydrolysis would be of interest.

The ruthenium powder treated with potassium in the presence of dinitrogen was subjected to reaction with water after removal of desorbable potassium and dinitrogen. The aqueous solution thus obtained was found to involve a dinitrogen complex of ruthenium as evidenced by IR absorption at 2200 and 2160 cm^{-1} for dinitrogen and by emission spectra for ruthenium. In addition, both hydrazine and ammonia were found in the distillate from the solution. Although little is known about the ligand in the water-soluble complex, either ammonia or hydrazine would be coordinated to Ru. The use of ethanol in place of water also gave hydrazine and dinitrogen complex, with the IR absorption being found at 2133 and 2174 cm^{-1}.[33] All the above results give support for the retention of N≡N bond in the absorbed state.

Cooperative Incorporation in Other Transition Metals

In view of the significance of the complex formation with ruthenium, other metals in powder form were examined for their ability to effect the cooperative incorporation of dinitrogen and potassium at 350 °C.[37] The dinitrogen uptakes observed are one or two orders of magnitude less than that on ruthenium. However,

as shown in Figure 7, they are linearly correlated with the potassium contents determined after removal of excess potassium by evacuation at 350 °C for 2 h. Since the slope of the line is close to unity, the cooperative incorporation of N_2 and K appears to take place in those metals. In fact the dinitrogen species was detected from the water extract of treated metals: the evaporated residue gave IR absorptions at 2160 and 2040 cm^{-1} for iron and 2160 and 2080 cm^{-1} for osmium.[37] For rhodium or iridium the cooperative incorporation is obscure, while an IR absorption band was found on Rh–K/Al$_2$O$_3$ treated with dinitrogen at 2040 cm^{-1}.[34]

In summary, ruthenium is outstanding in giving the potassium–dinitrogen complex, whereas osmium, iron, and cobalt appear to give analogous complexes. Interestingly, those metals are known as good catalysts for dinitrogen activation, with ruthenium being most active in the potassium-promoted metals. The ability to form the dinitrogen complex seems to be parallel to the catalytic activity for the dinitrogen fixation. This may be because the activation of dinitrogen is necessary to form the dinitrogen complex.

Prospects of Ruthenium as an Ammonia Synthesis Catalyst

It has been demonstrated that ruthenium is remarkably promoted by addition of alkali (metallic or oxide) for the activation of dinitrogen, although it has the drawback of suffering from inhibition by hydrogen. The high activity thus attained makes it possible to reduce the reaction temperature so that the total pressure may be lowered to attain a desired conversion. Thus there is a possibility to get out of the energy-consuming compression process. This would be an advantage of a ruthenium catalyst to be considered in the near future in connection with energy prices.

Another advantage of ruthenium is that it gives rise to less susceptibility to poisons such as H_2O and CO than iron, when promoted with basic oxides instead of metallic alkali. In fact, it has been demonstrated that ammonia synthesis can be carried out in the presence of water and carbon monoxide on ruthenium catalysts.[40] Thus the direct synthesis of ammonia from dinitrogen, carbon monoxide, and water is possible on ruthenium.

(39) M. Ohkita, K. Aika, and A. Ozaki, reported at the 37th annual meeting of the Chemical Society of Japan, 1978; Paper No. 4Q08.

(40) K. Shimazaki, K. Urabe, K. Aika, and A. Ozaki reported at the 37th annual meeting of the Chemical Society of Japan, 1978; Paper No. 1Q34; S. Naito and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1105 (1978).