An alkali-promoted ruthenium catalyst for the synthesis of ammonia, supported on thermally modified active carbon

Zbigniew Kowalczyk, Jan Sentek and Sławomir Jodzis
Department of Chemistry, Warsaw University of Technology, Koszykowa 75, 00-664 Warsaw, Poland

Elżbieta Mizera
Institute of Physics, Polish Academy of Sciences, Al. Lotników 32/46, 02-668 Warsaw, Poland

Jacek Góralski and Tadeusz Paryjczak
Institute of General and Ecological Chemistry, Technical University of Łódź, Żwirki 36, 90-924 Łódź, Poland

Ryszard Diduszko
Institute of Vacuum Technology, Długa 44/50, 00-241 Warsaw, Poland

Received 9 August 1996; accepted 15 January 1997

Ruthenium catalysts deposited on active carbon and pre-calcined at 1900°C in He atmosphere were studied. The precursors of the active phase were $RuCl_3{\cdot}0.5H_2O$ and $Ru_3(CO)_{12}$. Potassium and cesium (hydroxides or nitrates) were used as promoters. The catalysts were characterized by TEM, WAXS and H_2 chemisorption. Activity measurements in NH_3 synthesis were performed in a flow integral reactor under a pressure of 10 MPa at 470, 430, and 400°C ($H_2 : N_2 = 3 : 1$). It has been found that the alkali-promoted catalyst deposited on the thermally modified carbon is much more active than that based on untreated carbon. The form of the Ru precursor used in the manufacture of the K-promoted catalyst had no effect on its dispersion or activity. The promoting effect of potassium was comparable to that of cesium. A monotonous increase in the activity of alkali-promoted catalyst vs. Ru content (5–15%) was observed, accompanied by a decrease in dispersion.

Keywords: ammonia synthesis, ruthenium catalyst, carbon support, alkali promoters

1. Introduction

It is believed that ruthenium catalysts will form a new generation of catalysts for the synthesis of ammonia. Various supports, such as alumina [1–8], carbon-coated alumina [9,10], magnesia [1–3,11–14], and even zeolites [15,16] were used in the studies of ruthenium catalysts. It seems, however, that the use of ruthenium–carbon systems, promoted additionally with alkali metal oxides or with oxides of alkaline earth metals, is the most promising [17–19]. Such a catalyst, based on thermally modified active carbon, was successfully commercialized by BP, the Kellog and Engelhard group (Kellog advanced ammonia process [20,21]). Unfortunately, no detailed scientific data are available so far.

For this reason, an attempt was made to study in detail the catalytic properties of ruthenium catalysts supported on active carbon pre-treated thermally at 1900°C in helium. The kinetic characteristics of such a catalyst (9.1% Ru, and KOH as a promoter) in the reaction of NH_3 synthesis at low and high pressures were presented in a previous paper [22] and compared with the kinetic characteristics of a fused, triply promoted iron catalyst. The aim of the present work was to study the effect of various Ru precursors ($RuCl_3{\cdot}0.5H_2O$, $Ru_3(CO)_{12}$) and various alkali metal compounds (KOH, KNO_3, CsOH, $CsNO_3$) on the catalytic activity of Ru/C systems. Both the raw active carbon and thermally modified carbon were used as supports. The catalysts were characterized by transmission electron microscopy (TEM), wide angle X-ray scattering (WAXS) and by chemisorption of hydrogen. The activity in NH_3 synthesis was measured in a flow integral reactor operating at high pressure.

2. Experimental

2.1. Preparation of the catalysts

The starting material for the catalyst's support was a commercially available active carbon Norit RO 08, in a rod-shaped form (0.8 mm diameter, 3–5 mm length). A batch of the material was heated for 2 h at 1900°C in an atmosphere of helium at a pressure of 400 Pa [22,23]. The properties of the raw carbon used (symbol NS) and also of the thermally modified carbon (N1900), as characterized by sorption of nitrogen, high-pressure Hg porosimetry, WAXS, and SAXS, were described elsewhere [23]. The essential texture parameters are listed in table 1.

Ruthenium was deposited on the surface of the supports by the impregnation method (incipient wetness technique). Acetone and THF were the solvents for $RuCl_3 \cdot 0.5H_2O$ and $Ru_3(CO)_{12}$, respectively. The impregnated materials were dried in air, then reduced in hydrogen for about 16 h at 350°C. After cooling to room temperature in a hydrogen atmosphere, the Ru/C catalysts were divided into small portions (600 mg), which were then impregnated with solutions of alkali metal compounds (by the incipient wetness technique) and subjected to activity measurements. Various contents of the promoters were obtained by the use of solutions of different concentration.

All the catalysts thus prepared were given unified symbols, to specify the kind of carbon used, e.g. NS; the content of ruthenium (in wt% of Ru in unpromoted Ru/C material), e.g. Ru 9.1; and the molar ratio of the alkali metal to Ru, e.g. K10.

