New ammonia synthesis catalysts based on supported potassium carbonyl ruthenates as precursors of catalytically active ruthenium particles and potassium promoter

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Abstract

New supported "single-component" ruthenium catalysts for ammonia synthesis are reported. For preparation of the catalysts, various potassium carbonyl ruthenates such as $K_2[Ru_6(CO)_{18}]$ (K:Ru = 1:3), $K_4[Ru_4(CO)_{12}]$ (K:Ru = 1:1), $K_6[Ru_6(CO)_{16}]$ (K:Ru = 1:1), $K_6[Ru_4(CO)_{11}]$ (K:Ru = 1.5:1) and $K_2[Ru(CO)_4]$ (K:Ru = 2:1) were used as precursors of both catalytically active ruthenium particles and potassium promoter while graphite-like carbon "Sibunit" was utilized as a support. The studied catalysts have been compared in their activity with the previously described $K_2[Ru_4(CO)_{13}]$-based catalyst (K:Ru = 1:2) on "Sibunit". It has been established that the rate of the ammonia synthesis at 300 °C over these catalysts increases with the increase in the K:Ru ratio in the starting carbonyl metallate, reaching a maximum in the case of the $K_6[Ru_4(CO)_{11}]$-based sample. On further enhancement in the K:Ru ratio, i.e. when the $K_2[Ru(CO)_4]$ catalyst is used, the rate of the ammonia formation noticeably diminishes. The activity of the $K_2[Ru(CO)_4]$-based catalyst in the ammonia synthesis can be considerably augmented on the replacement of "Sibunit" by catalytic filamentous carbon CFC-III or MgO. The use of γ-Al_2O_3 or carbon-coated γ-Al_2O_3 as supports decreases the reaction rate. An introduction of metallic potassium into the $K_2[Ru(CO)_4]$ catalysts on "Sibunit" and CFC-III accelerates strongly the process of the ammonia synthesis. The highest activity is exhibited by the $K_2[Ru(CO)_4]$ + K system on "Sibunit" at the metallic potassium to carbon molar ratio of 0.08. On using this catalyst (3.55 g), the steady ammonia concentration in the gas flow at 300 °C and 1 atm amounts to 71.1% of the equilibrium value while at 350 and 400 °C the process of the ammonia synthesis fully reaches the equilibrium. In its efficiency in the ammonia production at 250–300 °C, the $K_2[Ru(CO)_4]$ + K catalyst on "Sibunit" carbon significantly exceeds the previously developed $K_2[Ru_4(CO)_{13}]$ + K catalyst on the same support.
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Keywords: Ammonia synthesis; Supported catalysts; Ruthenium; Potassium carbonyl metallates; Metallic potassium

1. Introduction

During the past decades, there has been a considerable progress in a field of low-temperature ammonia synthesis from dinitrogen and dihydrogen (see e.g. [1–16] and references cited therein). New types of catalysts precursors, supports and electron promoters for this process have been developed, novel impressive examples of synergistic effects in ammonia synthesis have been described, an important information on the mechanism of the dinitrogen activation and its hydrogenation has been obtained. As a result of these studies, new efficient catalysts exhibiting an increased activity in ammonia synthesis in the low-temperature region have been found.

As part of our ongoing research program on the development of low-temperature catalysts for ammonia synthesis (see review [11] and [12–16]), we have previously reported the first supported catalysts for this process based on potassium derivatives of anionic metal carbonyl clusters ($K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, $K_2[Fe_2(CO)_8]$). A remarkable feature of such clusters is their ability to serve as precursors of both catalytically active metal particles and

potassium promoter. Basing on this approach, we applied the above-mentioned $K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$ and $K_2[Fe_2(CO)_8]$ clusters for creating the first systems on carbon supports capable of catalyzing the dinitrogen hydrogenation in the absence of a specially added electron promoter [13,14]. The highest activity among these supported "single-component" ammonia synthesis catalysts was observed for the $K_2[Ru_4(CO)_{13}]$ samples which turned out to be active in the ammonia synthesis starting from 250 °C (1 atm). Further increase in the ammonia synthesis rate has been achieved on the replacement of carbon supports by highly basic magnesium oxide [13]. It has also been found that particularly effective ammonia synthesis catalysts can be obtained when the $K_2[Ru_4(CO)_{13}]$-, $K_2[Os_3(CO)_{11}]$- and $K_2[Fe_2(CO)_8]$-based systems on carbon supports are treated with metallic potassium as an additional electron promoter [14].

