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Anionic ruthenium cluster $K_2[Ru_4(CO)_{13}]$ as precursor of catalytically active ruthenium particles and potassium promoter. New efficient ammonia synthesis catalysts based on supported $K_2[Ru_4(CO)_{13}]$

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Abstract

New efficient potassium-promoted catalysts for ammonia synthesis are reported. For preparation of the catalysts, anionic ruthenium cluster $K_2[Ru_4(CO)_{13}]$ was used as a precursor of both catalytically active metal particles and potassium promoter while magnesium oxide and new original graphite-like active carbon CFC-1 were employed as supports. The catalysts found are capable of catalysing the ammonia synthesis starting from 250°C (1 atm) and exceed markedly in their activity at 300–400°C and atmospheric pressure the industrial ammonia synthesis catalyst (SA-1). Especially effective is the $K_2[Ru_4(CO)_{13}]$ catalyst on MgO. The replacement of MgO by γ-Al_2O_3 and SiO_2 results in a sharp decrease in activity of the catalyst in ammonia synthesis. This indicates the importance of the basic properties of a support for the achievement of high ammonia synthesis rates.

Keywords: Ammonia synthesis; Supported catalysts; Anionic ruthenium carbonyl clusters

As part of our continuing studies [1–9] on the development of catalysts for low-temperature ammonia synthesis we have previously described [6] the first catalysts on carbon support exhibiting activity in ammonia synthesis in the absence of a specially added electron promoter. For preparation of the catalysts, potassium derivatives of anionic metal carbonyl clusters of ruthenium, osmium and iron ($K_2[Ru_4(CO)_{13}]$, $K_2[Os_3(CO)_{11}]$, $K_2[Fe_2(CO)_8]$) on the original graphite-like active carbon 'Sibunit' [10] were used as precursors of catalytically active particles. The highest activity was observed for the $K_2[Ru_4(CO)_{13}]$ catalyst which turned out to be active in ammonia synthesis starting from 250°C (1 atm). It has been concluded that the role of electron promoter in these catalysts is played by potassium originated from the initial anionic cluster. Interestingly, the replacement of 'Sibunit' carbon by usual commercial active carbons resulted in a sharp decrease in activity and stability of the catalysts.

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Taking this fact into account we decided to study in more detail the effect of the nature of a support on the activity of the $K_2[Ru_4(CO)_{13}]$ catalyst in ammonia synthesis. As a result of these studies, considerably more efficient ammonia synthesis catalysts based on $K_2[Ru_4(CO)_{13}]$ have been found.

The catalysts were prepared by impregnation of the corresponding support with THF solution of $K_2[Ru_4(CO)_{13}]$ [11] followed by removal of THF at 20°C in vacuum. The amount of Ru loading was 9 wt%. Magnesium oxide (135 m^2 g^{-1}), γ-alumina (177 m^2 g^{-1}), silica (286 m^2 g^{-1}) as well as novel original graphite-like active carbon CFC-1 (100–120 m^2 g^{-1}) [12] were tested as supports. A characteristic feature of CFC-1 carbon differing it from 'Sibunit' is considerably higher ratio of edge surface area to basal plane surface area (75:25 for CFC-1, 25:75 for 'Sibunit'). Both types of the carbons are characterized by an increased amount of mesopores as well as very low content of sulphur, mineral admixtures and other impurities. Before impregnation, CFC-1 carbon was dried at 130°C in vacuum for 6–8 h, MgO was dried at 200°C in vacuum for 2 h, γ-Al_3O_3 and SiO_2 were heated at 400°C in a dihydrogen stream for 11 h. Experiments on ammonia synthesis were carried out in a flow-type glass reactor at 250–400°C and atmospheric pressure with use of stoichiometric N_2–H_2 mixture (flow rate = 10 l h^{-1}). The ammonia content in the gas was determined by the method described in Ref. [1]. All manipulations with $K_2[Ru_4(CO)_{13}]$ and the corresponding catalysts were conducted under Ar or in vacuum with careful exclusion of air oxygen and moisture.