2.2. Characterization of the catalysts

The TEM, WAXS and H_2 chemisorption studies were performed with samples previously tested in the reaction of ammonia synthesis at high pressure.

The TEM studies were performed with a Jeol JEM2000EX instrument, equipped with a double-tilted goniometer and operating at a 200 kV acceleration potential. Specimens for the measurements were prepared in the following way: a small amount of the catalyst sample was ground in an agate morter and dispersed in *n*-butanol. Drops of the suspension were placed on a holey carbon film supported by a Ni-grid. The small catalyst fragments collected on the grid were then examined by TEM methods: microdiffraction, bright-field (BF) and dark-field (DF) diffraction contrast, as well as high-resolution imaging.

Table 1
Textural parameters of the active carbons used [23]

Parameter [a]	Carbon		Measurement technique
	NS	N1900	
W_m (cm^3/g)	0.33	0.036	N_2 sorption
S_m (m^2/g)	890	62	
L_m (nm)	0.74	1.16	
V_m (cm^3/g)	0.73	0.61	mercury porosimetry
ρ_s (g/cm^3)	1.25	1.36	
S_p (m^2/g)	95	60	

[a] W_m, S_m and L_m denote volume, surface area and mean size of the micropores, respectively; V_m, ρ_s and S_p denote pore volume (macro- and mezopores), skeletal density and internal surface area (macro- and mezopores), respectively.

The WAXS measurements were carried out in the 2θ angle range of 30–145° using a Siemens diffractometer (type D500) equipped with a semiconductor detector Si[Li]. A chromium anode ($\lambda = 0.229$ nm) was used. The average size of the ruthenium crystallites was determined from line broadening by the Scherrer method. In this case, precise measurements of the Ru(110) reflection profiles situated near the angle of $2\theta = 116°$ were performed.

The hydrogen chemisorption measurements were carried out in an Ami-1 apparatus (Altamira Instrument) equipped with a six-way valve with a loop of 50 μl and a catharometric detector. The carrier gas was argon of 99.999% purity. The following procedure was applied to obtain a "clean" metal surface. A sample of the catalyst (0.2–0.4 g) was heated in hydrogen (obtained in a Packard hydrogen generator and dried) to 450°C and kept at that temperature for 30 min. After cooling to room temperature in hydrogen, the sample was subjected to temperature-programmed hydrogen desorption by raising the temperature to 450°C in argon (50 ml(STP)/min), maintaining that temperature for 30 min, and then cooling in argon down to room temperature. The ruthenium surface thus obtained was treated as a "clean" surface. The chemisorption of H_2 was measured at room temperature by the standard, flowing pulse method. The stoichiometry of H : Ru = 1 : 1 was assumed to determine the dispersion of ruthenium [24,25].

2.3. Activity measurements

The activity of the catalysts in the ammonia synthesis was measured in an integral flow reactor operating with a stoichiometric mixture of purified H_2 and N_2 at a pressure of 10 MPa [22]. In all the experiments the flow rate of the gas mixture was maintained constant at the level of 63×10^3 ml(STP)/h (105×10^3 ml(STP)/(g_{C+Ru} h)). The corresponding space velocities (SV) were about 45×10^3–55×10^3 1/h depending on the Ru content in the sample (the apparent specific density of the catalyst depends on the Ru content). The concentration of ammonia in the outlet gas, as a measure of the catalyst's activity, was determined interferometrically. Prior to the activity measurement the samples were activated in the synthesis gas at atmospheric pressure according to the standard procedure: heating to 400°C, maintaining at that temperature for 20 h, raising the temperature to 470°C, and maintaining this temperature for about 40 h. Then the synthesis gas was pressed to 10 MPa and the measurements were performed, typically for 24 h. In the case of the NSRu catalysts the effect of activation time on catalytic activity was also studied.

3. Results and discussion

3.1. TEM, WAXS and H_2 chemisorption

Figures 1 and 2 present the results of the TEM studies of the NSRu and N1900Ru unpromoted materials, respectively. First of all, distinct differences in the structure of the two supports used are evident. The raw carbon NS is amorphous (carbon reflections are not visible, figure 1c), whereas the N1900 material has a partly graphitized form (the so-called turbostratic structure), which is evidenced by the presence of C(002) reflections in the electron diffraction pattern (figure 2d). The stacks of a graphite-like structure, randomly oriented in the amorphous matrix of the N1900 carbon are well seen in figures 2a and 2b.

Ruthenium is highly dispersed in both the NSRu and the N1900Ru catalyst as shown in figures 1a, 1b and 2a, 2c. Mainly small particles of about few nanometers in size can be observed. Two such particles are shown in figure 1d. It should be noticed, however, that Ru particles in the latter catalyst (N1900Ru) are less uniform with respect to their size. Apart from small grains, also coarser grains of 10–15 nm, (see figures 2c and 2a – left upper corner) and even 20–30 nm (not presented in figure 2) have been observed in that material.

