Journal of Molecular Catalysis A: Chemical 165 (2001) 141–147

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

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The effect of Co and Ir on the activity of the $K_2[Fe_2(CO)_8]$- and $K_2[Ru_4(CO)_{13}]$-based systems in ammonia synthesis. The synergistic acceleration of the ammonia synthesis over the $K_2[Fe_2(CO)_8] + K$ catalysts by iridium

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Received 2 February 2000; received in revised form 17 July 2000

Abstract

The effect of Co and Ir on the ammonia synthesis over the $K_2[Fe_2(CO)_8] + K$ and $K_2[Ru_4(CO)_{13}] + K$ catalysts on graphite-like active carbon "Sibunit" has been investigated. The catalysts were prepared by depositing $K_2[Fe_2(CO)_8]$ and $K_2[Ru_4(CO)_{13}]$ onto the "Sibunit" carbon-supported Co and Ir, followed by thermal decomposition of the deposited cluster and treatment of the resulting sample with metallic potassium. The catalysts containing no potassium metal have been studied as well. It has been found that the presence of Co in the Ru catalysts substantially decreases the ammonia synthesis rate. Similar results have been obtained on testing the Ru–Ir samples. By contrast, the introduction of Ir in the $K_2[Fe_2(CO)_8] + K$ catalysts leads to a synergistic acceleration of the process of the ammonia synthesis. The strongest accelerating effect of Ir is observed at 200°C. A rise in the reaction temperature to 250, 300 and then to 350°C results in a gradual weakening of the Fe–Ir synergism. An important feature of the Fe–Ir catalysts found is their increased activity in the ammonia synthesis at 150°C. The presence of Co in the iron catalysts little affects, in general, the ammonia synthesis rate, although some acceleration of this process by Co at 350 and 400°C for the samples not treated with potassium metal can be noted.

Keywords: Ammonia synthesis; Supported catalysts; Anionic iron and ruthenium carbonyl clusters; Cobalt; Iridium; Synergism

1. Introduction

As part of our ongoing research aimed at the development of low-temperature catalysts for the ammonia synthesis (see [1–4]), we have previously described new ruthenium and iron catalysts for this process [1,4]. The catalysts were obtained by depositing $K_2[Ru_4(CO)_{13}]$ and $K_2[Fe_2(CO)_8]$ from THF solution onto active carbons of different types followed by thermal decomposition of the supported cluster in a flow of a N_2–H_2 mixture or H_2 and treatment of the resulting sample with potassium metal. An interesting peculiarity of thus-prepared $K_2[Fe_2(CO)_8] + K$ catalysts is their increased activity in the ammonia synthesis in the low-temperature region. These catalysts are able to accomplish the process of dini-

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PII: S1381-1169(00)00379-4

trogen hydrogenation with a noticeable rate even at 150°C and atmospheric pressure. The analogous $K_2[Ru_4(CO)_{13}] + K$ systems are much less efficient at 150–200°C and 1 atm than the $K_2[Fe_2(CO)_8] + K$ catalysts but considerably exceed them in activity at higher temperatures (250–350°C). It has also been found that when the original graphite-like active carbons "Sibunit" [5] and CFC-1 [6] are used as supports instead of usual commercial active carbons, the $K_2[Ru_4(CO)_{13}]$-supported samples acquire the ability to catalyse the ammonia synthesis (starting from 250°C) even in the absence of a specially introduced metallic potassium [1,3,4]. The similar $K_2[Fe_2(CO)_8]$ catalysts are active in the formation of ammonia only at 400°C.

As is known, one of the general approaches to an increase in the efficiency of a catalytic process is the use of bimetallic catalysts, containing two different transition metals capable of synergistic interaction. Taking this into account, we decided to exploit such an approach for an enhancement in the activity of the above-mentioned $K_2[Ru_4(CO)_{13}]$- and $K_2[Fe_2(CO)_8]$-based catalysts in the ammonia production. In the present paper, data on the influence of Co and Ir on the ammonia synthesis rate over these catalysts are reported. An important result of this study is the discovery of a remarkable synergistic acceleration of the ammonia synthesis over the $K_2[Fe_2(CO)_8] + K$ catalysts by iridium.

2. Results and discussion

For preparation of the catalysts, the above-noted graphite-like active carbon "Sibunit" (99.5% C) was used as a support. A characteristic feature of "Sibunit" carbon, differing it from the majority of usual commercial active carbons is an increased amount of mesopores as well as very low content of mineral admixtures and other impurities. The amount of Ru and Fe loading in the catalysts was 9 and 5 wt.%, respectively; the Co and Ir loadings were varied.

