Ammonia synthesis from dinitrogen and dihydrogen over the catalysts based on supported mononuclear potassium carbonyl ruthenate. Promoting effect of alkyllithium compounds

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New catalysts for the ammonia synthesis from dinitrogen and dihydrogen based on supported mononuclear potassium carbonyl ruthenate $K_2Ru[(CO)_4]$ as a precursor of catalytically active particles have been developed. Magnesium oxide and graphite-like active carbon Sibunit were used as supports, while aliphatic organolithium compounds (Bu^nLi and Bu^tLi) were employed as electron promoters in these catalysts. The systems with MgO as a support are the most efficient. The introduction of RLi into these systems allows one to considerably increase the ammonia synthesis rate. When using carbon Sibunit, the promoting effect of organolithium compounds is much weaker but the activity of such catalysts can be essentially increased by the introduction of an additional electron promoter, *viz.*, metallic potassium, into the system. All the catalysts tested are active in the ammonia synthesis at atmospheric pressure and temperatures ≥250 °C.

Key words: dinitrogen, dihydrogen, ammonia synthesis, catalysts, promoters, alkali metal carbonyl ruthenates, organolithium compounds, metallic potassium, magnesium oxide, carbon supports.

Considerable progress in the development of new approaches to the accomplishment of the low-temperature ammonia synthesis from dinitrogen and dihydrogen is observed in the recent decades (see reviews[1—6] and articles[7—20]). One of such approaches is based on the use of heterogeneous systems consisting of a transition metal compound or the metal itself (as a rule, on a support) and promoting additives of a strong electron donor (usually metallic potassium) as catalysts of this process.[1,5,9—12] It turned out that systems of such a type, being heterogeneous analogs of the well known liquid-phase nitrogen-fixing systems based on transition metal compounds and strong reducing agents (alkali metals; metal hydrides; organolithium, -magnesium, and -aluminum compounds; *etc.*, see reviews[21,22]) are capable indeed of catalyzing the gas-phase ammonia synthesis, the best catalysts exhibiting a noticeable activity in this process already at 110—150 °C and atmospheric pressure.[1,5,10,11]

In our works on creating the catalysts for the low-temperature ammonia synthesis, we proposed for the first time to use supported potassium carbonyl metallates ($K_2[Fe_2(CO)_8]$, $K_2[Ru(CO)_4]$, $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, and others) as precursors of catalytically active particles.[5,8—13] It was assumed that the thermal decomposition of the supported carbonyl metallates (with CO formation) would result in the generation of negatively charged potassium-containing transition metal species on the support surface, which should favor the efficient activation of dinitrogen. Productivity of such an "organometallic" approach was demonstrated by the preparation of the first catalysts on a carbon support (graphite-like carbon Sibunit[23] and others) capable of accomplishing the ammonia synthesis with sufficiently high rates even in the absence of a specially added electron promoter.[5,8,9,12] Among these novel catalysts, the ruthenium-containing systems were the most active. It was shown that in the series of the $K_2[Ru_6(CO)_{18}]$, $K_2[Ru_4(CO)_{13}]$, $K_4[Ru_4(CO)_{12}]$, $K_6[Ru_6(CO)_{16}]$, $K_6[Ru_4(CO)_{11}]$, and $K_2[Ru(CO)_4]$ catalysts on carbon Sibunit the ammonia synthesis rate increases with an increase in the K : Ru ratio in the starting carbonyl ruthenate attaining a maximum in the case of $K_6[Ru_4(CO)_{11}]$ (K : Ru = 1.5 : 1) and only slightly decreases on going to $K_2[Ru(CO)_4]$ (K : Ru = 2 : 1).[12] It was also found that the activity of these catalysts can be still

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1811—1815, September, 2011.

more increased by the replacement of Sibunit by considerably more basic magnesium oxide and especially when metallic potassium is introduced into the system.[9,12] The catalyst $K_2[Ru(CO)_4]+K$ on Sibunit turned out to be the most efficient.[12] Note that the role of the electron promoter in this and similar catalytic systems is actually fulfilled not by metallic potassium itself but by its adduct with aromatic fragments of the carbon support, *i.e.*, peculiar organopotassium compound. If MgO is used instead of Sibunit as a support in the $K_2[Ru(CO)_4]+K$ system, the ammonia synthesis rate decreases due to, apparently, the consumption of the alkali metal in the reduction of magnesium oxide under the conditions of catalyst preparation and testing.