Figure 3 presents typical WAXS patterns obtained for the Ru catalysts supported on both types of carbon. The differences in the structure of the supports are distinctly seen, in accord with the results of the TEM studies. The C(002) peak in the NS pattern is diffused (trace A – amorphous carbon), whereas the C(002) peak in the N1900 material is sharp (trace B – turbostratic carbon). Furthermore, the Ru(110) lines for the samples based on the amorphous NS carbon were weaker than those for the Ru/N1900 systems, as shown in figure 3. They were too weak to be used for the determination of the average crystallite size from the line broadening.

Table 2 shows the dispersion of ruthenium in some of the catalysts, as determined by XRD and hydrogen chemisorption. The unpromoted Ru/C samples were studied as well as those promoted with KOH or CsOH. It is readily seen that the samples based on the N1900 carbon (those containing 9% Ru) have similar dispersions. The average size of ruthenium crystallites is about 15 nm for unpromoted systems and somewhat less (about 10 nm) for the systems promoted with potassium or cesium. There is a good agreement between the results obtained by the XRD and the H_2 chemisorption methods in this group of catalysts. It should be also noticed that the dispersion of ruthenium in the N1900 material depends strongly on the Ru content (samples promoted with CsOH, table 2): the lower the Ru content the higher the metal concentration.

The results obtained for the catalysts deposited on the raw carbon NS are much less uniform. The lack of distinct Ru(110) lines in the X-ray diffraction patterns indicates that the dispersion of the metal is high, in agreement with the results of TEM studies. On the other hand, the amounts of hydrogen chemisorbed on the sam-

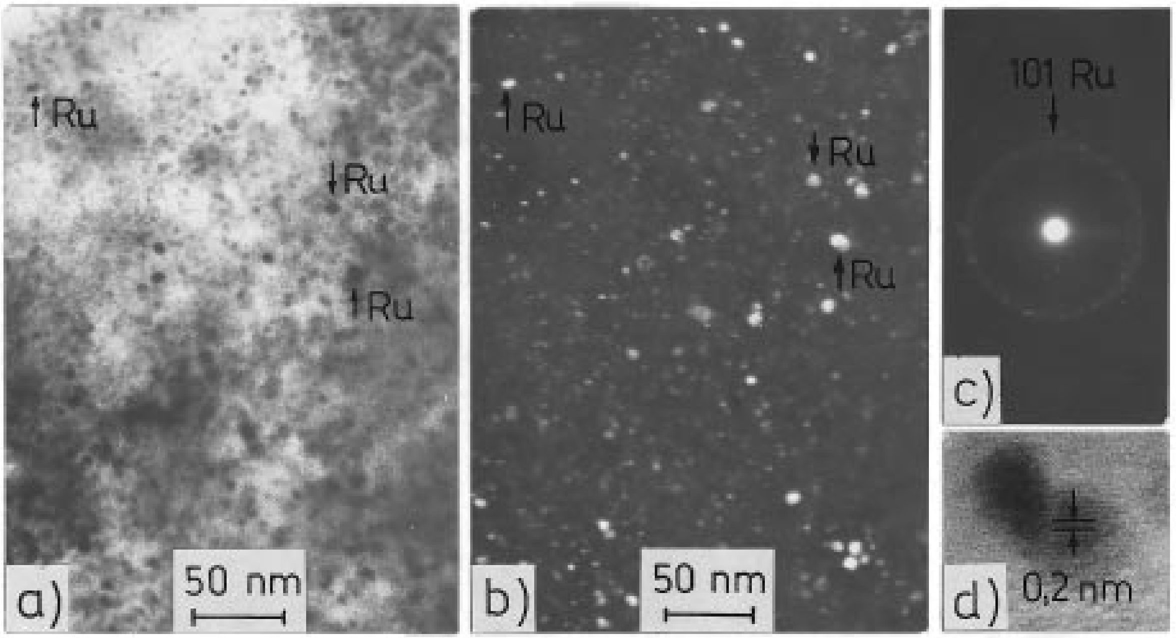

Figure 1. Ruthenium particles in the NSRu4.7 unpromoted catalyst, after 24 h activity test at 10 MPa (standard activation). (a) TEM bright-field (BF) micrograph of the Ru particles and corresponding selected area electron diffraction pattern (c), with visible 101Ru reflections, indicated by an arrow. Carbon reflections are not visible. (b) Dark-field (DF) image with a 101Ru reflection. (d) HRTEM image of (101) lattice plane fringes of a Ru particle of about 2 nm size.

