On the path to catalysts for the low-temperature ammonia synthesis

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A nontraditional approach to the development of catalysts for low-temperature ammonia synthesis is considered. The approach is characterized by application of catalysts representing heterogeneous analogs of the known homogeneous nitrogen-fixing systems based on transition metal compounds and strong electron donors. The use of this approach led to the development of catalysts that considerably surpass in their activity (at atmospheric pressure) the industrial catalyst for the ammonia synthesis. Some of the developed catalysts are active in the formation of ammonia from dinitrogen and dihidrogen even at 110—150 °C. The mechanisms of activation and hydrogenation of dinitrogen over these new catalysts are discussed.

Key words: dinitrogen, dihydrogen, ammonia synthesis, catalysts, promoters.

1. Introduction

The catalytic ammonia synthesis from dinitrogen and dihydrogen over an iron catalyst promoted by potassium, aluminum, and some other metal oxides is the main industrial method for nitrogen fixation. However, for kinetic and thermodynamic reasons, this process must be carried out at very high temperatures (400—550 °C) and pressures (280—320 atm). The high temperatures are needed to ensure reasonable reaction rates, but at high temperatures, the equilibrium concentration of ammonia in the gas decreases. An increase in the equilibrium content of ammonia can be attained by increasing pressure; however, this sharply increases the energy and material expenses, and, as a consequence, reduces the economy of the process. Thus, to increase crucially the efficiency of the process of ammonia synthesis, a new type of catalysts capable of hydrogenating dinitrogen at high rates at moderate temperatures and pressures is required. The development of these catalysts faces, however, severe difficulties caused by the extremely high chemical inertness of the N_2 molecule.

During the last decades, prospects for the solution of this important problem have taken shape. The first step was made in 1964, when it was shown that transition metal compounds are able to activate molecular nitrogen and make it undergo reduction in aprotic media at ambient temperatures and pressures.[1,2] This result, together with the synthesis of the first complex of dinitrogen with a transition metal compound $[Ru(NH_3)_5N_2]Cl_2$ accomplished in 1965,[3] marked the beginning of active development of the chemistry of molecular nitrogen in solutions (see, for example, reviews[4—6]) and created the basis for the accomplishment of low-temperature ammonia synthesis from dinitrogen and dihydrogen.

The currently known nitrogen-fixing systems, capable of reducing N_2 in aprotic media,[4,5] consist of two main components: a transition metal compound, which is needed for complexing and activating dinitrogen, and a sufficiently strong reducing agent serving as the source of electrons for reducing the activated N_2 molecule. Systems based on titanium, vanadium, chromium, molybdenum, tungsten, and iron compounds are the most active in nitrogen fixation. Alkali, alkaline earth, and rare earth metals, metal hydrides, organic derivatives of Li, Mg, and Al, adducts of aromatic hydrocarbons with alkali metals, *etc.* can be used as reducing agents. As a rule, the final products of the reaction are nitride derivatives in which a nitrogen atom is bound both to the transition metal atom of the initial salt or complex and to the metal atoms of the reducing agent. Hydrolysis of these nitrides yields ammonia. In some cases, it is possible to terminate the reaction at the stage of formation of the intermediate hydrazide derivative, whose hydrolysis affords hydrazine. Under optimum conditions, the reduction of N_2 occurs very efficiently to give ammonia in nearly quantitative yield even at room temperature and atmospheric pressure. Some of the systems are so active that they are capable of absorbing molecular nitrogen at high rates even at −70 to −100 °C.

Immediately after the discovery of these nitrogen-fixing systems, the question arose of whether these systems could be used as catalysts for hydrogenation of dinitrogen with dihydrogen under mild conditions. In 1965—1968, it was shown that the systems resulting from treatment of titanium alkoxides with triisobutylaluminum are able to reduce molecular nitrogen in solutions at room temperature with participation of molecular hydrogen.[7—9] Later, this reaction was trans-

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formed into a catalytic process.[4,10] The next important step was made in the late 60s — early 70s when it was found that similar systems can be used as heterogeneous catalysts for ammonia synthesis from N_2 and H_2.

At present, a large number of catalysts of this type are known, and vast information on the mechanism of their action in the ammonia synthesis has been accumulated. Catalysts have been prepared using various transition metal compounds: chlorides, oxides, acetylacetonates, phthalocyanine complexes, lamellar graphite compounds, anionic metal carbonyl clusters, *etc*. Alkali metals, sodium naphthalide, and organolithium compounds were tested as sources of electrons. The activity of the catalysts varies over a broad range depending on the nature of the transition metal and the reducing agent, the method of generation of the catalytically active species, and on other factors. The best of the catalysts found are considerably more active (under atmospheric pressure) than the industrial catalyst for the ammonia synthesis. Some catalysts are active even at 110—150 °C.

In the present review, the results of studies carried out in this important field are generalized.

2. Catalysts based on transition metal phthalocyanines

The first data concerning the use of the above-considered nitrogen-fixing systems in the gas-phase ammonia synthesis from dinitrogen and dihydrogen were published[11] in 1969. Donor-acceptor complexes of Fe, Co, Ni, Ti, Mo, Pt, Cu, and Zn phthalocyanines with alkali metals have been studied as catalysts. To prepare these complexes, the initial phthalocyanines were vaporized in high vacuum and deposited on thin sodium or potassium films supported on glass. The deposition gave deeply colored adducts of phthalocyanines with alkali metals; these adducts were tested in the ammonia synthesis. The testing was carried out in a circulating system at 20—260 °C and at a pressure of <600 Torr.

It turned out that the complex of iron phthalocyanine (PcFe) with sodium generated on glass is capable of catalyzing the synthesis of ammonia even at 110 °C, although the reaction occurs very slowly: only 0.26 cm^3 of NH_3 was formed over a period of 20 h (0.1 g of PcFe). As the temperature increased to 260 °C, the rate of formation of ammonia increased, and under these conditions, 4.6 cm^3 of NH_3 was produced in 20 h. Similar complexes of molybdenum, titanium, and cobalt phthalocyanines with Na and K were considerably less effective, and the complexes of copper, platinum, nickel, and zinc phthalocyanines with alkali metals exhibited only negligible activities in the ammonia synthesis. In the absence of an alkali metal, none of the phthalocyanines studied catalyzed hydrogenation of N_2 with H_2. In principle, the ammonia formed during testing of the catalysts might result from the N atoms of phthalocyanine rather than from dinitrogen. However, it was shown[11] that when a mixture of dinitrogen with dihydrogen is replaced by dihydrogen, ammonia is no longer detected in the gas phase. Unfortunately, this study on phthalocyanine catalysts[11] has not received further development.

3. Catalysts based on lamellar compounds of graphite with transition metals and their chlorides

In 1972, it was reported[12] that when lamellar compounds of graphite (LCG) with transition metal chlorides ($FeCl_3$, $RuCl_3$, $OsCl_3$, $MoCl_5$) are treated with alkali metals (Na, K, Rb) at 350 °C, systems able to catalyze the formation of ammonia from N_2 and H_2 at elevated temperatures (300—350 °C) are produced. Among the lamellar compounds tested, the LCG with $OsCl_3$ exhibited the highest activity, whereas the lowest activity was observed in the case of LCG with $MoCl_5$; in addition, rubidium and potassium are more effective than sodium. In the absence of an alkali metal, the systems were inactive. However, the lamellar compound of graphite with potassium containing no transition metal derivative proved to be able to catalyze hydrogenation of dinitrogen at 300 °C at a very low rate (three orders of magnitude lower than that with the system prepared from LCG with $FeCl_3$ and potassium).[11,12] The formation of a small amount of ammonia from dinitrogen and methane serving as a source of hydrogen was observed in the presence of the graphite—$FeCl_3$+K catalyst at 300—400 °C.[12]

Under the conditions used to prepare the catalysts in the study cited,[12] the starting LCG with transition metal chlorides could be reduced by alkali metals to give LCG with transition metals.[13] In these lamellar compounds, the transition metal atoms occurring in the interlayer space interact with the aromatic rings of graphite to give peculiar π-complexes.