The purpose of the present work is to study the possibility of the development of efficient catalysts for the gas-phase ammonia synthesis using supported $K_2[Ru(CO)_4]$ as a precursor of catalytically active particles and alkyllithium compounds (*n*-butyllithium, *tert*-butyllithium) as electron promoters. As it is known,[21] organolithium compounds can form highly active nitrogen-fixing systems with transition metal compounds that reduce molecular nitrogen in solutions already at room temperature and atmospheric pressure.

Experimental

All procedures involved in the synthesis of $K_2[Ru(CO)_4]$ and preparation of the catalysts were carried out in an argon atmosphere or *in vacuo* with careful exclusion of air oxygen and moisture. The initial $K_2[Ru(CO)_4]$ was synthesized by the reaction of $Ru_3(CO)_{12}$ with metallic potassium in liquid ammonia according to a procedure described earlier[24] and was deposited on graphite-like carbon Sibunit (carbon content 99.5%, surface area 440 $m^2\ g^{-1}$) or MgO (surface area 220 $m^2\ g^{-1}$) without isolation from the solution, after which the sample was dried *in vacuo* to a constant weight. A characteristic feature of Sibunit that distinguishes it from the most part of standard active carbons is a well-developed structure of mesopores, which is very essential for catalysis. Another important advantage of Sibunit is its high mechanical strength, thermal and mechanical resistance, and a low content of sulfur and other admixtures.[23] Prior to supporting, carbon Sibunit was dried *in vacuo* for 6 h at 130 °C, and magnesium oxide was dried *in vacuo* for 4 h at 200 °C. Liquid ammonia was purified by double recondensation over sodium under argon prior to use. The ratio Ru/support in the samples was 9 wt.%.

The catalysts were prepared as follows. After $K_2[Ru(CO)_4]$ was deposited on carbon Sibunit or MgO, the sample was heated at 300 °C in a dihydrogen flow for 4—6 h to remove CO from the supported carbonyl ruthenate. Then the sample obtained was impregnated with commercial solutions of Bu^nLi in hexane (15%, Merck) or Bu^tLi in pentane (1.5 mol L^{-1}, Aldrich), the mixture was stored for 5 min with shaking from time to time, the solvent was removed *in vacuo* at 20 °C, and the residue was dried *in vacuo* to a constant weight and then loaded into the reactor for tests in the ammonia synthesis. In some experiments, the samples of supported carbonyl ruthenate were treated with solutions of Bu^nLi or Bu^tLi without preliminary heating of $K_2[Ru(CO)_4]$ in an H_2 flow at 300 °C.

A treatment of the catalysts with metallic potassium was carried out at 120—130 °C according to a procedure described earlier.[9] The reaction with potassium yielded strongly pyrophoric powdered brown or dark brown samples, which were tested in the ammonia synthesis.

The catalysts were tested in the ammonia synthesis in a glass flow-type reactor (with fixed-bed sample) at 250—400 °C and atmospheric pressure. A stoichiometric dinitrogen—dihydrogen mixture was used in all experiments ($N_2 : H_2 = 1 : 3$, gas flow rate 10 L h^{-1}). The procedure of catalyst loading into the reactor excluded the contact of the sample with air. The activity of the catalyst was estimated by its productivity in ammonia formation (mL $NH_3\ h^{-1}\ g^{-1}$ cat.; STP) and by the ammonia content in the outlet gas flow (vol.%) in the stationary state.

The content of ammonia in the gas flow was determined by measuring the time necessary for the neutralization of a certain amount of an aqueous solution of H_2SO_4 of the known concentration with ammonia at constant flow rate of the dinitrogen—dihydrogen mixture, temperature, and pressure. The presence of ammonium ions in the analyzed solutions was monitored by the reaction with Nessler´s reagent. The repeated analyses of these solutions by the Kjeldahl method gave coinciding results. The results of six to eight measurements were averaged and rounded to the second decimal place to give the values of stationary concentrations of ammonia. The standard deviations from the average values were 0.002—0.008 vol.%.