In the present paper, new carbon-supported "single-component" ruthenium catalysts for ammonia synthesis based on various potassium carbonyl ruthenates such as $K_2[Ru_6(CO)_{18}]$, $K_4[Ru_4(CO)_{12}]$, $K_6[Ru_6(CO)_{16}]$, $K_6[Ru_4(CO)_{11}]$ and $K_2[Ru(CO)_4]$ are reported. The results obtained demonstrate a strong effect of the K:Ru ratio in the starting carbonyl ruthenate on the ammonia synthesis rate. It has been shown that the most efficient catalysts, derived from $K_6[Ru_4(CO)_{11}]$ and $K_2[Ru(CO)_4]$, exceed considerably in their activity at 300 °C and atmospheric pressure the aforementioned $K_2[Ru_4(CO)_{13}]$-based catalyst. The potassium metal-promoted $K_2[Ru(CO)_4]$ catalysts are also significantly more active than the corresponding $K_2[Ru_4(CO)_{13}] + K$ systems. The influence of the nature of a support on the rate of the ammonia synthesis over the $K_2[Ru(CO)_4]$ catalyst has also been described.

2. Experimental

All manipulations with potassium carbonyl ruthenates and the corresponding catalysts were carried out in an Ar atmosphere or in vacuum with careful exclusion of air oxygen and moisture. Tetrahydrofuran (THF) was purified in the usual manner and freshly distilled from sodium/benzophenone under Ar prior to use. The starting $K_2[Ru_6(CO)_{18}]$, $K_4[Ru_4(CO)_{12}]$ and $K_6[Ru_4(CO)_{11}]$ were prepared by the reactions of $Ru_3(CO)_{12}$ with potassium benzophenoneketyl in THF [17,18], the starting $K_6[Ru_6(CO)_{16}]$ was synthesized by the interaction of potassium benzophenoneketyl with $K_2[Ru_6(CO)_{18}]$ in THF [18], the starting $K_2[Ru(CO)_4]$ was obtained by the reaction of $Ru_3(CO)_{12}$ with potassium in liquid ammonia [19].

The supported Ru catalysts containing no metallic potassium were prepared by the impregnation of a support with a solution of the corresponding potassium carbonyl ruthenate in THF ($K_2[Ru_6(CO)_{18}]$) or dry methanol ($K_4[Ru_4(CO)_{12}]$, $K_6[Ru_6(CO)_{16}]$, $K_6[Ru_4(CO)_{11}]$, $K_2[Ru(CO)_4]$) followed by removal of a solvent at 20 °C in vacuum. Graphite-like

carbon "Sibunit" [20] (99.5% of C, BET surface area is ca. 440 m²/g), catalytic filamentous carbons CFC-I [21,22] (99.0% of C, 96 m²/g) and CFC-III [21,22] (99.5% of C, 315 m²/g) as well as MgO (220 m²/g), γ-Al$_2$O$_3$ (200 m²/g) and carbon-coated γ-Al$_2$O$_3$ (26% of C, 133 m²/g) were used as supports. Before impregnation, "Sibunit", CFC-I and CFC-III were dried at 130 °C in vacuum for 6 h, MgO was dried at 200 °C in vacuum for 2 h, γ-Al$_2$O$_3$ and carbon-coated γ-Al$_2$O$_3$ were heated at 400 °C in a dihydrogen stream for 10 h followed by evacuating at 300 °C for 1 h. The impregnation of "Sibunit", CFC-I, CFC-III and MgO with a solution of $K_2[Ru(CO)_4]$ was conducted also, using liquid ammonia as a solvent instead of dry methanol. In this case, the supported samples were heated for 0.5 h at 250 °C in a dihydrogen flow before their testing in ammonia synthesis. The replacement of methanol by liquid ammonia did not change essentially the activity of the $K_2[Ru(CO)_4]$ catalysts in ammonia synthesis.

For obtaining potassium metal-promoted Ru catalysts, the carbon-supported $K_2[Ru(CO)_4]$ underwent the thermal decomposition in a stream of H_2 (7.5 l/h) at 300 °C for 6 h to remove carbon monoxide ligands. Then, the resulting samples were treated at 120–130 °C with metallic potassium according to the procedure described in [14]. The reaction with potassium afforded dark brown (sometimes nearly black) strongly pyrophoric samples which were tested in ammonia synthesis.