The Ru–Co and Fe–Co catalysts unpromoted with metallic potassium were obtained by impregnation of carbon "Sibunit" with pentane solution of $Co_2(CO)_8$ followed by thermal decomposition of the supported carbonyl in vacuum and subsequent depositing $K_2[Ru_4(CO)_{13}]$ or, correspondingly, $K_2[Fe_2(CO)_8]$ from THF on the resulting Co-containing sample. The Ru–Ir and Fe–Ir catalysts unpromoted with potassium metal were prepared in a similar fashion, using $H_3IrCl_6{\cdot}nH_2O$ as a precursor of active iridium particles. After impregnation of "Sibunit" carbon with an aqueous solution of $H_3IrCl_6{\cdot}nH_2O$, the supported sample was reduced with dihydrogen. Then, the deposition of $K_2[Ru_4(CO)_{13}]$ or $K_2[Fe_2(CO)_8]$ from THF was carried out. For obtaining the potassium metal-promoted Ru–Co, Fe–Co, Ru–Ir and Fe–Ir catalysts, the deposited $K_2[Ru_4(CO)_{13}]$ and $K_2[Fe_2(CO)_8]$ undergone the thermal decomposition in a dihydrogen stream and the resulting samples were treated at 120–130°C with metallic potassium.

The experiments on the ammonia synthesis were performed in a flow-type glass reactor at 250–400°C and 1 atm using a stoichiometric N_2–H_2 mixture (flow rate = 10 l/h). Testing the catalysts was started from 250°C; then the temperature was successively raised to 300, 350 and 400°C. For some catalyst samples, the activity at 150 and 200°C was also measured. The results obtained were compared with those for the corresponding Ru and Fe catalysts not containing Co and Ir. The potassium metal-promoted Ir catalysts not containing Ru and Fe were tested as well. The introduction of metallic potassium in these catalysts was accomplished after reduction of the supported $H_3IrCl_6{\cdot}nH_2O$ with dihydrogen (see above).

2.1. The Ru–Co and Ru–Ir catalysts

In Table 1, the steady ammonia concentrations in the gas flow at 250–400°C for the Ru–Co and Ru–Ir catalysts are presented. The corresponding literature values [4] for the analogous Ru catalysts are also included in the Table for a comparison. The amount of Ru in the Ru, Ru–Co and Ru–Ir samples was 2.23–2.26 mmol. The Ru:Co and Ru:Ir molar ratios were 8.8:1 and 7.3:1, respectively (Co/support = 0.6 wt.%, Ir/support = 2.3 wt.%).

The analysis of the data of Table 1 shows that the presence of Co or Ir in the Ru catalysts leads, as a rule, to a decrease in the ammonia synthesis rate. The strongest reduction in the rate of the synthesis occurs on using the catalysts unpromoted with potassium metal. Here, a considerable lowering in the steady ammonia concentration in the gas on the addition of Co or Ir is observed in the whole studied temperature range,

Table 1
The effect of cobalt and iridium on the activity of the $K_2[Ru_4(CO)_{13}]$-based catalysts on carbon "Sibunit" in ammonia synthesis[a]

Catalyst	Amount of catalyst (g)	K:C (mol/mol)	Steady ammonia concentration (vol.%)			
			250°C	300°C	350°C	400°C
Ru	2.69	0	0.02	0.16	0.67	0.40
	3.16	0.05	0.37	1.01	0.73	0.42
	3.39	0.08	0.38	1.21	0.86	0.44
	3.70	0.11	0.28	1.10	0.86	0.44
Ru–Co	2.76	0	0.01	0.10	0.54	0.44
	3.20	0.05	0.21	0.75	0.70	0.44
	3.41	0.08	0.25	0.92	0.86	0.44
	3.65	0.11	0.19	0.93	0.86	0.44
Ru–Ir	2.79	0	0.01	0.10	0.51	0.42
	3.18	0.05	0.26	0.89	0.72	0.42
	3.40	0.08	0.36	1.16	0.86	0.42
	3.68	0.11	0.30	1.15	0.86	0.42

[a] Ru/support = 9 wt.%. The molar ratios K:C in the catalysts are given without taking into account the amount of potassium incorporated in the starting $K_2[Ru_4(CO)_{13}]$. The weight of the catalysts not containing a specially introduced metallic potassium was determined after their testing in ammonia synthesis at 250–400°C.

excluding 400°C where the process of the ammonia synthesis over all three catalysts practically attains the equilibrium.