Results and Discussion

The first experiments on using organolithium compounds as electron promoters for creating catalysts for the gas-phase ammonia synthesis have been described in the literature.[25] The authors treated the iron compounds ($FeCl_3$, $Fe(acac)_3$) on a carbon support (graphite, active carbon) with a large excess of a solution of *n*-butyllithium or phenyllithium and found that after solvent removal and drying the samples prepared can catalyze the ammonia synthesis, although with low rates. For instance, when using the most studied system $FeCl_3+Bu^nLi$ on graphite, the ammonia content in the gas flow at 300 °C and atmospheric pressure did not exceed ~0.011 vol.% ($W = 2000\ h^{-1}$, $N_2 : H_2 = 1 : 3$; $[NH_3]_e = 2.18$ vol.% (see Refs 26, 27)) whereas at 400 °C the ammonia content increased to ~0.109 vol.% ($W = 1100\ h^{-1}$), which is only ~25—26% of the corresponding equilibrium value (0.415 vol.%) (see Ref. 26), 0.44 vol.% (see Ref. 27)). The much higher ammonia synthesis rates were observed in the case of the catalysis of this process by the systems $K_2[Ru(CO)_4]+RLi$ (R = Bu^n, Bu^t) on Sibunit and MgO.

The data on the activity of the $K_2[Ru(CO)_4]+Bu^nLi$ and $K_2[Ru(CO)_4]+Bu^tLi$ catalysts on carbon Sibunit in the ammonia synthesis are presented in Table 1. The earlier published data[12] for the corresponding ruthenium catalyst based on $K_2[Ru(CO)_4]$, which was not promoted with

Table 1. Effect of additives of organolithium compounds on the activity of the catalyst based on $K_2[Ru(CO)_4]$ on Sibunit in the ammonia synthesis[a]

RLi	Amount of catalyst/g	RLi : Ru /mol mol^{-1}	Concentration of ammonia in gas (vol.%)				Productivity of catalyst /(mL of NH_3) h^{-1} (g of cat.)$^{-1}$			
			250 °C	300 °C	350 °C	400 °C	250 °C	300 °C	350 °C	400 °C
—	2.69[b]	0	0.03	0.36	0.81	0.41	1.1	13.4	30.1	15.2
Bu^{n}Li	2.95	2.0 : 1	0.04	0.36	0.81	0.42	1.4	12.2	27.5	14.2
	3.03	3.6 : 1	0.11	0.48	0.77	0.41	3.6	15.8	25.4	13.5
	3.17	5.5 : 1	0.06	0.36	0.72	0.42	1.9	11.4	22.7	13.3
	3.13[c]	3.6 : 1	0.07	0.51	0.84	0.43	2.2	16.3	26.8	13.7
	3.33[c]	7.1 : 1	0.06	0.56	0.81	0.38	1.8	16.8	23.7	11.4
	3.17[c,d]	10.0 : 1	0.03	0.38	0.78	0.42	1.0	12.0	24.6	13.3
	3.61[c]	14.2 : 1	0.01	0.09	—	0.31	0.3	2.5	—	8.6
Bu^{t}Li	2.93	1.0 : 1	0.03	0.37	0.84	0.42	1.0	12.6	28.7	14.3
	3.05	2.0 : 1	0.06	0.43	0.81	0.44	2.0	14.1	26.6	14.4
	2.97[d]	3.7 : 1	0.06	0.36	0.75	0.43	2.0	12.1	25.3	14.5
	3.11	7.0 : 1	0.00	0.18	0.49	0.41	0.0	5.8	15.8	13.2

[a] The content of Ru in the samples was 2.24 mmol, Ru/support = 9 wt.%, the weight of the catalysts was determined after their tests in the ammonia synthesis at 250—400 °C.