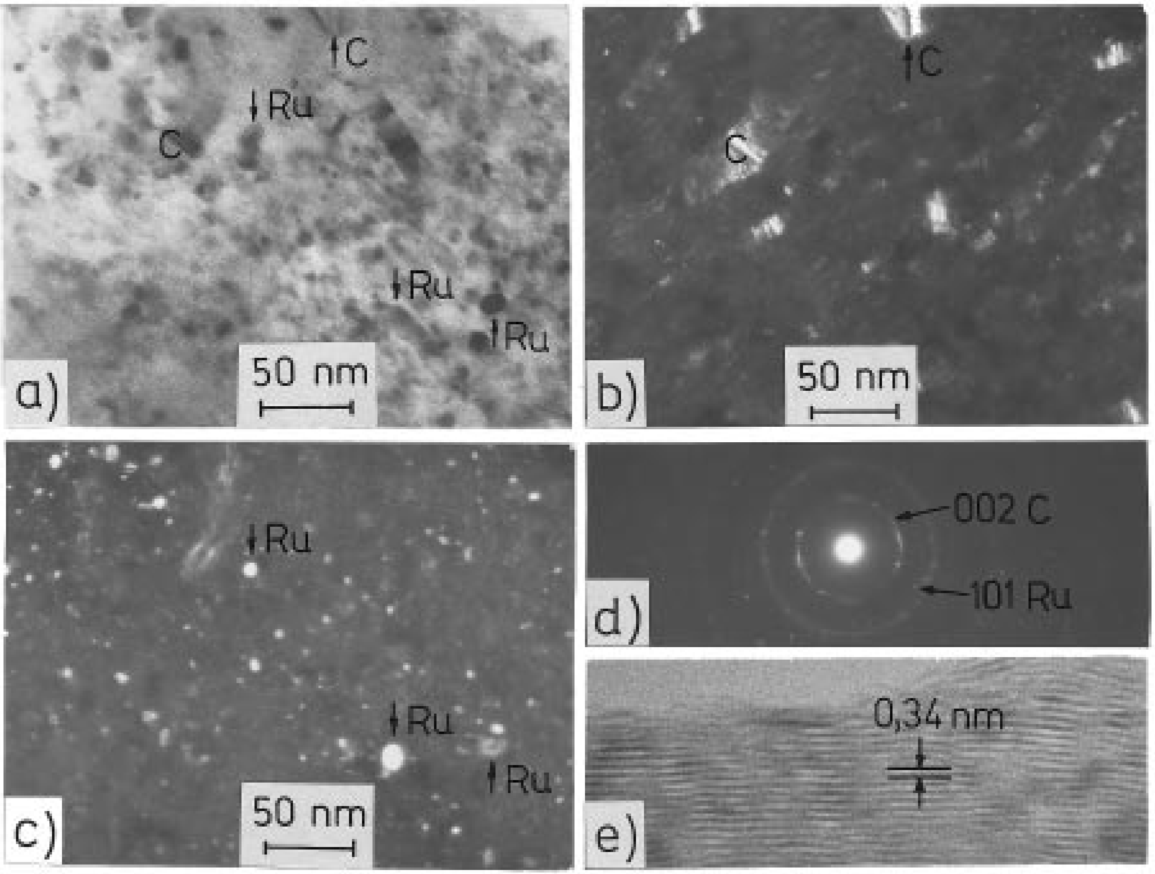

Figure 2. Ruthenium particles in the N1900Ru4.7 unpromoted material after 24 h activity test at 10 MPa (standard activation). (a) TEM bright-field (BF) micrograph of the sample and (d) corresponding selected area diffraction pattern with reflections of carbon and ruthenium. The spots indicated by arrows (d) are 002C and 101Ru. Weak reflections 100 and 002 of Ru are visible. Dark-field images (DF) (b) and (c) are taken with a small aperture in a region of the diffraction pattern corresponding to 002C (d) and 101Ru (d), respectively. Note the existence of graphite-like stacks (b) and ruthenium particles (c) indicated by arrows (dark-field images of graphite stacks (b) and ruthenium (c) are bright, respectively). (e) HRTEM image of (002) lattice plane fringes of the ordered part of carbon (graphite like structure) in the N1900 support.

ples activated according to the standard procedure are small. The corresponding values of D are less than 1% for the unpromoted sample and about 3.6% for the sample promoted with potassium. A long maintenance of the promoted catalyst under the conditions of NH_3 synthesis leads, however, to a substantial increase in the dispersion D to the value of about 40% (sample NSRu4.7K10(d), table 2). We conclude, therefore, that ruthenium deposited on the NS carbon is highly dispersed, but the surface of the material was poisoned for H_2 chemisorption when the samples had been activated according to the standard procedure. Such a poisoning was observed recently by Boehm [26] for rhodium supported on carbon blacks. There was no or very little hydrogen chemisorption, whereas the CO adsorption was high. When graphitized carbon black was used as a support, the H_2 and CO chemisorption agreed with each other. According to Boehm's hypothesis [26] the surface of the metal was poisoned in the first case by carbon–hydrogen surface complexes that were formed on poorly organized carbon surfaces by hydrogen spillover and reverse diffusion to the metal surface. These surface complexes are more strongly bound than hydrogen, but more weakly than CO.

The above interpretation can also be applied to our NSRu catalysts, since the NS carbon was poorly organized, as evidenced by TEM and WAXS. After a long time of activation at 470°C the ruthenium surface became clean, probably due to methanation of the CH_x surface complexes, and, therefore, active for H_2 chemisorption (sample NSRu4.7K10(d)). Further studies are necessary to verify the above hypothesis.