The catalytic activities of systems based on individual LCG with Fe, Os, and their chlorides as well as with $RuCl_3$ in ammonia synthesis have been studied in detail.[14—16]

It was found that unlike pure metallic iron, the LCG with Fe does not catalyze the formation of ammonia from dinitrogen and dihydrogen up to 400 °C. However, treatment of this compound with excess metallic potassium at 350 °C affords catalysts that are active in the synthesis of ammonia.[14,16] Systems based on LCG with Os, $FeCl_3$, $OsCl_3$, and $RuCl_3$ treated with potassium also catalyze hydrogenation of dinitrogen at elevated temperatures. All of these catalysts ehxibit the highest activities at 400 °C. The activity at 250 °C is either low or equal to zero. According to the results presented in Ref. 12, the LCG with potassium containing no transition metal exhibits only negligible activity in this process over the whole temperature range studied (250—400 °C).

The content of an alkali metal in the system has a strong effect on the activity of the catalysts.[14,16] As the content of potassium in the graphite—Fe+K catalyst increases, the steady-state concentration of ammonia in the gas flow increases and reaches a maximum at a K : Fe ratio of (5—7) : 1 (K : C ≈ 1 : 4.5). Further increase in the content of potassium diminishes the activity of the catalyst. A similar dependence is observed for the graphite—$FeCl_3$+K catalyst.

The above-described systems proved also to be able to catalyze the isotope exchange in dinitrogen at elevated temperatures.[16] The graphite—$OsCl_3$+K and graphite—$RuCl_3$+K systems are the most active in this process; in the presence of these catalysts, the reaction occurs at a noticeable rate even at 250 °C. In the case of LCG with Fe treated with potassium, the exchange proceeds only at 350 °C. The maximum activity of the graphite—Fe+K system in the isotope exchange is observed at the same content of potassium as that in the ammonia synthesis. In the absence of alkali metal, the isotope exchange does not occur.

The promoting effect of potassium on the LCG with Fe can be understood[14] by taking into account the fact that transfer of electrons from the transition metal to an N_2 molecule is significant for the activation of dinitrogen.[9] In the LCG with Fe, the metal donates the electron density to the carbon framework of graphite.[13] This results in a partial positive charge on the iron atoms and, as a consequence, in complete loss of the catalytic activity in the ammonia synthesis and isotope exchange in dinitrogen. The introduction of a strong electron donor such as metallic potassium would not only neutralize this unfavorable electron-withdrawing effect of graphite but also induce some negative charge on the iron atoms.

The promoting effect of potassium can be accomplished both upon its direct interaction with a transition metal and through the carbon framework of graphite.[14,16] In fact, the conditions under which the catalysts are prepared (350 °C) permit the insertion of potassium into the interlayer space of graphite to give LCG with potassium in which the aromatic rings of graphite carry a negative charge. At the same time, in the LCG with Fe, the atomic orbitals of iron also markedly interact with the aromatic framework of graphite.[13]

It has been assumed[14] that the decrease in the catalytic activity in the presence of a large excess of potassium is due either to the decrease in the accessible surface of iron caused by adsorption of excess alkali metal (not inserted into graphite) on the surface of the catalyst or to the formation of a stable nitride, difficult to hydrogenate, similar to that observed previously in the interaction of N_2 with iron and lithium.[17]

A study of the state of iron in the graphite—Fe+K catalyst by Mössbauer spectroscopy has shown that it exists in two forms.[15,16] One of them is responsible for a sextet of lines with the parameters of α-iron; the isomeric shift of the sextet does not depend on the amount of potassium in the system. The second form accounts for a singlet (15—20% of the total area of the spectrum), whose isomeric shift is more negative than that of the α-iron. As the content of potassium increases, the isomeric shift of the singlet changes and passes through a minimum at a K : Fe ratio of (5—7) : 1 (K : C ≈ 1 : 4.5). The same ratio corresponds to the maximum catalytic activity in the ammonia synthesis and isotope exchange. It can be assumed that such a change in the isomeric shift of the singlet is due to the increase in the electron density on iron atoms resulting from the transfer of electrons from potassium atoms to iron. Apparently, the initial decrease in the isomeric shift is due to the predominant transfer of electrons to the 4s atomic orbitals of iron, while its following increase is caused by saturation of the 4s orbitals and subsequent filling of the 3d orbitals. The observed correlation between the isomeric shift of the singlet and the catalyst activities in the ammonia synthesis and isotope exchange might imply that the "singlet" form of iron participates in the hydrogenation of N_2. However, the quantitative contribution of this species to the overall catalytic activity of the system is still unknown, and it cannot be ruled out that α-iron is also involved in the synthesis of ammonia.

4. Supported catalysts based on transition metal chlorides and oxides as precursors of catalytically active species

Much more efficient catalysts for ammomia synthesis than those considered above have been found by the authors of Ref. 18. Subsequently, these catalysts have been studied in detail[19—30] in order to elucidate the mechanism of their action in the activation and hydrogenation of N_2.

The catalysts were prepared in the following way:[18—20] transition metal chlorides (or OsO_4 in the case of osmium-containing systems) were deposited onto various supports from aqueous solutions and then reduced with dihydrogen for several hours at elevated temperatures. The reduced samples were treated *in vacuo* with metallic potassium vapor at 400 °C and then heated for 4—5 h at 400 °C in a circulating system in an He stream, in order to attain uniform distribution of the alkali metal in the sample. As supports, active carbon (AC), γ-alumina, Celite, glass, and silicon carbide were used. The amount of the transition metal in the samples was 0.5—10% (w/w) with respect to the support. The catalysts were tested in a circulating system at 600 Torr using a stoichiometric H_2—N_2 mixture.

The testing showed that the highest activity in the ammonia synthesis at 250 °C is exhibited by the Ru+K and Os+K systems on carbon.[18—20] These catalysts are considerably more effective than the conventional doubly promoted iron catalyst for the ammonia synthesis. Similar catalysts based on Fe, Rh, Ir, Mo, Re, and Co are less active than the ruthenium and osmium systems and also than the doubly promoted iron catalyst. Nickel- and platinum-containing systems exhibit very low activities, and the Pd+K, Mn+K, and Ti+K systems on carbon are absolutely inactive in the ammonia synthesis even at

450 °C. The most effective system, Ru+K on carbon, catalyzes the ammonia synthesis even at 146 °C (the rate of the synthesis was ~0.015 cm^3 of NH_3 h^{-1} g^{-1}).[18]

It should be noted that whereas Ru, Os, Fe, Re, Mo, Co, and Ni as bulk metals can themselves catalyze the ammonia synthesis,[31–33] metallic Rh, Ir, and Pd are inactive in this process, and Pt is active only at very high temperatures and pressures. Thus, the addition of potassium to the Rh, Ir, and Pt supported on carbon makes these metals active in the ammonia synthesis even at 250 °C and at a pressure close to atmospheric.

In a study of the influence of the nature of the support on the activity of the Ru+K system in the ammonia synthesis at 290 °C, it was shown that in terms of their efficiency, the supports tested can be arranged in the following series:[19]

AC > γ-Al_2O_3 ≫ glass > Celite > SiC.

The best catalysts were obtained using active carbon and γ-alumina, which ensure higher degrees of dispersion of Ru, owing to their greater specific surface areas. However, apparently, the role of active carbon and alumina is not merely to increase the accessible surface of Ru in the catalyst.[19] It has been assumed that active carbon acts simultaneously as the medium for the transfer of electrons from potassium to a transition metal. In fact, it was found[34] that similarly to graphite, active carbon can react with alkali metals on heating to give adducts. These adducts could serve as a sort of storage systems for the electrons during their transfer to a transition metal.[19] A similar function of the electron storage tank could be accomplished by γ-alumina. However, in this case, it cannot be ruled out that alumina is partially reduced by metallic potassium to give metallic aluminum.