[b] Supported $K_2[Ru(CO)_4]$ was not heated in an H_2 flow at 300 °C. Preliminary heating of supported $K_2[Ru(CO)_4]$ at this temperature in an H_2 flow exerts almost no effect on the activity of the sample in the ammonia synthesis.

[c] Prior to impregnation with a solution of Bu^{n}Li, supported $K_2[Ru(CO)_4]$ was not heated at 300 °C in an H_2 flow.

[d] The catalyst weight is somewhat underestimated because of a small loss of the sample upon its discharging from the reactor.

an organolithium compound, are also given for a comparison. The tests of the catalysts were started from 250 °C, and then the temperature was successively increased to 300, 350, and 400 °C.

The data presented show that $K_2[Ru(CO)_4]$ on Sibunit exhibits a sufficiently high activity in the dinitrogen hydrogenation with dihydrogen even in the absence of a specially added electron promoter. The process occurs with a noticeable rate already at 250 °C, and at 300 °C the stationary concentration of ammonia in the gas attains 0.36 vol.%, which is 16.5% of the equilibrium value. At 350 and 400 °C the ammonia synthesis reaction on this non-promoted catalyst nearly reaches equilibrium (at 350 °C $[NH_3]_e = 0.864$ vol.%).[26]

When *n*-butyllithium is introduced into the system, its activity in the ammonia formation at 250 and 300 °C first increases with an increase in the amount of the organolithium compound, reaches a maximum at the ratio Bu^{n}Li : Ru = 3.6 : 1, and then begins to decrease. The highest accelerating effect of Bu^{n}Li is observed at 250 °C. Under these conditions, the ammonia content in the outlet gas flow and the synthesis rate increase by a factor of 3—4 compared to the activity of the non-promoted sample. At 300 °C additives of Bu^{n}Li also accelerate the process but to a less extent. The stationary ammonia concentration in the gas flow at this temperature was increased from 0.36 to 0.48 vol.% (22% of the equilibrium value), *i.e.*, by a factor of 1.3. At 350 °C the catalyst activity decreases with an increase in the content of Bu^{n}Li. At 400 °C the stationary concentration of ammonia in the outlet gas mixture remained close to the equilibrium value at all Bu^{n}Li : Ru ratios.

In the case of the catalysts in which $K_2[Ru(CO)_4]$ on Sibunit underwent no thermal decomposition at 300 °C in an H_2 flow before the treatment with *n*-butyllithium, the rate of NH_3 synthesis also passes through a maximum as the amount of alkyllithium increases in the system (see Table 1). If the synthesis of NH_3 is carried out at 250 °C, the use of this method for catalyst preparation decreases the catalytic activity of the sample; however, at 300 °C the activity, on the contrary, even somewhat increases. Indeed, as can be seen from Table 1, the ammonia content in the gas at 300 °C is, in this case, already 0.56 vol.% (~26% of the equilibrium value), which is substantially higher than an analogous value (0.48 vol.%) obtained when the standard procedure of catalyst preparation was used.

The catalyst $K_2[Ru(CO)_4]$+Bu^{t}Li behaves similarly in the ammonia synthesis, but the promoting effect of this organolithium compound is somewhat weaker than the effect of *n*-butyllithium (see Table 1).

The catalytic activity of the $K_2[Ru(CO)_4]$+Bu^{n}Li system on carbon Sibunit in the ammonia synthesis can be still more increased by the introduction of the second electron promoter, namely, metallic potassium. The preparation of such doubly promoted catalysts included the thermal decomposition of supported $K_2[Ru(CO)_4]$ in an H_2 flow at 300 °C, the impregnation of the obtained sample with a solution of Bu^{n}Li in hexane (Bu^{n}Li : Ru = 3.6 : 1),

Table 2. Effect of metallic potassium additives on the activity of the catalyst $K_2[Ru(CO)_4]+Bu^nLi$ on Sibunit in the ammonia synthesis[a]