On the introduction of metallic potassium in the Ru–Co and Ru–Ir catalysts, their activity in the ammonia synthesis is sharply increased, reaching a maximum at the same potassium to carbon molar ratio (0.08) as in the case of the corresponding Ru system. However, these potassium metal-promoted Ru–Co and Ru–Ir catalysts with the optimal K:C molar ratio are less efficient (at 250–300°C) than the analogous Ru sample as well. The greatest retarding effect is caused here by Co. The additive of Ir reduces the ammonia synthesis rate to a lesser extent. In the case of the catalysts unpromoted with metallic potassium, Co and Ir are close in their inhibiting influence on the process of the ammonia synthesis.

The use of the catalysts with a larger potassium content (K:C = 0.11) decreases the rate of the ammonia formation. At such potassium amount, the Ru–Co catalyst is again less active (at 250–300°C) than the analogous Ru sample, however, the Ru–Ir system shows here slightly higher efficiency. At 350 and 400°C, the Ru–Co and Ru–Ir systems with the K:C molar ratios of 0.08 and 0.11 exhibit practically the same activity as the similar Ru catalysts because the steady ammonia concentrations in the gas flow at these temperatures reach in fact the corresponding equilibrium values.

2.2. The Fe–Co catalysts

The obtained results on the activity of the Fe–Co systems in the ammonia synthesis are given in Table 2, together with the corresponding data for the analogous Fe samples. The catalysts contained 2.23–2.24 mmol of Fe. The Fe:Co molar ratios were 8.7:1 (Co/support = 0.6 wt.%) and 2.2:1 (Co/support = 2.4 wt.%). In the previously studied iron catalysts based on $K_2[Fe_2(CO)_8]$ [4], the Fe content was 3.9–4.0 mmol (Fe/support = 9 wt.%).

The data presented show that in the absence of metallic potassium, the rate of the ammonia synthesis over the Fe–Co catalysts is low even at high temperatures. However, the analogous Fe catalyst is still less efficient under the same conditions. Thus, at 400°C the steady ammonia concentration in the gas on using the Fe–Co system unpromoted with potassium metal (Co/support = 0.6 wt.%) is 3.5 times higher than that in the case of the similar Fe sample. The Fe–Co system exhibits also some activity at 350°C while the Fe catalyst is completely inactive at this temperature. The corresponding Co catalyst does not form ammonia at 350°C as well and its activity at 400°C is negligible ($[NH_3] < 0.01$ vol.%). Thus, the addition of Co to Fe results here in a synergistic acceleration of the process of the ammonia synthesis. Unfortunately, this Fe–Co synergism is manifested to a noticeable extent only

Table 2
The effect of cobalt on the activity of the $K_2[Fe_2(CO)_8]$-based catalysts on carbon "Sibunit" in ammonia synthesis[a]

Catalyst	Amount of catalyst (g)	Co loading (wt.%)	K:C (mol/mol)	Steady ammonia concentration (vol.%)			
				250°C	300°C	350°C	400°C
Fe	2.91[b]	0	0	0	0	0	0.02
	4.17		0.17	0.16	0.29	0.44	0.42
	4.43		0.20	0.17	0.33	0.47	0.38
	4.58		0.23	0.19	0.35	0.47	0.35
Fe–Co	2.77	0.6	0	0	0	0.01	0.07
	3.85		0.14	0.14	0.29	0.42	0.40
	4.16		0.17	0.16	0.30	0.44	0.40
	4.40		0.20	0.17	0.36	0.52	0.42
	4.59		0.23	0.15	0.35	0.48	0.40
Fe–Co	2.79	2.4	0	0	0	0.005	0.04
	4.14		0.17	0.13	0.32	0.46	0.40

[a] Fe/support = 5 wt.%. The molar ratios K:C are given without taking into account the amount of potassium incorporated in the starting $K_2[Fe_2(CO)_8]$. The weight of the catalysts not containing a specially introduced metallic potassium was determined after their testing in ammonia synthesis at 250–400°C.

[b] Fe/support = 9 wt.%, the amount of Fe is 4 mmol [4].

at elevated temperatures (350–400°C). When the Co loading in the Fe–Co catalyst is enhanced to 2.4 wt.%, its accelerating effect on the ammonia synthesis is lowered.