Catalytic tests were carried out in a flow-type glass reactor at 250–400 °C and atmospheric pressure with the use of a stoichiometric N_2–H_2 mixture (flow rate = 10 l/h). The catalysts were tested at first at 250 °C; then the temperature was successively raised to 300, 350 and 400 °C. The measure of the activity of the catalysts was the ammonia content in the outlet gas and the rate of the ammonia formation (ml NH$_3$ h^{-1} g^{-1} cat., STP) in the steady state.

The ammonia concentrations in the gas flow were determined by measuring the time which is necessary to neutralize a definite amount of an aqueous HCl (or H_2SO_4) solution of a known concentration with ammonia at constant flow rate, temperature and pressure. From the results of these measurements, the contents of ammonia in the gas were calculated. The presence of ammonia in the analyzed solutions was controlled by the reaction with the Nessler reagent. The repeated analyses of these solutions by the Kjeldal method gave the same NH$_3$ contents. The values of steady ammonia concentrations were averaged over six to eight measurements and rounded to two decimal figures. The standard deviations from the average values were within 0.002–0.008 vol.%.

3. Results and discussion

In Table 1, the steady ammonia concentrations in the gas flow and the ammonia synthesis rates at 250–400 °C for the $K_2[Ru_6(CO)_{18}]$, $K_4[Ru_4(CO)_{12}]$, $K_6[Ru_6(CO)_{16}]$,

Table 1

Steady ammonia concentrations in the gas flow (vol.%) and ammonia synthesis rates (ml NH_3 h^{-1} g^{-1} cat., STP) over the catalysts based on different potassium carbonyl ruthenates on "Sibunit" carbon

Carbonyl ruthenate	Amount of catalyst (g)	Ammonia concentration				Ammonia synthesis rate			
		250 °C	300 °C	350 °C	400 °C	250 °C	300 °C	350 °C	400 °C
$K_2[Ru_6(CO)_{18}]$	2.70	<0.01	0.03	0.21	0.39	<0.4	1.1	7.8	14.4
$K_2[Ru_4(CO)_{13}]$	2.69	0.02	0.16	0.67	0.40	0.7	5.9	24.9	14.9
$K_4[Ru_4(CO)_{12}]$	2.80	0.02	0.22	0.75	0.41	0.7	7.9	26.8	14.6
$K_6[Ru_6(CO)_{16}]$	2.72	0.02	0.22	0.75	0.41	0.7	8.1	27.6	15.1
$K_6[Ru_4(CO)_{11}]$	2.92	0.04	0.43	0.86	0.44	1.4	14.7	29.5	15.1
$K_2[Ru(CO)_4]$	2.69	0.03	0.36	0.81	0.41	1.1	13.4	30.1	15.2

The ruthenium content in the catalysts ∼2.22–2.24 mmol; Ru/carbon = 9 wt.%; the weight of the catalysts was determined after their testing in ammonia synthesis at 250–400 °C.

$K_6[Ru_4(CO)_{11}]$ and $K_2[Ru(CO)_4]$ catalysts on carbon "Sibunit" are presented. The corresponding literature values [13,14] for the analogous $K_2[Ru_4(CO)_{13}]$ catalyst on the same support are also included in the table for a comparison. All the samples contained 2.23–2.24 mmol of Ru. The Ru/carbon ratio was 9 wt.%.

The results obtained show that the rate of the ammonia synthesis over these catalysts is strongly dependent on the nature of the supported potassium carbonyl ruthenate. In the series of the $K_2[Ru_6(CO)_{18}]$ (K:Ru = 1:3), $K_2[Ru_4(CO)_{13}]$ (K:Ru = 1:2), $K_4[Ru_4(CO)_{12}]$ (K:Ru = 1:1), $K_6[Ru_6(CO)_{16}]$ (K:Ru = 1:1) and $K_6[Ru_4(CO)_{11}]$ (K:Ru = 1.5:1) catalysts, the reaction rate increases with an increase in the K:Ru ratio in the starting ruthenium compound, reaching a maximum in the case of the $K_6[Ru_4(CO)_{11}]$-based sample. This result demonstrates an important role of an increased electron density on Ru atoms for the effective dinitrogen activation. However, on further increase in the K:Ru ratio, i.e. when the $K_2[Ru(CO)_4]$ sample (K:Ru = 1:1) is used, the rate of the process noticeably diminishes, thus indicating the existence of other factors (besides the K:Ru ratio) affecting the ammonia forming capacity of the system.