3.2. Results of activity measurements

Table 3 presents the results of kinetic measurements of three catalysts supported on the raw NS carbon. Two of them were promoted with KOH. Because of the low activity of the samples the kinetic tests were performed only at 470°C and, after long activation, also at 430°C. As can be seen (table 3), the unpromoted NSRu material proved to be completely inactive, in agreement with literature data [17]. Also, the activation process of the promoted catalysts was very slow. A stable NH_3

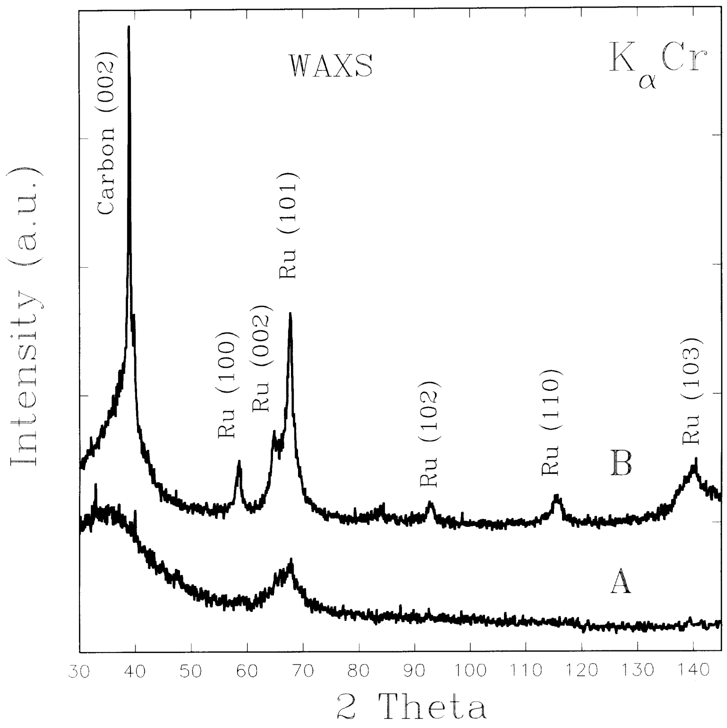

Figure 3. Typical WAXS patterns for ruthenium catalysts after the activity measurements; (A) NSRu4.7; (B) N1900Ru9.1.

concentration in the outlet gas is not attained as after about one week of additional (in excess to the normal procedure) activation of the samples at 470°C. As results from the combination of the kinetic and hydrogen chemisorption data the turnover frequency (TOF) for one of the two promoted samples (NSRu4.7K10(d)) is then equal to about 0.045 1/s at 470°C and about 0.02 1/s at 430°C.

In contrast to the above, the catalysts supported on the N1900 carbon attained quickly a stable level of activity. Some of the samples were tested for five days and no decrease in the percentage of ammonia was observed. Hence, the activation procedure enabled to obtain reliable kinetic data. The most important results for this group of catalysts are presented below.

Figure 4 shows the effect of potassium (used as

Table 2
Size of metal crystallites as determined by XRD and H_2 chemisorption

Catalyst[a]	Precursor of active phase	XRD crystallite size L (nm)	H_2 chemisorption		
			H_2 uptake (μmol/g_{C+Ru})	dispersion D (%)	crystallite size L_1 (nm)
NSRu4.7	$RuCl_3{\cdot}0.5H_2O$	–	2	0.8	170
NSRu4.7K10	$RuCl_3{\cdot}0.5H_2O$	–	8.8	3.6	45
NSRu4.7K10(d)	$RuCl_3{\cdot}0.5H_2O$	–	93	40	3.2
N1900Ru9.1	$RuCl_3{\cdot}0.5H_2O$	14	46	10.4	12
N1900Ru9.1	$Ru_3(CO)_{12}$	16	34	7.6	17
N1900Ru9.1K3.7	$RuCl_3{\cdot}0.5H_2O$	12	60	13.5	9.5
N1900Ru9.1K3.7	$Ru_3(CO)_{12}$	16	58	13.1	9.8
N1900Ru4.7Cs7	$RuCl_3{\cdot}0.5H_2O$	–	46	19.8	6.5
N1900Ru9.1Cs3.7	$RuCl_3{\cdot}0.5H_2O$	–	65	14.5	8.8
N1900Ru16.6Cs2	$RuCl_3{\cdot}0.5H_2O$	–	75.5	9.2	13.9

[a] All the samples were previously tested in the ammonia synthesis reactor (standard activation; 24 h activity measurement at 10 MPa pressure). Sample labeled as (d) was activated additionally to the standard procedure for ten days at 470°C before activity measurement.