The introduction of metallic potassium in the catalysts leads again to a sharp increase in the ammonia synthesis rate. In the case of the Fe–Co systems (Co/support = 0.6 wt.%), the highest activity is attained at the K:C molar ratio of 0.20. The maximum of the activity of the Fe catalysts is shifted towards greater potassium contents in the sample.

From the comparison of the data of Table 2 it follows that on using the potassium metal-promoted systems, the addition of Co to Fe little affects in general the ammonia synthesis rate. For example, at the K:C molar ratio of 0.17 and Co loading of 0.6 wt.%, there are no essential differences in activity of the Fe–Co and Fe catalysts at 250–400°C at all. An increase in the Co content to 2.4 wt.% somewhat diminishes the synthesis rate at 250°C but slightly enhances it at 300 and 350°C. When the K:C molar ratio is 0.20, the presence of Co in the sample (Co/support = 0.6 wt.%) leads to some increase in the efficiency of the ammonia formation at 300–400°C; however, at 250°C the Co–Fe and Fe catalysts of such composition show the same activity. At the K:C ratio of 0.23, the additive of Co somewhat retards the process of the ammonia synthesis at 250°C but accelerates it a little at 400°C. At 300 and 350°C, the Fe–Co system does not differ practically in its activity from the corresponding Fe catalyst.

2.3. The Fe–Ir catalysts

For studying the effect of Ir on the activity of the $K_2[Fe_2(CO)_8]$-based systems in the ammonia synthesis, the catalysts with the Fe:Ir molar ratios of ca. 7.4:1 (Ir/support = 2.3 wt.%), 3.4:1 (Ir/support = 5.1 wt.%) and 2.4:1 (Ir/support = 7.1 wt.%) were prepared and tested. The amount of Fe in the catalyst samples was again 2.23–2.24 mmol. The activity of the Ir catalysts not containing Fe was measured as well. The results obtained are presented in Table 3.

Unlike the Fe–Co catalysts unpromoted with potassium metal (see above), the analogous Fe–Ir systems are close in their activity in the ammonia synthesis to the corresponding Fe sample. Here also, the process proceeds only at 400°C, the rate of the ammonia formation even under such drastic conditions being very low. Thus, Ir, in contrast to Co, does not accelerate the reaction of the ammonia synthesis over the Fe catalyst in the absence of metallic potassium.

Different behavior is demonstrated by the catalysts promoted with potassium metal. Here, an introduction of Ir in the systems considerably enhances their efficiency in the ammonia synthesis.

Table 3
The effect of iridium on the activity of the $K_2[Fe_2(CO)_8]$-based catalysts on carbon "Sibunit" in ammonia synthesis[a]

Catalyst	Amount of catalyst (g)	Ir loading (wt.%)	K:C (mol/mol)	Ammonia concentration (vol.%)					
				150°C	200°C	250°C	300°C	350°C	400°C
Fe	2.91[b]	0	0	–	–	0	0	0	0.02
	4.17		0.17	–	0.05	0.16	0.30	0.44	0.42
	4.43		0.20	–	–	0.17	0.33	0.47	0.38
	4.58		0.23	–	–	0.19	0.35	0.47	0.35
Fe–Ir	3.87	2.3	0.14	–	0.07	0.21	0.40	0.58	0.39
	4.16		0.17	–	0.10	0.24	0.42	0.59	0.37
	4.37		0.20	–	–	0.22	0.41	0.54	0.39
Ir	3.94	2.3	0.17	–	0	0	0.01	0.01	0.02
Fe–Ir	2.86	5.1	0	–	–	0	0	0	0.01
	4.01		0.14	–	–	0.27	0.49	0.64	0.42
	4.19		0.17	0.02	0.12	0.30	0.55	0.68	0.40
	4.49		0.20	–	–	0.28	0.47	0.59	0.40
Ir	4.01	5.1	0.17	–	0	0	0.01	0.02	0.02
Fe–Ir	2.91	7.1	0	–	–	0	0	0	0.02
	4.03		0.14	–	–	0.34	0.59	0.79	0.43
	4.32		0.17	0.03	0.15	0.36	0.63	0.80	0.43
	4.52		0.20	–	–	0.35	0.60	0.78	0.44
Ir	4.06	7.1	0.17	–	0	0.002	0.02	0.03	0.03

[a] Fe/support = 5 wt.%. The catalyst amounts indicated in the Table relate to testing the samples at 250–400°C. For determination of the activity at 150 and 200°C independent experiments were conducted. The amounts of catalysts in these experiments were approximately the same as those in the corresponding tests at 250–400°C. The molar ratios K:C are given without taking into account the amount of potassium incorporated in the starting $K_2[Fe_2(CO)_8]$. The weight of the catalysts not containing a specially introduced metallic potassium was determined after their testing in ammonia synthesis.