The results of the experiments are presented in Table 1. The catalysts were tested at first at 250°C, then the temperature was successively raised to 300, 350 and 400°C. As seen from the Table 1, all the samples obtained like the $K_2[Ru_4(CO)_{13}]$ on 'Sibunit' carbon are able to catalyse ammonia synthesis in the absence of a specially added promoter but they differ strongly from each other in their activity. The highest ammonia synthesis rates are observed in the case of the $K_2[Ru_4(CO)_{13}]$ catalysts on magnesium oxide and carbon CFC-1. These catalysts are considerably more active than the analogous catalyst on 'Sibunit' carbon. Especially active is the $K_2[Ru_4(CO)_{13}]$ catalyst on MgO. On using this catalyst (2.7 g) the steady ammonia concentration in the gas flow at 300°C and 1 atm amounts to ~23% of an equilibrium value while at 350 and 400°C the process of ammonia synthesis fully reaches the equilibrium. Both the $K_2[Ru_4(CO)_{13}]$ catalysts (on MgO and CFC-1) exceed markedly in their activity at 300–400°C and atmospheric pressure the industrial ammonia synthesis catalyst (SA-1). Thus, at 300°C and space velocity of 2500 h^{-1}, the ruthenium sample on MgO gives ~3.4-times higher ammonia concentration in the gas (0.76 vol% or ~35% of an equilibrium value) than the industrial catalyst (0.22 vol%) under the same condi-

Table 1
Steady ammonia concentrations in the gas flow (vol%) and ammonia synthesis rates (ml NH_3 h^{-1} g^{-1} cat., STP) for the $K_2[Ru_4(CO)_{13}]$ catalysts on carbon and oxide supports[a]

Support	Amount of catalyst (g)	Ammonia concentration				Ammonia synthesis rate			
		250°	300°	350°	400°	250°	300°	350°	400°
Sibunit	2.69	0.02	0.16	0.67	0.40	0.7	5.9	24.9	14.9
CFC-1	2.75	0.03	0.33	0.70	0.38	1.1	12.0	25.5	13.8
MgO	2.70	0.03	0.50	0.86	0.44	1.1	18.5	31.9	16.3
γ-Al_2O_3	2.73	0	0.02	0.09	0.39	0	0.7	3.3	14.3
SiO_2	2.70	0	0.02	0.13	0.33	0	0.7	4.8	12.2

[a]The ruthenium content in the catalysts ~2.2–2.3 mg-at; the weight of the catalysts was determined after their testing in ammonia synthesis at 250–400°C.

Table 2
Comparison of the activities of the $K_2[Ru_4(CO)_{13}]$ catalyst on MgO and industrial ammonia synthesis catalyst SA-1 ($W = 2500$ h^{-1})

Catalyst	Ammonia concentration (vol%)			
	250°	300°	350°	400°
$K_2[Ru_4(CO)_{13}]$/MgO	0.06	0.76	0.86	0.44
SA-1	0.08	0.22	0.33	0.31

tions (Table 2). Data for $K_2[Ru_4(CO)_{13}]$/MgO catalyst presented in Table 1 correspond to space velocity value of 4630 h^{-1}.

The replacement of MgO as support by γ-Al_2O_3 and SiO_2 results in a sharp decrease in activity of the $K_2[Ru_4(CO)_{13}]$ catalyst in ammonia synthesis (Table 1). This may indicate the importance of the basic properties of a support for the achievement of high ammonia synthesis rates. Similar conclusion has been made by Aika et al. [13] on studying the ammonia synthesis catalysts based on neutral ruthenium cluster $Ru_3(CO)_{12}$ as the catalyst precursor. One may suggest that on passing from γ-Al_2O_3 and SiO_2 to highly basic MgO, a significant enhancement in the electron density on ruthenium atoms occurs which favours the effective dinitrogen activation and, as a consequence, the efficient work of the catalyst in ammonia synthesis. In all probability, this accelerating effect of magnesium oxide is analogous in its nature to that of potassium promoter generated from the initial anionic cluster $K_2[Ru_4(CO)_{13}]$. In both cases, the electron donation (from magnesium oxide and potassium promoter, respectively) to the active ruthenium particles is apparently the reason of an increase in the ammonia synthesis rate.

Thus, the use of $K_2[Ru_4(CO)_{13}]$ in combination with a suitable support enables to design catalysts exhibiting considerable activity in ammonia synthesis even in the absence of a specially introduced electron promoter. This result allows to consider the anionic clusters of similar type as very promising precursors for the development of catalysts for low-temperature ammonia synthesis.

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