Amount of catalyst/g	K : C /mol mol^{-1}	Concentration of ammonia in gas (vol.%)				Productivity of catalyst /(mL of NH_3) h^{-1} (g of cat.)$^{-1}$			
		250 °C	300 °C	350 °C	400 °C	250 °C	300 °C	350 °C	400 °C
3.03[b]	0	0.11	0.48	0.77	0.41	3.6	15.8	25.4	13.5
3.51	0.05 : 1	0.21	0.87	0.77	0.42	6.0	24.8	21.9	12.0
3.81	0.08 : 1	0.26	0.98	0.86	0.41	6.8	25.7	22.6	10.8
3.95	0.10 : 1	0.19	0.78	0.84	0.41	4.8	19.8	21.3	10.4

[a] The content of Ru in the samples was 2.23—2.24 mmol, Ru/support = 9 wt.%, the mole ratio Bu^nLi : Ru = 3.6 : 1. The mole ratios K : C are given without taking into account the amount of potassium in the initial carbonyl ruthenate.

[b] The weight of the catalyst was determined after its testing in the ammonia synthesis at 250—400 °C.

and the treatment with various quantities of metallic potassium. The results of tests of the catalysts are presented in Table 2, which show that the introduction of one more electron promoter into the system results in a considerable increase in the synthesis rate. The best results are observed at the mole ratio of the metallic potassium and carbon of the support equal to 0.08 : 1. When this K : C ratio is used, the ammonia content in the gas flow at 250 °C increases by a factor of 2.4, and at 300 °C it attains 0.98 vol.%, which is ~45% of the equilibrium value. At 350 and 400 °C the ammonia synthesis reaction reaches practically complete equilibrium. A further increase in the amount of metallic potassium in the sample decreases the rate of the process. As compared to the earlier[12] studied catalyst $K_2[Ru(CO)_4]+K$ on Sibunit without alkyllithium, the above-mentioned system $K_2[Ru(CO)_4]+Bu^nLi+K$ exhibits a lower activity in the ammonia synthesis.

The replacement of Sibunit by MgO in the $K_2[Ru(CO)_4]+Bu^nLi$ and $K_2[Ru(CO)_4]+Bu^tLi$ systems results in a sharp enhancement of the promoting effect of an organolithium compound. In the case of the *n*-butyllithium system, the sample with the ratio Bu^nLi : Ru = = 3.8 : 1 shows the maximum activity at 250 °C (Table 3). Under these conditions, the stationary concentration of ammonia in the gas flow (0.16 vol.%) and the synthesis rate are higher by a factor of ~5 than those in the case of the non-promoted catalyst. At 300 °C the maximum of the catalyst activity is observed in the range of the ratios Bu^nLi : Ru = (3.8—5.5) : 1 (see Table 3). In the presence of such amounts of the organolithium promoter, the $K_2[Ru(CO)_4]+Bu^nLi$ system on MgO exceeds in its efficiency at this temperature the corresponding non-promoted sample by a factor of 2.3—2.5. On using the $K_2[Ru(CO)_4]+Bu^nLi$ system on MgO the ammonia content in the outlet gas mixture attains 1.12—1.13 vol.% at 300 °C, which is 51—52% of the corresponding equilibrium value. At 350 and 400 °C the ammonia synthesis reaction practically reaches the equilibrium. If the amount of Bu^nLi in the system is further increased, the catalyst activity again decreases substantially. The $K_2[Ru(CO)_4]+Bu^tLi$ system on MgO shows somewhat lower activity than the analogous *n*-butyllithium system. In the both cases, unlike the above-mentioned catalysts on Sibunit, the use of the samples in which supported $K_2[Ru(CO)_4]$ was not thermally decomposed at 300 °C before the introduction of alkyllithium results in a strong decrease in the rate of dinitrogen hydrogenation at 250—400 °C.