[b] Fe/support = 9 wt.%, the amount of Fe is 4 mmol [4].

The degree of the acceleration of the ammonia synthesis by Ir is dependent on the reaction temperature and the amount of iridium and potassium in the sample. At 250–350°C, the greatest accelerating effect of Ir is manifested at the potassium to carbon molar ratio of 0.17. Such content of potassium promoter in the Fe–Ir catalysts is optimal for these temperatures. At the constant potassium content, the efficiency of the system in the ammonia production increases with an increase in the amount of Ir. As seen from Table 3, when the Ir loading becomes equal to 7.1 wt.%, the steady ammonia concentration in the gas at 250°C over the Fe–Ir catalyst (K:C = 0.17) reaches a value of 0.36 vol.% (8.3 ml NH_3 h^{-1} g^{-1} cat, STP) which is about 2.3 times higher than that over the Fe catalyst under the same conditions. Even stronger acceleration of the ammonia synthesis by Ir is observed at 200°C. Here, the Fe–Ir catalyst (Ir/support = 7.1 wt.%) proves to be three times more effective ($[NH_3]$ = 0.15 vol.%; 3.5 ml NH_3 h^{-1} g^{-1} cat, STP) than the corresponding Fe catalyst. A remarkable feature of the Fe–Ir system with the Ir loading of 7.1 wt.% is its increased activity in the ammonia formation at 150°C ($[NH_3]$ = 0.03 vol.%; 0.7 ml NH_3 h^{-1} g^{-1} cat, STP). When the content of Ir decreases to 5.1 wt.%, the rate of the synthesis at 150°C diminishes. It is important to note that the analogous Ir samples produce no ammonia at all at 150–200°C in the absence of Fe and their activity at 250°C is either equal to zero or negligible. Thus, the addition of Ir to Fe exerts a synergistic effect on the reaction of the ammonia synthesis from dinitrogen and dihydrogen. In its activity in dinitrogen hydrogenation at 150–200°C, the above Fe–Ir catalyst (Ir/support = 7.1 wt.%) is apparently the most efficient among the presently known catalysts for this process.

At 300 and 350°C, the Fe–Ir synergism in the ammonia synthesis is observed as well but the situation is complicated here because of instability of the Fe–Ir systems at these temperatures. Thus, at 300°C the ammonia concentration in the gas over the Fe–Ir catalyst (Ir/support = 7.1 wt.%, K:C = 0.17), after reaching its maximum value of 0.63 vol.% in 35 min, then starts decreasing and in 6 h drops to 0.53 vol.%. Similar decrease in the ammonia content with time (from 0.80 to 0.58 vol.% in 4 h) occurs at 350°C. In Table 3, the maximum values of the ammonia concentration at 300 and 350°C for the Fe–Ir catalysts are presented. It should be noted that at 150–250°C the Fe–Ir systems are much more stable and their activity at these temperatures remains practically unchanged for several hours. The corresponding Fe catalysts are quite stable in the whole studied temperature range (200–400°C).

A rise in the reaction temperature from 250 to 300°C and 350°C leads to further weakening of the Fe–Ir synergism. For example, at 300°C the Fe and Ir samples give in sum 2.1 times lower ammonia concentration in the gas stream than the analogous Fe–Ir catalyst (Ir/support = 7.1 wt.%, K:C = 0.17) at the point of maximum, while at 350°C the overall activity of the Fe and Ir samples is only 1.8 times smaller than the maximum activity of the Fe–Ir system under the same conditions.