Table 3
Activity of the NSRu4.7K$_i$ catalysts vs. time of activation[a] at 470°C; precursor $RuCl_3{\cdot}0.5H_2O$, promoter KOH. In parentheses the corresponding values of TOF (1/s) are given

Catalyst	NH_3 in the outlet gas (%)				
	(a) 470°C	(b) 470°C	(c) 470°C	(d) 470°C	(d) 430°C
NSRu4.7K0	0.00	–	–	0.00	–
NSRu4.7K10	0.05	–	0.70	0.65 (0.045)	0.30 (0.02)
NSRu4.7K15	0.08	0.60	0.80	0.75	0.35

[a] (a) Standard activation, (b) standard activation +3 days at 470°C, (c) standard activation +6 days at 470°C, (d) standard activation +10 days at 470°C (after 10 days of additional activation the activity was measured both at 470 and at 430°C).

KOH) on the activity of the system containing 9.1% of ruthenium. The precursor of the active phase was $RuCl_3$. As one might expect [17], the activity of the catalyst in the ammonia synthesis depends on the amount of the promoter used. Flat maxima appear at all temperatures tested. The optimum ratio of K^+/Ru is about 2–4, and the unpromoted material is completely inactive. The use of ruthenium carbonyl (figure 5) instead of $RuCl_3$ gives catalysts with properties very close to those described above. This identity concerns not only optimal potassium contents in the systems compared, but also the activities at corresponding temperatures or, more precisely, the concentrations of ammonia in the outlet gas. Thus, ruthenium chloride is as effective a precursor of the active phase as ruthenium carbonyl and it can be alternatively employed in the preparation of catalytically active Ru/C systems. It is worth to remind here that Ru/Al_2O_3 catalysts prepared from Ru carbonyl were much more active in the NH_3 synthesis than those prepared from $RuCl_3$ [7,18], probably due to a higher dispersion [7], or both higher dispersion and lack of Cl [18].

A substantial supplement to the results shown in figures 4 and 5 is table 4, which presents the TOF values calculated from the kinetic and H_2 chemisorption data obtained for the potassium-promoted catalysts derived from $RuCl_3$ and from $Ru_3(CO)_{12}$. The TOF values, identical for both samples (table 4), suggest that the Cl^- ions are completely removed from the system, in the form of HCl, during the reduction of the chloride precursor. Attention should be payed, however, to the much higher TOF values obtained for the N1900RuK system than for the NSRuK system (by more than one order of magnitude both at 470 and 430°C). One may suppose that in the latter case only a small part of the Ru surface area exposed for the chemisorption of H_2 is promoted with potassium. The other part would then be inactive, giving no contribution to the overall rate of the process. It is also possible that ruthenium deposited on the turbostratic carbon exhibits sites which are significantly different from those in the NSRu system. These sites, when pro-

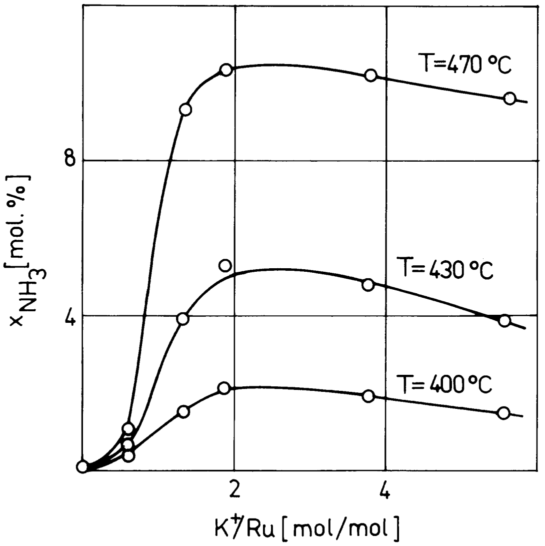

Figure 4. Activity of a $RuCl_3{\cdot}0.5H_2O$-derived Ru catalyst supported on the N1900 carbon vs. K^+/Ru molar ratio; $Ru/(Ru + C) = 9.1\%$, KOH as a promoter (24 h activity measurement at 10 MPa).

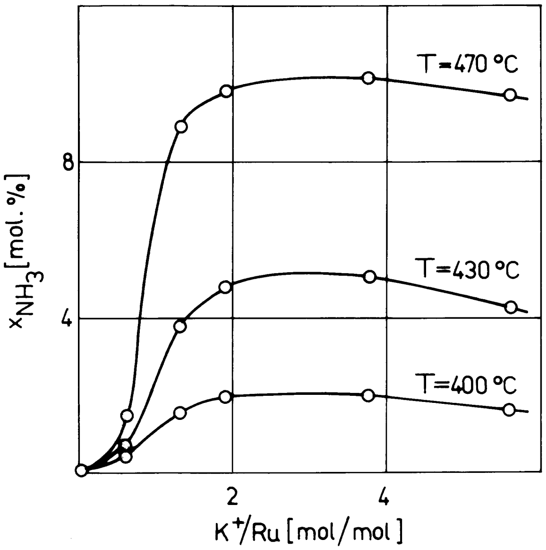

Figure 5. Activity of a $Ru_3(CO)_{12}$-derived Ru catalyst supported on the N1900 carbon vs. K^+/Ru molar ratio; $Ru/(Ru + C) = 9.1\%$, KOH as a promoter (24 h activity measurement at 10 MPa).