The important role of the metallic potassium in these systems is illustrated by the fact that in the absence of potassium, the rate of hydrogenation of N_2 dramatically decreases or even becomes equal to zero. Among these catalysts, non-promoted with potassium, the highest activity is exhibited by ruthenium on γ-Al_2O_3, in whose presence the ammonia synthesis occurs at a low rate at 400 °C. In the case of Ru on Celite or glass, the rate of the reaction is even lower, and Ru on carbon or silicon carbide containing no potassium are totally inactive in ammonia synthesis even at 400 °C. Similar results have been obtained for Os, Fe, and other active transition metals. Having been deposited on carbon, all these metals completely lose their catalytic activities in the ammonia synthesis.[18,30]

The inhibiting effect of the carbon support on the ammonia synthesis is apparently caused by the electron-withdrawing nature of the active carbon resulting in the generation of partial positive charge on the transition metal atoms, which hampers efficient activation of dinitrogen.[19,24] As in the case of the LCG-based systems considered above, the introduction of potassium into the catalyst results apparently in neutralization of this positive charge and in the appearance of partial negative charge on the transition metal atoms. It should be noted in this connection that bulk transition metals can also be promoted by metallic potassium.[19,28–30] For example, the rate of the ammonia synthesis over powdered Ru at 350 °C increases approximately 66-fold after treatment of the catalyst with potassium vapor.

Study of the influence of the amount of potassium on the activity of the Ru+K system supported on carbon in the ammonia synthesis at 290 °C showed that at constant amounts of ruthenium and carbon in the sample, the rate of the reaction first increases following an increase in the quantity of the alkali metal but then gradually decreases.[19] At the same time, when the contents of potassium and carbon in the catalyst are constant, the rate of the ammonia synthesis (cm^3 NH_3 h^{-1}) is nearly proportional to the content of ruthenium. When there is no deposited transition metal, *i.e.*, when the adduct of active carbon with potassium is used, the reaction does not occur even at 400 °C. Apparently,[19] the increase in the activity of the carbon-supported Ru+K catalyst following an increase in the content of potassium is due to the increase in the electron density on the transition metal atoms caused by the transfer of electrons from potassium. The maximum catalytic activity corresponds to saturation of carbon with potassium. The decrease in the activity of the system upon further increase in the content of the alkali metal was explained[19] by the agglomeration of potassium on the surface of the catalyst.

The role of potassium as the electron promoter in these systems is also indicated by the data[19] on the influence of the nature of the alkali metal on the catalytic activity of carbon-supported ruthenium. It was found that at the same content of Ru in the catalyst, the promoting effect of Cs is considerably stronger than that of K. In turn, the promoting effect of potassium sharply exceeds that of sodium. For example, at 290 °C, the Ru+Cs catalyst supported on carbon (2.5 % w/w Ru) is 2.5 times more active than a similar catalyst, Ru+K. The latter is almost 10 times more active than the Ru+Na catalyst on carbon. Thus, the catalytic activity of ruthenium on carbon in the ammonia synthesis increases with increase in the electron-donating ability of the alkali metal, *i.e.*, in the series Cs > K > Na. It is of interest that in the case of cesium, the dependence of the catalyst activity on the amount of the alkali metal does not pass through a maximum (as was observed for potassium) but gradually flattens out.

In studying the isotope exchange in dinitrogen over ruthenium—potassium catalysts, it was found that the highest activity in this reaction is exhibited by the Ru+K system on carbon, in whose presence the exchange occurs at a noticeable rate even at 220 °C.[21,24,25] As the temperature increases, the isotope exchange is accelerated. The activity of the Ru+K catalyst on γ-Al_2O_3 is strongly exceeded by that of Ru+K on carbon, and the unsupported Ru+K system is approximately 10 times less active than the Ru+K catalyst on γ-Al_2O_3 (at 320 °C).[24] In the absence of potassium, the rate of the isotope exchange on bulk Ru or Ru on γ-Al_2O_3 sharply decreases;[21,24] in this case, too, Ru on γ-Al_2O_3 is somewhat more active than bulk Ru.[24] Carbon-supported ruthenium containing no potassium does not catalyze the isotope exchange in dinitrogen at all, as it does not catalyze the ammonia synthesis.[21]

Thus, in the case of supported systems, the introduction of potassium also exerts a promoting effect on both the ammonia synthesis and the isotope exchange in dinitrogen. It is noteworthy that the promoting effect of potassium on these two reactions is manifested in different degrees. For example, upon treatment of bulk ruthenium with potassium, the rate of isotope exchange at 400 °C increases 480-fold, whereas the rate of hydrogenation of N_2 under the same conditions increases by a factor of only 25.[24,25] As a result, the rate of the ammonia synthesis over the Ru+K catalyst is lower than the rate of isotope exchange, although in the absence of potassium, the ammonia synthesis on bulk Ru occurs faster than the isotope exchange. A similar situation is observed for the Ru+K catalyst on carbon. In this case, the rate of the ammonia synthesis is about half that of the isotope exchange (at 220—280 °C), despite the fact that the apparent activation energies of these two reactions are approximately equal.[21]

The kinetic data obtained in a study of the isotope exchange[24] show that the addition of potassium to Ru supported on γ-Al_2O_3 results in the first order of the reaction being replaced by a fractional order, which approaches unity as the temperature increases. The isotope exchange in dinitrogen in the presence of other ruthenium—potassium catalysts also obeys fractional-order kinetics with respect to the pressure of N_2 (0.5 in the case of Ru+K on carbon at 280 °C and 0.44—0.79 in the case of unsupported Ru+K at 320—380 °C).[21,24,25] Based on these data, it was concluded that the introduction of potassium increases the strength of adsorption of N_2 by ruthenium due to the transfer of electrons from the alkali metal to the transition metal and then to the adsorbed N_2 molecule. Data on the isotope exchange[25] also imply that, although the rate of hydrogenation of adsorbed dinitrogen is relatively low, the rate of the ammonia synthesis is still limited by the step of dissociative chemisorption of N_2.

Study of the effect of dihydrogen on the isotope exchange in N_2 showed that the isotope exchange catalyzed by bulk ruthenium is accelerated in the presence of H_2, whereas that catalyzed by the γ-Al_2O_3-supported Ru is retarded by the introduction of dihydrogen.[25] A similar deceleration of the isotope exchange in the presence of H_2 is observed for potassium-containing systems (Ru+K on carbon, Ru+K on γ-Al_2O_3, and Ru+K without a support).[21,25]

The inhibition of isotope exchange over ruthenium—potassium catalysts by dihydrogen can be caused by two reasons.[25]

First, the introduction of dihydrogen, which forms very strong adsorption compounds with ruthenium, decreases the number of vacant adsorption sites on the surface of the metal; this should decrease the adsorbed amount of dinitrogen and, hence, retard the isotope exchange.

Second, the isotope exchange in dinitrogen in the presence of H_2 should be accompanied by the formation of ammonia, which is able to convert metallic potassium into the corresponding amide or imide, whose electron-donating abilities are much lower than that of the metal itself. The decrease in the amount of potassium in the catalyst should diminish the negative charge on the ruthenium atoms, and this, in turn, should hamper the chemisorption of dinitrogen and decrease the rate of the exchange. The content of the alkali metal in the system can also diminish through its reaction with dihydrogen to form potassium hydride.

The fact that the rate of the isotope exchange in dinitrogen over bulk ruthenium containing no potassium increases in the presence of dihydrogen is due to the favorable electron-donating effect of the NH_x species, which arise as intermediates during the reaction of dinitrogen with the dihydrogen on the catalyst surface. However, as noted above, in the case of Ru on γ-Al_2O_3, where similar electron-donating NH_x species can also be formed, the isotope exchange in dinitrogen is no longer accelerated in the presence of dihydrogen, but is, conversely, retarded. Apparently, the NH_x species formed in this system lose their electron-donating capacity upon interaction with the acidic sites of the support.