The highest activity in the dinitrogen hydrogenation is exhibited by the $K_6[Ru_4(CO)_{11}]$- and $K_2[Ru(CO)_4]$-based catalysts. On using the $K_6[Ru_4(CO)_{11}]$ catalyst, the steady ammonia concentration in the gas stream at 300 °C attains a value of 0.43 vol.% which is 2.7 times higher than that

observed over the previously described $K_2[Ru_4(CO)_{13}]$ catalyst under the same conditions. At 350 and 400 °C, the process of the ammonia synthesis over the $K_6[Ru_4(CO)_{11}]$ catalyst fully reaches the equilibrium. The $K_2[Ru(CO)_4]$-based catalyst is about 2.3 times more active at 300 °C than the $K_2[Ru_4(CO)_{13}]$ sample. The $K_4[Ru_4(CO)_{12}]$ and $K_6[Ru_6(CO)_{16}]$ catalysts, being characterized by the same K:Ru ratio (1:1), are close to each other in their activity. On going from the least effective $K_2[Ru_6(CO)_{18}]$ catalyst to the most efficient $K_6[Ru_4(CO)_{11}]$ catalyst, the rate of the ammonia formation at 300 °C increases by more than one order of magnitude.

The effect of the nature of a support on the ammonia synthesis rate has been studied on the example of the more accessible $K_2[Ru(CO)_4]$ catalyst. As supports, use was made of the CFC-I and CFC-III carbons [21,22] as well as MgO, γ-Al_2O_3 and carbon-coated γ-Al_2O_3. In all the samples, the Ru/support ratio was 9 wt.%.

As seen from Table 2, the replacement of "Sibunit" carbon in the $K_2[Ru(CO)_4]$-based catalyst by CFC-III and MgO leads to a considerable increase in the rate of the ammonia formation. Particularly active is the catalyst on CFC-III which gives 1.5 times greater ammonia concentration in the gas flow at 300 °C (0.53 vol.%) than the analogous sample on "Sibunit". Interestingly, highly basic magnesium oxide, affording as a rule significantly more efficient Ru catalysts for ammonia synthesis than those on carbon supports (see e.g. [13,23]), yields here noticeably less active catalysts at

Table 2

Steady ammonia concentrations in the gas flow (vol.%) and ammonia synthesis rates (ml NH_3 h^{-1} g^{-1} cat., STP) over the $K_2[Ru(CO)_4]$-based catalyst on different supports

Support	Amount of catalyst (g)	Ammonia concentration				Ammonia synthesis rate			
		250 °C	300 °C	350 °C	400 °C	250 °C	300 °C	350 °C	400 °C
"Sibunit"	2.69	0.03	0.36	0.81	0.41	1.1	13.4	30.1	15.2
CFC-I	2.93	0.03	0.35	0.68	0.40	1.0	11.9	23.2	13.7
CFC-III	2.92	0.04	0.53	0.84	0.41	1.4	18.2	28.8	14.0
MgO	2.85	0.03	0.45	0.86	0.44	1.1	15.8	30.2	15.4
γ-Al_2O_3/C	2.85	0.01	0.19	0.61	0.44	0.4	6.7	21.4	15.4
γ-Al_2O_3	2.87	0.01	0.11	0.62	0.44	0.3	3.8	21.6	15.3

The ruthenium content in the catalysts ∼2.22–2.24 mmol; Ru/carbon = 9 wt.%; the weight of the catalysts was determined after their testing in ammonia synthesis at 250–400 °C.