Table 4
TOF values and corresponding percentages of NH_3 (in parentheses) for potassium-promoted ruthenium catalysts supported on N1900 carbon; Ru/(Ru + C) = 9.1%; promoter KOH. (24 h test of activity at 10 MPa)

Catalyst	Precursor	TOF (1/s)		
		470°C	430°C	400°C
N1900Ru9.1K3.7	$RuCl_3{\cdot}0.5H_2O$	1.05 (10.1)	0.50 (4.8)	0.25 (1.9)
N1900Ru9.1K3.7	$Ru_3(CO)_{12}$	1.08 (10.1)	0.53 (4.9)	0.25 (1.9)

moted with potassium, show a very high activity. In such a case the difference observed in TOF would be an indirect consequence of differences in the structure of the supports: amorphous in the NS material and a graphite-like, partly ordered structure in N1900. Further investigations are necessary to elucidate this problem. It can only be stated that the catalytic properties of the promoted Ru/C system are strongly dependent on the kind of carbon used for its preparation.

Figure 6 illustrates the effect of the kind of alkaline promoter (KOH, CsOH) on the activity of the system N1900Ru4.7. The diagram presented is concerned with samples that contain optimum amounts of the promoters. As can be seen, the activity of the catalyst promoted with cesium is slightly higher than that with potassium. An analogous relationship (not presented in the paper) was obtained for the samples with a higher content of ruthenium (9.1%). It should be noticed, however, that the H_2 chemisorption for the Cs-promoted sample (9.1% Ru) was also slightly higher (see table 2). The optimum ratio of both K^+ or Cs^+ to Ru was in the former case (4.7% Ru) about twice as high as that in the latter one (9.1% Ru). Hence, the ratios of the alkali metal to carbon were almost identical. One might suppose, therefore that the optimum content of the alkali metal (K^+ or Cs^+) is more related to the texture of the carbon support than to the content of the active phase. The effect of nitrates of cesium or potassium used as a precursors of the alkaline promoter is comparable to that for the systems involving the hydroxides, and therefore it was not illustrated.

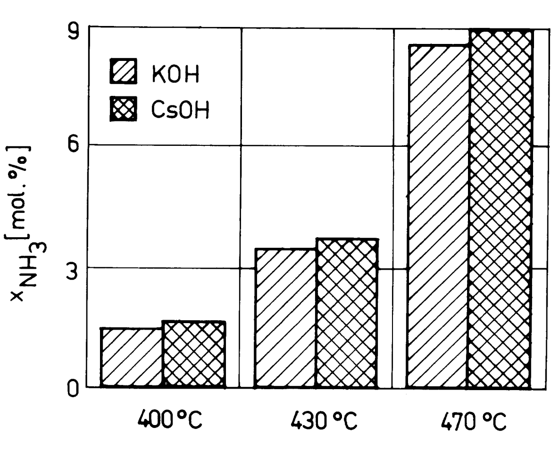

Figure 6. Activity of a $RuCl_3{\cdot}0.5H_2O$-derived catalyst promoted with KOH or CsOH; Ru/(Ru + C) = 4.7% (24 h activity measurement at 10 MPa).

Figure 7 presents the activity of the N1900 catalyst promoted with CsOH as a function of ruthenium content in the material. The increase in Ru content was accompanied by a monotonous increase in the conversion, which was at lower temperatures (400 and 430°C) roughly proportional to the number of Ru surface atoms determined by H_2 chemisorption (see table 2). Hence, the TOF values (0.2–0.25 1/s and about 0.5 1/s at 400 and 430°C, respectively) are independent of the ruthenium dispersion. It should be noticed that the ammonia concentration in the outlet gas for the catalyst containing 16.6% Ru at 470°C was very close to its equilibrium value (13.7%), despite of the fact that the space velocity was relatively high (about 55×10^3 1/h). Such a result accounts for a high activity of the ruthenium catalyst deposited on the thermally modified carbon.

4. Conclusions

A ruthenium catalyst supported on the pre-calcined carbon N1900 (1900°C, helium atmosphere) and promoted with alkali metal compounds is much more active in the synthesis of ammonia at high pressures than a catalyst supported on similarly promoted raw, amorphous carbon. Unpromoted catalysts of this kind were completely inactive.