Important results were obtained in a study of the products of interaction of N_2 with the above-mentioned catalysts for the ammonia synthesis. It was found that the Ru+K system on carbon can efficiently absorb gaseous N_2 at temperatures above 235 °C (300 Torr).[22] The quantity of the absorbed N_2 depends strongly on the content of potassium in the system and increases upon an increase in the excess of potassium. Study of the kinetics of the reaction of dinitrogen with the Ru+K system on carbon at 300 °C showed that the initial relatively fast absorption of N_2, which stops after several hours, is replaced by very slow absorption of dinitrogen, which still goes on even after 160 h at 300 °C.[27] A similar situation is characteristic of the reaction of dinitrogen with the Ru+K catalyst on γ-Al_2O_3 at 380 °C. It is significant that neither Ru on carbon or γ-Al_2O_3 in the absence of potassium nor potassium on carbon or γ-Al_2O_3 in the absence of ruthenium can absorb N_2 under the same conditions.

It should be noted that the number of nitrogen atoms absorbed by the catalyst can exceed the number of Ru atoms in the catalyst sample.[22,27] For instance, in the case of the Ru+K system on γ-Al_2O_3, this ratio reaches 1.6 g-atom of N per g-atom of Ru after 96 h at 350 °C,[27] while for the Ru+K system on carbon, this ratio is 1.36 g-atom N per g-atom of Ru (260 °C, 6 h).[22] Based on these results, it was suggested that the interaction of dinitrogen with the catalyst is not restricted to the adsorption of N_2 on the surface but occurs more deeply, *i.e.*, as absorption or corrosion chemisorption.

The Ru+K catalyst without a support also proved to absorb N_2 starting from 250 °C;[28,29] in this case, too, the initial relatively fast absorption of N_2 is replaced by much slower absorption, which still occurs even after 40—50 h. The total number of the sorbed nitrogen atoms is 6—9 times greater than the number of surface Ru atoms.[29] When the sample obtained after the reaction with N_2 is heated *in vacuo* (0.06 Torr) at 350 °C for 6 h, only 1.5% of the sorbed dinitrogen can be desorbed. This indicates that the sorbed nitrogen is bound to the catalyst practically irreversibly. Similar results were obtained for the Ru+K catalyst on γ-Al_2O_3.

In a study of the reactivity of the sorbed nitrogen, it was found that on heating, it can be hydrogenated with dihydrogen to give ammonia. However, the reaction occurs very slowly. Thus in the case of the Ru+K system on γ-Al_2O_3, hydrogenation of the nitrogen preabsorbed by the catalyst (during 90 h at 380 °C) becomes noticeable only above 200 °C, and at 380 °C, only 57% of the sorbed nitrogen can be converted into ammonia even over a period of 100 h.[27] The low rate of hydrogenation of the sorbed nitrogen is also characteristic of the Ru+K system on carbon; in this case, the degree of conversion of sorbed (166 h, 300 °C) nitrogen into ammonia is only 47% after 96 h at 300 °C.[27]

In addition to hydrogenation, nitrogen sorbed by the Ru+K catalyst on carbon (at 300 °C for 160 h) can also undergo isotope exchange with labeled gaseous $^{15}N_2$. The reaction occurs at a low rate even at 300 °C. Like the absorption of dinitrogen by the catalyst, the isotope exchange includes an initial stage of relatively fast exchange (30—40 min at 300 °C) and a subsequent stage of very slow exchange. As a result, after 2 h at 300 °C, the degree of approach to the equilibrium of the isotope exchange is 39%, and after 5 h, it is only 42%. If the absorption of dinitrogen by the catalyst is carried out at 300 °C over a shorter period (20 h instead of 160 h), the subsequent isotope exchange of $^{15}N_2$ with the sorbed nitrogen sharply accelerates, and at 300 °C, the equilibrium is practically reached as soon as after 2 h. This indicates that the catalyst contains at least two different forms of sorbed nitrogen; one of them (formed rapidly and less firmly bound to the catalyst) readily undergoes isotope exchange with $^{15}N_2$ and, probably, is easily hydrogenated, whereas the other one (formed slowly and bound more firmly to the catalyst) enters with difficulty into isotope exchange with $^{15}N_2$ and cannot be readily hydrogenated. It was suggested[27] that nitrogen atoms of the latter type are those sorbed within the bulk of the catalyst rather than on its surface.

In the case of the Ru+K system supported on γ-Al_2O_3, nitrogen absorbed by the catalyst (350 °C, 96 h) undergoes isotope exchange with gaseous $^{15}N_2$ starting from 270 °C.[27] Although the rate of the process is very low even at 350 °C, the reaction still proceeds somewhat faster than hydrogenation of the absorbed nitrogen. However, the rate of isotope exchange of sorbed nitrogen with $^{15}N_2$ is approximately two orders of magnitude lower (at 355 °C) than the rate of isotope exchange in gaseous nitrogen, which is observed even at 250 °C.

Investigation of the nature of nitrogen sorbed by the Ru+K catalyst on γ-Al_2O_3 by IR spectroscopy showed that heating the catalyst in an atmosphere of N_2 at 200 °C results in the appearance of an absorption band at 2020—2050 cm^{-1} in the IR spectra; the intensity of this band sharply increases when the temperature of heating increases to 350 °C.[23,26] Based on experiments with $^{15}N_2$, the band in question was assigned to the stretching vibrations of the N_2 molecule coordinated to ruthenium, and the measurement of the extinction coefficient of this νNN band led to the conclusion[26] about the end-on type of coordination of dinitrogen to the metal, *viz.*, Ru—N≡N.

As the content of potassium in the catalyst increases, the intensity of the νNN band increases, while the band itself gradually shifts to longer wavelengths (from 2050 to 2020 cm^{-1}). However, when K is replaced by Na, the νNN band shifts to shorter wavelengths (by 6—10 cm^{-1}), and its intensity decreases. All the foregoing demonstrates the importance of the transfer of electrons from an alkali metal to ruthenium and then to N_2 for the formation of the coordination bond between ruthenium and dinitrogen.

The intensity of the νNN band observed in the IR spectrum upon the interaction of N_2 with the Ru+K catalyst on γ-Al_2O_3 virtually does not change after prolonged (for 24 h) evacuation of the sample at room temperature, and when the sample is kept for 3 h at 350 °C in an atmosphere of He, the intensity of this band decreases only by 50%, which points to a highly strong coordination of N_2 with ruthenium.

The most interesting feature of the Ru—N_2 species formed in the Ru+K system on γ-Al_2O_3 is that on heating, they react with H_2 to give ammonia.[23,26] According to the IR spectroscopy data, hydrogenation of dinitrogen bound to ruthenium becomes obvious at temperatures above 260 °C, when the intensity of the νNN band in the spectrum gradually decreases, and ammonia appears in the gas phase. When the temperature is increased to 350 °C, the rate of hydrogenation increases but it is still rather low, so that under these conditions, the νNN band completely disappears only after 4.5 h.

Similar νNN bands indicating the formation of dinitrogen complexes are exhibited in the IR spectra on heating N_2 with the Re+K and Rh+K catalysts on γ-Al_2O_3 at 350 °C.[23,26] However, these bands are shifted by 4—20 cm^{-1} to shorter wavelengths compared to the νNN bands exhibited by the ruthenium-containing system and are less intense; this correlates with the fact that the Rh+K and Re+K catalysts on γ-Al_2O_3 are less active in the ammonia synthesis than Ru+K on γ-Al_2O_3.

The dinitrogen complexes formed in the interaction of N_2 with these catalysts contain apparently not only a transition metal and nitrogen but also potassium. This assumption is supported by the data obtained in a study of the reaction of N_2 with the Ru+K system without a support.[28,29] It was found that if a mixture of powdered ruthenium with potassium is kept at 350 °C for 40 h in an He atmosphere, and the resulting sample is then evacuated at the same temperature, potassium is completely removed from the catalyst over a period of only 2 h. At the same time, when a mixture of ruthenium and potassium is kept in a dinitrogen atmosphere under the above-mentioned conditions (40 h, 350 °C) and then the resulting sample is evacuated at 350 °C, a considerable part of the potassium remains bound to the catalyst and is not removed during the evacuation. This means that metallic potassium directly participates in the reaction of Ru with N_2 and is apparently incorporated in the resulting nitrogen-containing product.