Table 3
Steady ammonia concentrations in the gas flow (vol.%) and ammonia synthesis rates (ml NH_3 h^{-1} g^{-1} cat., STP) at different metallic potassium to carbon molar ratios for the $K_2[Ru(CO)_4] + K$ and $K_2[Ru_4(CO)_{13}] + K$ catalysts on active carbons

Carbonyl ruthenate	Carbon support	Amount of catalyst (g)	K:C (mol/mol)	Ammonia concentration				Ammonia synthesis rate			
				250 °C	300 °C	350 °C	400 °C	250 °C	300 °C	350 °C	400 °C
$K_2[Ru(CO)_4]$	"Sibunit"	2.69	0	0.03	0.36	0.81	0.41	1.1	13.4	30.1	15.2
		3.35	0.050	0.40	1.52	0.86	0.44	11.9	45.4	25.7	13.1
		3.55	0.080	0.47	1.55	0.86	0.44	13.2	43.7	24.2	13.4
		3.77	0.104	0.34	1.29	0.86	0.44	9.0	34.2	22.8	11.7
$K_2[Ru_4(CO)_{13}]$	"Sibunit"	2.69	0	0.02	0.16	0.67	0.40	0.7	5.9	24.8	14.9
		3.16	0.052	0.37	1.01	0.73	0.42	11.7	32.0	23.1	13.3
		3.31	0.064	0.41	1.10	0.81	0.44	12.4	33.2	24.5	13.3
		3.39	0.080	0.38	1.21	0.86	0.44	11.2	35.7	25.4	13.0
		3.70	0.106	0.28	1.10	0.86	0.44	7.6	29.7	23.2	11.9
$K_2[Ru(CO)_4]$	CFC-III	2.92	0	0.04	0.53	0.83	0.41	1.4	18.2	28.4	14.0
		3.54	0.080	0.35	1.44	0.86	0.41	9.9	40.7	24.3	11.6

The ruthenium content in the catalysts ~2.22–2.24 mmol; Ru/carbon = 9 wt.%.

250 and 300 °C than that on CFC-III carbon. The use of γ-Al_2O_3 and carbon-coated γ-Al_2O_3 as supports instead of "Sibunit" decreases the reaction rate.

Data on the effect of potassium metal upon the activity of the $K_2[Ru(CO)_4]$-based catalysts on carbons "Sibunit" and CFC-III in the ammonia synthesis are given in Table 3, together with the corresponding literature data for the analogous $K_2[Ru_4(CO)_{13}] + K$ systems on "Sibunit" carbon [14]. The amount of Ru in the samples was 2.23–2.24 mmol, the Ru/carbon ratio was again 9 wt.%. A decrease in this ratio to 6 wt.% lowered the synthesis rate. The activity of the catalysts fell down as well when the temperature of preheating of the supported $K_2[Ru(CO)_4]$ in a dihydrogen stream (see Section 2) was decreased from 300 to 250 °C.

The data of Table 3 show that the introduction of potassium metal in the catalysts increases sharply their efficiency in the ammonia formation. In the case of the $K_2[Ru(CO)_4] + K$ catalyst on carbon "Sibunit", the maximum of the activity is observed at the metallic potassium to carbon molar ratio of 0.08. Both an increase and a decrease in this ratio diminish the reaction rate. On using the optimal K:C ratio, the steady ammonia concentration in the gas at 300 °C over the $K_2[Ru(CO)_4] + K$ catalyst on "Sibunit" reaches 1.55 vol.% which corresponds to 71% of an equilibrium value. Under the same conditions, the $K_2[Ru_4(CO)_{13}] + K$ catalyst gives at 300 °C ca. 1.3 times lower ammonia concentration in the gas (1.21 vol.%), and at 250 °C it is also noticeably less efficient than the $K_2[Ru(CO)_4] + K$ system. At 350 and 400 °C, the reaction of the ammonia synthesis over the $K_2[Ru(CO)_4] + K$ catalyst totally attains the equilibrium. The $K_2[Ru(CO)_4] + K$ system on CFC-III carbon is somewhat less effective at 250 and 300 °C than the analogous sample on "Sibunit" but noticeably exceeds in its activity at 300 °C the above $K_2[Ru_4(CO)_{13}] + K$ catalyst on "Sibunit" carbon. In the absence of ruthenium, the above carbon supports treated with metallic potassium exhibit only negligible activity or are totally inactive in the ammonia formation at 250–400 °C.

Thus, the results of this study demonstrate that it is possible to enhance strongly the ammonia synthesis rate changing the K:Ru ratio in the supported potassium carbonyl ruthenate. An additional increase in the efficiency of the process can be achieved by changing the nature of a support and, especially, by introducing potassium metal into the system. At present, we are studying the nature of particles responsible for the activity of the catalysts found in the ammonia synthesis.

Acknowledgements

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