Thus, additives of *n*-butyllithium and *tert*-butyllithium exert an accelerating effect on the ammonia synthesis under the action of the catalysts based on supported $K_2[Ru(CO)_4]$. The greatest promoting effect of alkyllithium compounds is observed when MgO is used as a support. In all cases, the activity of the catalysts passes through a maximum with the increasing amount of the organolithium compound introduced. Similar dependences with a maximum were observed previously for various iron and ruthenium catalysts on a carbon support promoted with metallic potassium (see the corresponding works cited in the review[5]). It is assumed that an initial increase in the ammonia synthesis rate with an increase in the potassium content in these catalysts is due to an increase in the electron density on the transition metal atoms in consequence of their interaction with the resulting carbon—potassium adduct. Such an increase in the electron density, as already mentioned, should favor the efficient activation of dinitrogen. The observed decrease in the catalytic activity of the system on further increase in the amount of potassium is explained by a decrease in the accessibility of the transition metal particles caused by covering the sample surface with an excess of the alkali metal, which is already incapable of forming adducts with the carbon support. The extreme character of the dependence of the activity of the $K_2[Ru(CO)_4]+RLi$ systems in the ammonia synthesis on the amount of alkyllithium can be due to similar reasons.

As it is known,[28a] aliphatic organolithium compounds can react with molecular hydrogen to form lithium hydride and the corresponding alkane. The thermal decom-

Table 3. Effect of additives of organolithium compounds on the activity of the catalyst based on $K_2[Ru(CO)_4]$ on MgO in the ammonia synthesis[a]

RLi	Amount of catalyst/g	RLi : Ru /mol mol^{-1}	Concentration of ammonia in gas (vol.%)					Productivity of catalyst /(mL of NH_3) h^{-1} (g of cat.)$^{-1}$				
			250 °C	300 °C	320 °C	350 °C	400 °C	250 °C	300 °C	320 °C	350 °C	400 °C
—	2.85[b]	0	0.03	0.45	—	0.86	0.44	1.1	15.8	—	30.2	15.4
Bu^nLi	2.87	2.0 : 1	0.06	0.40	0.76	0.86	0.42	2.1	13.9	26.5	28.9	14.6
	2.94	3.8 : 1	0.16	1.12	1.30	0.86	0.41	5.4	38.1	44.2	29.3	14.0
	3.06	5.5 : 1	0.14	1.13	1.24	0.84	0.41	4.6	36.9	40.5	27.5	13.4
	3.05[c]	7.1 : 1	0.13	1.09	1.21	0.84	0.39	4.3	35.7	39.7	27.5	12.8
Bu^tLi	2.96	3.8 : 1	0.12	0.85	1.04	0.81	0.43	4.1	28.7	35.1	27.4	14.5
	3.02	6.8 : 1	0.09	1.09	1.21	0.84	0.40	3.0	36.1	40.1	27.8	13.3
	3.08	10.2 : 1	0.01	0.39	0.62	0.71	0.40	0.3	12.7	20.1	23.1	13.0
	3.14[d]	3.8 : 1	—	0.37	—	0.78	0.39	—	11.8	—	24.8	12.4

[a] The content of Ru in the samples was 2.24 mmol, Ru/support = 9 wt.%, the weight of the catalysts was determined after their testing in the ammonia synthesis at 250—400 °C.

[b] Supported $K_2[Ru(CO)_4]$ was not heated in an H_2 flow at 300 °C.

[c] The catalyst weight is somewhat underestimated because of a small loss of the sample upon its discharging from the reactor.

[d] Magnesium oxide was first impregnated with a solution of Bu^nLi and then heated in an H_2 flow at 300 °C for 5 h, after which $K_2[Ru(CO)_4]$ was supported.

position of alkyllithium compounds can also yield LiH.[28b] Based on these data, we assume that the true electron promoter in the $K_2[Ru(CO)_4]+Bu^nLi$ and $K_2[Ru(CO)_4]+Bu^tLi$ systems is not the organolithium compound itself but lithium hydride formed from it under the conditions of tests of the catalysts. A somewhat lower activity of the $K_2[Ru(CO)_4]+Bu^tLi$ system in the ammonia synthesis compared to that of the $K_2[Ru(CO)_4]+Bu^nLi$ system is possibly explained by the fact that *tert*-butyllithium is less efficiently adsorbed on the catalytically active sites than *n*-butyllithium because of steric hindrances created by the bulky *tert*-butyl group.

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Received December 7, 2010;
in revised form March 25, 2011