According to measurements, the molar ratio of the amount of dinitrogen absorbed by the Ru+K catalyst to the amount of potassium firmly attached to the catalyst is close to unity.[28,29] This led to the assumption that the reaction of N_2 with Ru and K yields a nitrogen-containing product of the composition $[KRuN_2]_n$. Since the number of nitrogen atoms sorbed by the catalyst (and, hence, the number of the firmly fixed potassium atoms as well) exceeds the number of surface ruthenium atoms by a large factor (see above), it was concluded that the formation of $[KRuN_2]_n$ occurs over the whole bulk of ruthenium, and it is this reaction that constitutes the slow stage of the dinitrogen absorption by the catalyst.

It should be noted that, unlike the stoichiometric ratio, $K : N_2 = 1$, which was found experimentally, the $Ru : N_2$ ratio in the product was not determined but was postulated to be equal to unity resorting to the indirect data obtained for the reaction of N_2 with the Ru+K system on γ-Al_2O_3 in which the amount of dinitrogen absorbed during 96 h at 350 °C reaches 0.8 moles per 1 g-atom of Ru (see above).[27] Thus, actually it is assumed that the reaction of N_2 with the Ru+K system on γ-Al_2O_3 yields a nitrogen-containing compound with the same composition, $[KRuN_2]_n$, as in the case of the unsupported Ru+K catalyst. Correspondingly, the νNN band observed at 2020—2050 cm^{-1} in the IR spectrum of the products of the reaction of dinitrogen with the Ru+K catalyst on γ-Al_2O_3, was attributed[27] to the stretching vibrations of the NN-bond in the compound $[KRuN_2]_n$, which is thus regarded as a dinitrogen complex of ruthenium.

The presence of an NN bond in $[KRuN_2]_n$ is indicated by the fact that hydrolysis of the products of reaction of N_2 with the Ru+K system gives substantial amounts of hydrazine and gaseous nitrogen, together with ammonia.[28,29] The yield of hydrazine is 11.8 mol.%, and that of ammonia is 9.5 mol.%, which corresponds to conversion of ~16% of the absorbed amount of dinitrogen. Unfortunately, the amount of gaseous nitrogen evolved during the hydrolysis was not determined.

The formation of dinitrogen and hydrazine on the hydrolysis of $[KRuN_2]_n$ could occur *via* protonation of the dinitrogen ligand, which carries a partial negative charge on the nitrogen atoms. Protonation of this type (by acids or even alcohols) is well-known for complexes of dinitrogen with transition metal compounds (see, for example, Ref. 35).

Catalysts for the ammonia synthesis prepared by depositing transition metal compounds onto various supports (active carbon, graphite, zeolite) followed by reduction of the resulting supported samples by solutions of organolithium and organosodium compounds have been described.[36] As transition metal compounds, Fe^{III}, Ru^{III}, Mo^{V}, and Ti^{IV} chlorides, K_2OsCl_6, $KReO_4$, and Fe^{III} and Ti^{III} acetylacetonates were utilized; *n*-butyllithium, phenyllithium and sodium naphthalenide were used as the reducing agents. The activity of these catalysts is low. The K_2OsCl_6+$C_{10}H_8^-Na^+$ system supported on graphite is the most active ($[NH_3] = 0.0142\%$ (v/v) at 370 °C and at 1 atm, $N_2 : H_2 = 1 : 3$, $W = 1300$ h^{-1}). The $RuCl_3$+$C_{10}H_8^-Na^+$ and $FeCl_3$+PhLi systems on graphite and $FeCl_3$+Bu^nLi on active carbon are less efficient. Other catalysts exhibit only negligible (if any) activity in the ammonia synthesis.

5. Supported catalysts based on the potassium derivatives of anionic metal carbonyl clusters

The potassium derivatives of anionic metal carbonyl clusters are quite promising for the catalysis of the ammonia synthesis, because they are potential precursors of not only highly dispersed transition metal particles but also of a potassium promoter.

The possibility of using such clusters for the development of highly efficient catalysts for the ammonia synthesis has been studied in detail.[37—44] Catalysts of two types were invesigated. The first type included catalysts not promoted by additives of alkali metals. The second type contained metallic potassium specially introduced as a promoting additive.

For the preparation of the catalysts, the following supports were used: magnesium oxide, γ-alumina, silica, carbonized magnesium oxide, various commercial active carbons (SKT, AG-5, BAU, *etc.*), and original graphite-like active carbons "Sibunit"[45] and CFC-1.[46] The experiments on the ammonia synthesis were carried out in a flow-type reactor at 250—400 °C and atmospheric pressure using a stoichiometric dinitrogen—dihydrogen mixture (flow rate 10 L h^{-1}). The catalysts were tested starting from 250 °C; then the temperature was successively raised to 300, 350, and 400 °C. For some catalyst samples, the activity at 150—200 °C was also measured. Among the clusters tested ($K_2[Fe_2(CO)_8]$, $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, $K_2[Mo_2(CO)_{10}]$, $K_2[W_2(CO)_{10}]$, *etc.*), the highest efficiency was exhibited by $K_2[Fe_2(CO)_8]$, $K_2[Ru_4(CO)_{13}]$, and

$K_2[Os_3(CO)_{11}]$. The catalysts based on these clusters are considered below.

5.1. Catalysts containing no promoting additives of an alkali metal

The catalysts were prepared by impregnation of supports with THF solutions of $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, and $K_2[Fe_2(CO)_8]$ followed by removal of the solvent at 20 °C *in vacuo*. The Ru/support and Fe/support ratio in the catalysts was 9% (w/w), and the Os/support ratio was 17.2% (w/w).

As noted above, ruthenium and osmium on active carbon prepared by the reduction of supported $RuCl_3$ and OsO_4 with dihydrogen are inactive in the ammonia synthesis even at 400 °C unless they are promoted by the addition of an alkali metal.[18,19,30] However, it has been found[40—44] that if the carbon-supported ruthenium and osmium catalysts are prepared using $K_2[Ru_4(CO)_{13}]$ and $K_2[Os_3(CO)_{11}]$ (instead of $RuCl_3$ and OsO_4), the resulting systems are able to catalyze efficiently the ammonia synthesis even in the absence of a specially added alkali metal or any other electron promoter. Apparently, the potassium incorporated in the initial anionic cluster acts as a promoter in these catalysts.

The best results were obtained for the ruthenium cluster on the graphite-like active carbons "Sibunit" and CFC-1. Both catalysts proved to be active in the ammonia synthesis starting from 250 °C. Especially effective is $K_2[Ru_4(CO)_{13}]$ on the CFC-1 carbon.[43] In its activity at 300—400 °C and 1 atm ($W = 2500\ h^{-1}$), this catalyst exceeds the industrial catalyst for the ammonia synthesis (SA-1). The osmium cluster $K_2[Os_3(CO)_{11}]$ supported on graphite-like carbons is less active than $K_2[Ru_4(CO)_{13}]$: it catalyzes the ammonia synthesis starting from 300 °C. The iron-containing cluster $K_2[Fe_2(CO)_8]$ exhibits activity in this process only at 400 °C. When the graphite-like active carbons are replaced by conventional carbon SKT, the activities and stabilities of the catalysts sharply decrease.[39,40]

An even more efficient ruthenium catalyst for the ammonia synthesis is obtained by supporting $K_2[Ru_4(CO)_{13}]$ on highly basic magnesium oxide.[41,43] At 300 °C and space velocity of 2500 h^{-1}, this catalyst is 3.4 times more active than the industrial catalyst. The use of γ-Al_2O_3 or SiO_2 instead of MgO dramatically decreases the efficiency of the catalyst,[41,43] indicating that the basic properties of the support are significant for ensuring high rates of the ammonia synthesis. Apparently, on passing from γ-Al_2O_3 and SiO_2 to highly basic MgO, the electron density on the Ru atoms substantially increases, and this is exactly the reason for the observed acceleration of the ammonia synthesis (*cf.* Ref. 47). Thus, in this catalytic system, MgO is not merely a support but also acts as a peculiar electron promoter (together with the potassium incorporated in the starting ruthenium cluster).