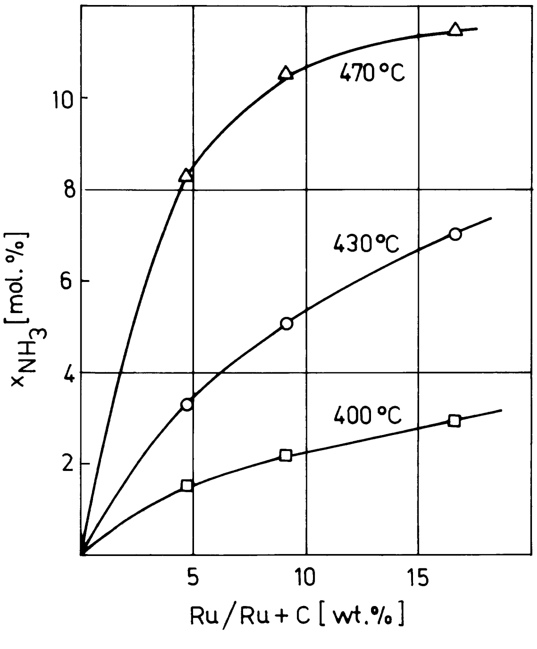

Figure 7. Activity of a $RuCl_3{\cdot}0.5H_2O$-derived catalyst vs. ruthenium content; CsOH as a promoter (24 h activity measurement at 10 MPa).

Ruthenium chloride used as a precursor of the active phase was as effective as ruthenium carbonyl. Both the dispersion *D* and the TOF values obtained for the $RuCl_3$-derived catalyst based on the N1900 carbon and promoted with K^+ were almost identical with those found for the Ru carbonyl-derived material.

Potassium and cesium hydroxides and nitrates can be used alternatively as precursors of the alkali promoters. The activity of Cs^+-promoted catalyst was only slightly higher than that of the catalyst promoted with K^+, probably due to higher dispersion of ruthenium in the former.

A monotonous increase in activity vs. ruthenium content (5–15%) in the N1900RuCs catalyst was observed, roughly proportional to the amount of Ru surface atoms (per gram of $C + Ru$).

Acknowledgement

The authors benefited from discussions with Professor H.P. Boehm.

References

[1] H. Baris, M. Gliński, J. Kijeński, A. Wokaun and A. Baiker, Appl. Catal. 28 (1986) 295.

[2] J. Kubota and K. Aika, J. Phys. Chem. 98 (1994) 11293.

[3] K. Aika, M. Kumasaka, T. Oma, O. Kato, H. Matsuda, N. Watanabe, K. Yamazaki, A. Ozaki and T. Onishi, Appl. Catal. 28 (1986) 57.

[4] K. Aika, K. Shimazaki, Y. Hattori, A. Ohya, S. Ohshima, K. Shirota and A. Ozaki, J. Catal. 92 (1985) 296.

[5] S. Murata and K. Aika, J. Catal. 136 (1992) 118.

[6] S. Murata and K. Aika, J. Catal. 136 (1992) 110.

[7] P. Moggi, G. Predieri, G. Albanesi and S. Papadopulos, Appl. Catal. 53 (1989) L1–L4.

[8] P. Moggi, G. Albanesi, G. Predieri and G. Spoto, Appl. Catal. A 123 (1995) 145.

[9] S. Masthan, P.S. Prasad, K.S. Rama Rao and P. Kanta Rao, J. Mol. Catal. 67 (1991) L1–L5.

[10] K.S. Rama Rao, S. Khaja Masthan, P.S. Sai Prasad and P. Kanta Rao, Appl. Catal. 73 (1991) L1–L5.

[11] K. Aika, A. Ohya, A. Ozaki, Y. Inoue and I. Yasumori, J. Catal. 92 (1985) 305.

[12] K. Aika, T. Takano and S. Murata, J. Catal. 136 (1992) 126.

[13] F. Rosowski, O. Hinrischen, M. Muhler and G. Ertl, Catal. Lett. 36 (1996) 229.

[14] O. Hinrischen, F. Rosowski, M. Muhler and G. Ertl, Chem. Eng. Sci. 51 (1996) 1683.

[15] K. Chao, L. Lin and M. Yang, Catal. Lett. 38 (1996) 279

[16] J. Wellenbüscher, M. Muhler, W. Mahdi, U. Sauerlandt, J. Schütze, G. Ertl and R. Schlögl, Catal. Lett. 25 (1994) 61.

[17] J.K. Aika, H. Hori and A. Ozaki, J. Catal. 27 (1972) 424.

[18] K. Aika, T. Kawahara, S. Murata and T. Onishi, Bull. Chem. Soc. Jpn. 63 (1990) 1221.

[19] US Patent 4,163,775, British Petroleum (1979).

[20] US Patent 4,568,532 (1984).

[21] US Patent 4,479,925 (1984).

[22] Z. Kowalczyk, S. Jodzis and J. Sentek, Appl. Catal. A 138 (1996) 83.

[23] Z. Kowalczyk, J. Sentek, S. Jodzis, R. Diduszko, A. Presz, A. Terzyk, Z. Kucharski and J. Suwalski, Carbon 34 (1996) 403.

[24] R.A. Dalla Betta, J. Catal. 34 (1974) 57.

[25] K.C. Taylor, J. Catal. 38 (1975) 299.

[26] H.P. Boehm, in preparation.