The observed decrease in activity of the Fe–Ir catalysts at 300 and 350°C with time can be explained by the fact that at these temperatures the gradual decomposition of the Fe–Ir particles responsible for the Fe–Ir synergism in the ammonia synthesis takes place. The nature of these active particles is now under investigation. As our preliminary studies have shown, the introduction of Rh in the $K_2[Fe_2(CO)_8]$-based systems results also in a synergistic acceleration of the process of the ammonia synthesis. Thus, at 200°C the Fe–Rh catalyst promoted with potassium metal (Fe/support = 5 wt.%, Rh/support = 2.1 wt.%, K:C = 0.17, 2.24 mmol Fe) exhibits 2.5 times higher activity in dinitrogen hydrogenation than the corresponding Fe catalyst under the same conditions. The analogous Rh sample does not catalyse the ammonia synthesis at 200°C in the absence of Fe. As in the case of the Fe–Ir catalysts, a rise in the reaction temperature leads to a weakening of the Fe–Rh synergism. One may assume that the role of Ir and Rh in the Fe–Ir and Fe–Rh systems consists in the acceleration of the step of hydrogenolysis of the intermediate amide (or imide) derivatives which are formed in the $K_2[Fe_2(CO)_8] + K$ catalyst during the ammonia synthesis [1,13,14]. However, special studies are required for the elucidation of this important question.

3. Experimental

All manipulations with $K_2[Fe_2(CO)_8]$, $K_2[Ru_4(CO)_{13}]$ and the corresponding catalysts were carried out in an Ar atmosphere or in vacuum with careful exclusion of air oxygen and moisture. Tetrahydrofuran was purified in the usual manner and freshly distilled from sodium/benzophenone under Ar prior to use. Pentane was dried over molecular sieves and then outgassed. The starting $K_2[Ru_4(CO)_{13}]$ was prepared by the reaction of $Ru_3(CO)_{12}$ with potassium benzophenoneketyl in THF under Ar [7]. The initial $K_2[Fe_2(CO)_8]$ was obtained by the interaction of $Fe(CO)_5$ with potassium graphite (C_8K) in THF under Ar [8,9].

For preparation of the supported Co samples not containing Ru and Fe, the procedure described in detail in Ref. [10] was utilized. The “Sibunit” carbon having a surface area of ca. 440 m^2/g and a pore volume of ca. 0.5 cm^3/g was impregnated with a solution of $Co_2(CO)_8$ (Merck) in pentane. The volume of the impregnating solution was so little as to reach only a minor layer over the support. The resulting slurry was allowed to stand at room temperature for 3 h after which the solvent was removed in vacuum at the same temperature. The obtained sample was then placed into the furnace preheated to 260°C where it was kept for 1 h under conditions of constant outgassing of CO evolved. All the operations on preparing the Co samples were performed in vacuum without being exposed to air. For this purpose, a special all-sealed glass equipment [11] was used.

For obtaining the supported Ir samples not containing Ru and Fe, a weighed amount of “Sibunit” was loaded into a rotated cylindrical reactor and impregnated with an aqueous solution of $H_3IrCl_6 \cdot nH_2O$. The impregnating solution of the appropriate concentration was fed into a nozzle and sprayed into the reactor. The volume of the impregnating solution, V, was calculated as $V = 0.9V_{\mathrm{liq}}m$, where V_{liq} is the total pore volume (cm^3/g) of “Sibunit” carbon (obtained from the data on water adsorption) and *m* is the mass of carbon (g). The sample was unloaded and dried in air at 117°C. The reduction stage was conducted in a glass tube reactor with fixed-bed catalyst. The sample was charged into the reactor, after which argon was passed through the catalyst at room temperature for about 15 min. Dihydrogen was then substituted for argon and the sample was reduced in a flow of H_2 (80 ml/min) during 2 h at the temperature elevated to 400°C, followed by keeping the sample at this temperature in a dihydrogen stream for another 2 h. Then the temperature was brought down to 120°C and argon was substituted for dihydrogen. The sample was cooled to room temperature and unloaded in the stream of Ar.

The deposition of $K_2[Ru_4(CO)_{13}]$ and $K_2[Fe_2(CO)_8]$ from THF onto the supported Co and Ir samples was carried out as described in [4]. Before depositing, the Ir samples were additionally heated at 160°C in flowing dihydrogen (7.5 l/h) for 90–100 min. The thermal decomposition of the supported $K_2[Ru_4(CO)_{13}]$ and $K_2[Fe_2(CO)_8]$ was conducted in a dihydrogen stream (7.5 l/h) for 6 h at 300 and 200°C, respectively.

An introduction of metallic potassium in the samples was carried out according to the procedure developed in [4]. The ammonia concentration in the gas flow was determined by the method described in [12].

For other details concerning the preparation of the catalysts and conditions of the ammonia synthesis experiments, see Section 2.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (the Project code 99-03-32396).

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