5.2. Catalysts promoted by metallic potassium

The catalysts promoted by metallic potassium[37—39,41,44] were prepared in the following way. First $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, and $K_2[Fe_2(CO)_8]$ supported on active carbon were heated for several hours in a flow of a dinitrogen—dihydrogen mixture or dihydrogen in order to remove the carbonyl ligands from the metal. The temperature of heating was 300 °C for the ruthenium and osmium complexes and 200 °C for the iron complex. Then the resulting samples were treated with metallic potassium at 120—130 °C in an argon atmosphere with vigorous stirring. Under these conditions, metallic potassium smoothly reacted with active carbon to give dark-brown highly pyrophoric powders, which were tested in the ammonia synthesis.

The testing showed that in all cases, the introduction of metallic potassium sharply increases the activity of the catalysts in the ammonia synthesis.[37,39,41,44] An especially strong accelerating effect of the alkali metal was observed for iron-containing samples. In studying the $K_2[Ru_4(CO)_{13}]$+K and $K_2[Fe_2(CO)_8]$+K catalysts on "Sibunit,"[41,44] it was found that at constant contents of the transition metal and carbon in the system, the activities of both catalysts pass through a maximum with increase in the amount of potassium in the system; in the case of the ruthenium catalyst, the content of the alkali metal corresponding to the maximum catalytic activity is substantially smaller (K : C = 1 : 12.5—16.7) than that in the case of the iron catalyst (K : C = 1 : 5).* Probably iron supported on carbon requires much stronger electron promotion for the ammonia synthesis than ruthenium on carbon.

A characteristic feature of the $K_2[Fe_2(CO)_8]$+K catalysts is their increased activity in the ammonia synthesis in the low-temperature region. Thus hydrogenation of N_2 over the $K_2[Fe_2(CO)_8]$+K catalyst on the AG-5 carbon occurs at a noticeable rate (0.3 $cm^3\ NH_3\ h^{-1}\ g^{-1}$) even at 150 °C and atmospheric pressure, and at 250 °C, this catalyst is 2.5 times more active than the industrial catalyst for the ammonia synthesis ($W = 2500\ h^{-1}$).[37] The $K_2[Ru_4(CO)_{13}]$+K catalysts on carbon are less efficient at 150—200 °C than the similar $K_2[Fe_2(CO)_8]$+K systems, but they are considerably more active at higher temperatures (250—350 °C).[39,41,44]

The dependence of the activity of the $K_2[Fe_2(CO)_8]$+K catalyst on the SKT carbon in the ammonia synthesis on the amount of potassium also passes through a maximum,[37,48] but this maximum is shifted to even higher contents of the alkali metal than that observed for the similar catalyst on "Sibunit." It should be noted that the position of the maximum does not depend on the content of iron in the catalyst (at least, in the Fe/carbon = 4.5—9.0% (w/w) range), be-

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* Here and below, the K : C ratios in the samples do not include potassium incorporated in the starting anionic cluster.

ing determined only by the molar ratio of potassium to carbon. The optimum K : C ratio is 1 : (3.7—3.8). The results obtained led to the conclusion that the actual donor of electrons in these systems is not the potassium itself but its adduct with active carbon, similar to the well-known adducts of alkali metals with graphite and aromatic hydrocarbons.

A significant point in elucidation of the mechanisms of activation and subsequent hydrogenation of dinitrogen was the fact that the ammonia synthesis over such catalysts can be accomplished stepwise.[38] Thus if the $K_2[Fe_2(CO)_8]+K$ catalyst on the SKT carbon is heated for 7 h at 250 °C in a flow of N_2, and then H_2 is passed through the sample at the same temperature (after removal of N_2), ~0.4 mole of ammonia per 1 g-atom of Fe is formed. The repeated heating of the catalyst in a flow of dinitrogen and then in a flow of dihydrogen results again in the formation of ammonia, and such cycles of stepwise hydrogenation can be repeated many times.

In a study of the processes occurring during the interaction of dinitrogen with these systems, it was found that hydrolysis of the $K_2[Fe_2(CO)_8]+K$ catalyst after its heating in a flow of N_2 at 250 °C also affords ammonia.[48] Since the products of hydrolysis contained no hydrazine, it was concluded that during the reaction of the catalyst with dinitrogen, the latter is reduced to nitride derivatives, which serve as the source of ammonia during the hydrolysis. It was shown by special experiments[48] that these nitrides are also responsible for the formation of ammonia during the interaction of the sample with dihydrogen.

The efficiency of the reduction of dinitrogen to nitrides (which can be evaluated based on the yield of ammonia after the hydrolysis) depends strongly on the content of potassium in the catalyst.[48] It is significant that this dependence also passes through a maximum, which is observed at the same K : C ratio (1 : 3.7—3.8), as in the case of the ammonia synthesis from dinitrogen and dihydrogen. In the absence of specially introduced potassium, the catalyst completely loses its activity in the reduction of N_2 to nitrides at 250 °C.

The yields of ammonia formed on the hydrolysis are quite large; at sufficiently long reaction times, they approach a value of 2 moles per 1 g-atom of Fe.[48] The formation of the so large amounts of ammonia with respect to iron clearly indicates that the reduction of dinitrogen in the $K_2[Fe_2(CO)_8]+K$ system on the SKT carbon occurs, at least partially, due to electrons of metallic potassium, or, more precisely, its adduct with carbon. Since the adduct of potassium with carbon alone was found to be inert with respect to N_2 at 250 °C, it can be concluded that iron also participates in the reduction of dinitrogen by activating the N_2 molecule. Thus, the processes occurring during the interaction of the $K_2[Fe_2(CO)_8]+K$ catalyst on SKT with dinitrogen are apparently quite similar to the reactions of reduction of N_2 in liquid-phase nitrogen-fixing systems,[4,9] with the only difference being that in the latter case, the reduction occurs in solution rather than on the surface of a catalyst.

Subsequent studies have shown that during the ammonia synthesis from N_2 and H_2 over the $K_2[Fe_2(CO)_8]+K$ catalyst on SKT, large amounts of a nitrogen-containing product, capable of forming ammonia under the action of dihydrogen or upon hydrolysis, are also accumulated in the sample.[38,48] It was found that when H_2 is passed at 250 °C through the catalyst after hydrogenation of N_2 at the same temperature for 3 h at a steady rate, ammonia appears again in the gas flow. The quantity of ammonia increases with time and, after 18 h, it reaches ~1.2 mole per 1 g-atom of Fe, and the reaction is not yet completed up to this moment. When H_2 is replaced by Ar, ammonia is no longer detected in the gas flow. This indicates that the formation of ammonia in the reaction with dihydrogen is due not to thermal desorption of NH_3 from the catalyst surface but to hydrogenation of an intermediate nitrogen-containing product resulting from the reaction of the dinitrogen—dihydrogen mixture with the catalyst during the ammonia synthesis.

The rate of formation of this intermediate product is substantially higher than the rate of formation of the nitride derivative in the reaction of the catalyst with pure N_2.[48] This is indicated by a comparison of the time dependences of the yields of ammonia on the hydrolysis for the reactions of the catalyst with an N_2—H_2 mixture and with N_2 alone. Thus the hydrolysis of the catalyst preheated for 1.5 h at 250 °C in a flow of N_2 yields only 0.3 mole of NH_3 per 1 g-atom of Fe, whereas in the case where the catalyst had reacted with a dinitrogen—dihydrogen mixture, the yield of ammonia after the hydrolysis is 1.3—1.4 mole of NH_3 per 1 g-atom of Fe under the same conditions.

Based on the obtained results,[48] it was suggested that dihydrogen actively interferes in the interaction of dinitrogen with the catalyst even at the early stages by accelerating the process and participating in the dinitrogen reduction, together with the adduct of carbon with potassium. If this is really so, then the nitrogen-containing intermediate, which is formed in the catalyst during the ammonia synthesis and serves as the source of ammonia in the hydrolysis, should contain N—H bonds, *i.e.*, this should be an amide or imide derivative rather than a nitride, as in the case of the reaction of the catalyst with pure dinitrogen. It can be believed that in the formation of this amide (or imide), the role of the reducer of dinitrogen is accomplished by the product of interaction of dihydrogen with the potassium—carbon adduct, most likely, potassium hydride. A similar accelerating effect of dihydrogen on the reduction of N_2 has been observed previously for liquid-phase nitrogen-fixing systems $Ti(OR)_4+Bu^i{}_3Al$ (R = Et, Bu^n) and $TiX_4+Bu^i{}_3Al+AlBr_3$ (X = Cl, Bu^nO),[7,8,10] in which dihydrogen was shown to actually participate in the reduction of dinitrogen (together with the organoaluminum compound) to form products containing N—H bonds.

The isotope exchange in dinitrogen over the $K_2[Fe_2(CO)_8]$+K catalyst on the SKT carbon is also accelerated in the presence of dihydrogen, and in this case too, the plots for the exchange efficiency both in the absence and in the presence of H_2 pass through a maximum at a K : C ratio of 1 : (3.7—3.8).[49] The isotope exchange over this catalyst requires much higher temperatures (350 °C) than the ammonia synthesis and the reduction of dinitrogen to nitrides. Apparently, the ammonia synthesis and the isotope exchange in dinitrogen over the $K_2[Fe_2(CO)_8]$+K catalyst are characterized by different rate-determining steps. It is known that in the case of the conventional ammonia synthesis catalyst based on bulk iron, the isotope exchange in dinitrogen occurs at the same temperatures as the ammonia synthesis and that the rates of these two processes are close.[32,33] The latter indicates that the rate of both reactions is limited by the same step, namely, chemisorption of dinitrogen.

Thus, the results presented above show that the $K_2[Fe_2(CO)_8]$+K system on SKT carbon is able to accomplish on heating at least three processes: catalytic ammonia synthesis from N_2 and H_2, reduction of N_2 to nitrides and the isotope exchange in dinitrogen. The efficiencies of these three reactions depend on the amount of potassium in the catalyst and pass through a maximum at the same K : C ratio. The presence of dihydrogen in the gas accelerates both the reduction of dinitrogen by the catalyst and the isotope exchange in dinitrogen. However, the latter occurs at considerably higher temperatures than the reduction of N_2 by the catalyst or the ammonia synthesis.

A comparison of the $K_2[Fe_2(CO)_8]$+K catalyst on the SKT carbon with liquid-phase nitrogen-fixing systems based on transition metal compounds and strong reducing agents demonstrates similarity of the behavior of these two types of systems, indicating that the mechanisms of their reactions with dinitrogen have common features. It can be assumed that the first step of the reaction of N_2 with the $K_2[Fe_2(CO)_8]$+K system on the SKT carbon includes complexation of an N_2 molecule with iron-containing active sites. Then the coordinated dinitrogen molecule is reduced by electrons from the potassium—carbon adduct to yield nitrides, which are converted into ammonia upon hydrolysis. The ability of these nitrides to undergo hydrogenolysis to ammonia with regeneration of the active sites makes it possible to accomplish cyclic ammonia synthesis on this catalyst.

The catalytic synthesis of ammonia from N_2 and H_2 in the presence of the $K_2[Fe_2(CO)_8]$+K system also includes apparently the step of complexation of N_2 with Fe atoms; however, the subsequent reduction of the coordinated N_2 molecule occurs probably through the action of potassium hydride, which could result from the reaction of dihydrogen with the adduct of carbon with potassium. The reduction of dinitrogen with potassium hydride affords amides or imides, whose hydrogenolysis under the action of dihydrogen gives ammonia.

6. Conclusion

The data presented in this review demonstrate the fruitfulness of using the ideas and methods of the chemistry of molecular nitrogen in solutions for the accomplishment of low-temperature ammonia synthesis from dinitrogen and dihydrogen. The studies carried out in recent decades resulted in the development of a new type of catalysts for the ammonia synthesis that are characterized by increased activities in the low-temperature region. The catalysts are heterogeneous analogs of the well-known homogeneous nitrogen-fixing systems based on transition metal compounds and strong electron donors. The best results have been obtained for supported ruthenium, osmium, and iron catalysts treated with alkali metals. The potassium-containing catalysts, which are highly active in the ammonia synthesis, have been studied in the greatest detail. The replacement of potassium by cesium gives even more active systems, but they have been scarcely studied.

One of the functions accomplished by metallic potassium in these new catalysts is the creation of increased electron density on the transition metal atoms, which is necessary for efficient activation of dinitrogen. In the industrial catalyst for the ammonia synthesis, this function is performed by potassium oxide; however, the effect of metallic potassium should be much stronger.

Yet another possible role of metallic potassium in the functioning of these catalysts is due to the fact that, unlike K_2O, it is a strong reducing agent. As a consequence, on introduction of metallic potassium, a system can acquire the ability to reduce molecular nitrogen to, for example nitrides, as was observed for the $K_2[Fe_2(CO)_8]$+K system on SKT carbon. In the presence of dihydrogen, a considerable part of the metallic potassium is apparently converted into potassium hydride, and this provides conditions for the occurrence of the ammonia synthesis by a mechanism that includes reduction of dinitrogen by potassium hydride to amide or imide derivatives followed by their hydrogenolysis by dihydrogen to give free ammonia.

Regarding the practical use of the developed catalysts, the prospects for metallic potassium are obviously not very good. Therefore, in the late 70s, intense studies were started in Japan and Great Britain (British Petroleum) aimed at the replacement of metallic potassium in the catalysts under consideration by other promoters that would be more plausible from the practical viewpoint (see, for example, Refs. 50—54). These studies resulted in the development of new supported ruthenium catalysts for the ammonia synthesis, containing alkali or alkaline earth metal oxides (or hydroxides) as the electron promoters. The best of these catalysts are substantially more efficient than the industrial catalyst for the ammonia synthesis, but regarding the activity in the low-temperature region, they are considerably inferior to those promoted by metallic potassium. One of these new ruthenium catalysts was used by the

M. W. Kellog company together with British Petroleum to develop a new industrial technology for the ammonia synthesis, which may replace in the future the currently used Haber—Bosch process. The use of the new catalyst allows the ammonia synthesis to be conducted at much lower pressures (70—105 atm), but the reaction temperatures still remain fairly high (350—470 °C)[55].

Further research aimed at the development of catalysts for low-temperature ammonia synthesis would make it possible to solve this important problem.

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References

1. M. E. Vol'pin and V. B. Shur, *Dokl. Akad. Nauk SSSR*, 1964, **156**, 1102 [*Dokl. Chem.*, 1964 (Engl. Transl.)].
2. M. E. Vol'pin, V. B. Shur, and M. A. Ilatovskaya, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1964, 1728 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1964, **13**, 1644 (Engl. Transl.)].
3. A. D. Allen and C. V. Senoff, *J. Chem. Soc., Chem. Commun.*, 1965, 621.
4. M. E. Vol'pin and V. B. Shur, in *New Trends in the Chemistry of Nitrogen Fixation*, Eds. J. Chatt, L. M. da Câmara Pina, and R. L. Richards, Acad. Press, London, 1980, p. 67.
5. T. A. Bazhenova and A. E. Shilov, *Coord. Chem. Rev.*, 1995, **144**, 69.
6. M. Hidai and Y. Mizobe, *Chem. Rev.*, 1995, **95**, 1115.
7. M. E. Vol'pin, M. A. Ilatovskaya, E. I. Larikov, M. L. Khidekel', Yu. A. Shvetsov, and V. B. Shur, *Dokl. Akad. Nauk SSSR*, 1965, **164**, 331 [*Dokl. Chem.*, 1965 (Engl. Transl.)].
8. Yu. A. Shvetsov, L. G. Korableva, G. N. Nechiporenko, M. A. Ilatovskaya, and M. L. Khidekel', *Dokl. Akad. Nauk SSSR*, 1968, **178**, 400 [*Dokl. Chem.*, 1968 (Engl. Transl.)].
9. M. E. Vol'pin and V. B. Shur, in *Organometallic Reactions*, Eds. E. Becker and M. Tsutsui, Wiley, New York, 1970, **1**, 55.
10. M. E. Vol'pin, M. A. Ilatovskaya, and V. B. Shur, *Kinet. Katal.*, 1970, **11**, 333 [*Kinet. Catal.*, 1970, **11** (Engl. Transl.)].
11. M. Sudo, M. Ichikawa, M. Soma, T. Onishi, and K. Tamaru, *J. Phys. Chem.*, 1969, **73**, 1174.
12. M. Ichikawa, T. Kondo, K. Kawase, M. Sudo, M. Soma, T. Onishi, and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1972, 176.
13. Yu. N. Novikov and M. E. Vol'pin, *Usp. Khim.*, 1971, **40**, 1568 [*Russ. Chem. Rev.*, 1971, **40** (Engl. Transl.)].
14. V. A. Postnikov, L. M. Dmitrienko, R. F. Ivanova, N. L. Dobrolyubova, M. A. Golubeva, T. I. Gapeeva, Yu. N. Novikov, V. B. Shur, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 2642 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24** (Engl. Transl.)].
15. A. V. Nefed'ev, R. A. Stukan, V. A. Postnikov, V. B. Shur, Yu. N. Novikov, and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 2376 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1976, **25** (Engl. Transl.)].
16. M. E. Vol'pin, Yu. N. Novikov, V. A. Postnikov, V. B. Shur, B. Bayerl, L. Kaden, M. Wahren, L. M. Dmitrienko, R. A. Stukan, and A. V. Nefed'ev, *Z. Anorg. Allg. Chem.*, 1977, **428**, 231.
17. W. G. Frankenburg, *Catalysis*, 1955, **3**, 186.
18. A. Ozaki, K. Aika, and H. Hori, *Bull. Chem. Soc. Jpn.*, 1971, **44**, 3216.
19. K. Aika, H. Hori, and A. Ozaki, *J. Catal.*, 1972, **27**, 424.
20. K. Aika, I. Yamaguchi, and A. Ozaki, *Chem. Lett.*, 1973, 161.
21. K. Urabe, K. Aika, and A. Ozaki, *J. Catal.*, 1974, **32**, 108.
22. K. Aika and A. Ozaki, *J. Catal.*, 1974, **35**, 61.
23. M. Oh-Kita, K. Aika, K. Urabe, and A. Ozaki, *J. Chem. Soc., Chem. Commun.*, 1975, 147.
24. K. Urabe, K. Aika, and A. Ozaki, *J. Catal.*, 1975, **38**, 430.
25. K. Urabe, K. Aika, and A. Ozaki, *J. Catal.*, 1976, **42**, 197.
26. M. Oh-Kita, K. Aika, K. Urabe, and A. Ozaki, *J. Catal.*, 1976, **44**, 460.
27. K. Urabe, K. Shiratori, and A. Ozaki, *J. Catal.*, 1978, **55**, 71.
28. A. Ohya, K. Urabe, and A. Ozaki, *Chem. Lett.*, 1978, 233.
29. A. Ohya, K. Urabe, K. Aika, and A. Ozaki, *J. Catal.*, 1979, **58**, 313.
30. A. Ozaki, *Acc. Chem. Res.*, 1981, **14**, 16.
31. A. Ozaku and K. Aika, in *A Treatise of Dinitrogen Fixation*, Eds. R. W. F. Hardy, F. Bottomley, and R. C. Burns, Wiley, New York, Chichester, Brisbane, Toronto, 1979.
32. L. D. Kuznetsova, L. M. Dmitrienko, P. D. Rabina, and Yu. A. Sokolinskii, *Sintez ammiaka* [*Ammonia Synthesis*], Khimiya, Moscow, 1982 (in Russian).
33. K. Tamaru, in *New Trends in the Chemistry of Nitrogen Fixation*, Eds. J. Chatt, L. M. da Câmara Pina, and R. L. Richards, Acad. Press, London, 1980, p. 13.
34. M. Ishizuka, K. Aika, and A. Ozaki, *J. Catal.*, 1970, **16**, 97.
35. R. L. Richards, in *New Trends in the Chemistry of Nitrogen Fixation*, Eds. J. Chatt, L. M. da Câmara Pina, and R. L. Richards, Acad. Press, London, 1980, p. 199.
36. V. V. Karpov and G. I. Kozub, *Kinet. Katal.*, 1976, **17**, 1334 [*Kinet. Catal.*, 1976, **17** (Engl. Transl.)].
37. V. B. Shur, S. M. Yunusov, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, 1984, **277**, 884 [*Dokl. Chem.*, 1984 (Engl. Transl.)].
38. V. B. Shur, S. M. Yunusov, S. Rummel, M. Wahren, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, 1987, **292**, 1409 [*Dokl. Chem.*, 1987 (Engl. Transl.)].
39. V. B. Shur, S. M. Yunusov, E. S. Kalyuzhnaya, and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, 1991, **320**, 353 [*Dokl. Chem.*, 1991 (Engl. Transl.)].
40. V. B. Shur, S. M. Yunusov, V. K. Puri, H. Mahapatra, B. Sen, D. K. Mukhergee, E. S. Kalyuzhnaya, I. A. Fokina, V. A. Likholobov, and M. E. Vol'pin, *Izv. Akad. Nauk, Ser. Khim.*, 1992, 1452 [*Bull. Russ. Acad. Sci., Div. Chem. Sci.*, 1992, 1137 (Engl. Transl.)].
41. V. B. Shur, S. M. Yunusov, and V. A. Likholobov, *The 14th International Conference on Catalysis* (The Taniguchi Foundation), November 5—10, 1995, Kobe, Japan, Abstracts, p. 9.
42. S. M. Yunusov, V. A. Likholobov, and V. B. Shur, *Appl. Cat. A: General*, 1997, **158**, L35.
43. S. M. Yunusov, B. L. Moroz, A. S. Ivanova, V. A. Likholobov, and V. B. Shur, *J. Molec. Catal. A: Chemical*, 1998, in press.
44. S. M. Yunusov, E. S. Kalyuzhnaya, H. Mahapatra, V. K. Puri, V. A. Likholobov, and V. B. Shur, *J. Molec. Catal. A: Chemical*, 1998, in press.

45. Yu. I. Yermakov, V. F. Surovikin, G. V. Plaksin, V. A. Semikolenov, V. A. Likholobov, L. V. Chuvilin, and S. V. Bogdanov, *React. Kinet. Catal. Lett.*, 1987, **32**, 435.
46. V. A. Likholobov, V. B. Fenelonov, L. G. Okkel, O. V. Goncharova, L. V. Avdeeva, V. I. Zaikovskii, G. G. Kuvshinov, V. A. Semikolenov, N. K. Duplyakin, O. N. Baklanova, and G. V. Plaksin, *React. Kinet. Catal. Lett.*, 1995, **54**, 381.
47. K. Aika and S. Murata, *J. Catal.*, 1992, **136**, 126.
48. V. B. Shur, S. M. Yunusov, M. A. Ilatovskaya, S. Rummel, and M. E. Vol'pin, *Dokl. Akad. Nauk*, 1994, **336**, 631 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
49. V. B. Shur, S. M. Yunusov, M. A. Ilatovskaya, S. Rummel, and M. E. Vol'pin, *Dokl. Akad. Nauk*, 1994, **336**, 789 [*Dokl. Chem.*, 1994 (Engl. Transl.)].
50. A. Ozaki, K. Urabe, K. Shimazaki, and S. Sumiya, *Stud. Surf. Sci. Catal.*, 1979, **3**, (*Prep. Catal.* 2), 381.
51. K. Aika, K. Shimazaki, Y. Hattory, A. Ohya, S. Ohshima, K. Shirota, and A. Ozaki, *J. Catal.*, 1985, **92**, 296.
52. K. Aika, A. Ohya, A. Ozaki, Y. Inoue, and I. Yasumory, *J. Catal.*, 1985, **92**, 305.
53. J. J. McCarrol, S. R. Tennison, and N. P. Wilkinson, UK Patent, 2136704A (1984).
54. K. Aika, T. Kawahara, S. Murata, and T. Onishi, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1221.
55. *Chem. Eng. NY*, 1993, March, 19.

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