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Ammonia synthesis over the Ba-promoted ruthenium catalysts supported on boron nitride

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Barium promoted ruthenium catalysts deposited on the boron nitride supports were characterised (XRD, O_2 and CO chemisorption) and tested in NH_3 synthesis. Prior to use, the raw BN materials marked as BNS (Starck, 96 m^2/g) and HCV (Advanced Ceramics Corporation Cleveland USA, 40 m^2/g) were heated in an ammonia stream at 700–800 °C for 120 h. As a result, the oxygen content was reduced from 7.0 at% (BNS) to 3.5 at% (BNS_{NH3}) and from 3.8 to 2.7 at% (HCV_{NH3}), as evidenced by XPS. The kinetic studies of NH_3 synthesis (63 or 90 bar; H_2:N_2 = 3:1) revealed that the catalysts based on the modified supports were more active, respectively, than those derived from starting nitrides, the difference being especially pronounced in the case of BNS and BNS_{NH3}. Studies of the catalysts activation have shown, in turn, that the stabilisation in a H_2:N_2 = 3:1 mixture at 1 bar is very slow, i.e. the reaction rate increases slowly versus time on stream even at a high temperature of 550 – 600 °C. Stabilisation is faster and the NH_3 synthesis rates are higher when the activation is performed with an ammonia rich mixture (10% NH_3 in H_2:N_2 = 3:1) flowing under high pressure of 90 bar. It is suggested that boron oxide (an impurity) acts as a deactivating agent for Ba–Ru/BN and that the reaction between NH_3 and B_2O_3 ($B_2O_3 + 2NH_3 = 2BN + 3H_2O$) is responsible for the activity increase. A poisoning mechanism of B_2O_3 is discussed.

KEY WORDS: ammonia synthesis; ruthenium catalyst; boron nitride supports; support modification with ammonia.

1. Introduction

Although the ammonia synthesis from hydrogen and nitrogen has been commercialised almost 100 years ago, it still remains a very important but also a high energy consuming industrial process [1]. The catalytic NH_3 synthesis is very attractive as a model reaction in the fundamental studies, too [2]. For the above reasons, the researchers from industrial centres and academia are still active in the field of NH_3 synthesis and they try to work out a completely new catalyst [1,3–10] or to improve the formula and properties of the conventional iron one [11–15]. Among several new catalytic systems investigated in the last 30 years, only ruthenium supported on high surface area graphite (HSAG) was implemented to the industrial practice so far. A combination of both conventional iron (first catalytic bed) and modern Ru/C catalyst (last three beds) in a so-called Kellog Brown & Root Advanced Ammonia Process (KBRAAP) was shown to be very advantageous [16,17], i.e. the pressure in ammonia loops could be significantly reduced (to 90 bar), thus resulting in a lower energy consumption. The KBRAAP catalyst has been operating successfully in several retrofitted as well as totally new plants, some of them being of high capacity (about 2000 ton/day) [16].

The commercialisation of the Ru/HSAG catalyst has resulted in intensive studies of ruthenium catalysts deposited on various supports such as magnesia [18–30], magnesium–aluminum spinel [31–34], zeolites [35–38] or carbon [39–55], Recently, Jacobsen [56] and Hansen *et al.* [57] from H. Topsoe have revealed that ruthenium supported on boron nitride and promoted with barium is the most efficient catalytic system for NH_3 synthesis that has ever been found. Our paper is also devoted to the Ba–Ru/BN catalysts or, more precisely, to their catalytic properties in NH_3 synthesis. To get a closer insight into the role of the BN substrate, both the effect of the support modification with ammonia at high temperature and that of the activation procedure were examined.

The kinetic measurements of NH_3 synthesis were supplemented with the characterisation studies of the BN supports (XRD, XPS) and catalysts (XRD, oxygen and carbon monoxide chemisorption).

2. Experimental

2.1. The BN supports

Two commercial boron nitride powders of 190 m^2/g (marked as BNS) and of 40 m^2/g (marked as HCV) BET surface areas were received from H.C. Starck GmbH and Advanced Ceramics Corporation Cleveland USA,

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respectively. Both starting materials were additionally modified by heating in an ammonia stream according to the temperature scheme: 700 °C for 100 h + 800 °C for 20 h. As a result, the BET surface area of BNS increased significantly – to 270 m^2/g and that of HCV increased slightly – to 42.5 m^2/g. The four different BN materials, labelled throughout the text as: BNS, BNS_{NH3}, HCV and HCV_{NH3} were used as supports for the catalysts preparation.

2.2. The catalysts

The unpromoted Ru/BN catalysts were prepared by the incipient wetness impregnation of the BN powders using ruthenium carbonyl ($Ru_3(CO)_{12}$) as the Ru precursor. One of the samples was derived from ruthenium nitroso nitrosyl ($Ru(NO)(NO)_3$). The metal loading in the samples was ca. 9.0 or 4.3 wt%. In order to obtain barium promoted catalysts, the Ru/BN specimens were impregnated with aqueous solutions of barium salts (nitrate, nitrite, acetate) or hydroxide to get the molar ratios of Ba:Ru = 0.5:1 (9% Ru) and Ba:Ru = 1:1 or 3:1 for 4.3% Ru. After drying, the catalysts were pressed into pellets, crushed and sieved into the grain fraction of 0.2–0.63 mm. To distinguish easily among the catalysts, all of the samples were labelled with unified symbols that specified the Ba:Ru molar ratio, ruthenium loading (wt%) and kind of boron nitride, e.g., Ba1Ru4.3/HCV_{NH3}.

2.3. Kinetic studies of NH_3 synthesis

The activity measurements were carried out in a flow differential reactor operating under a constant pressure of 63 or 90 bar. The reactor was fed either with an ammonia free H_2:N_2 = 3:1 mixture ($x_1 = 0$) or with a H_2 + N_2 mixture supplemented with ammonia ($x_1 = 8\%$ at 63 bar or $x_1 = 9.5\%$ at 90 bar). Most of the kinetic tests were performed using pure gas ($x_1 = 0$). Under standard conditions of temperature and gas flow rate (63 dm^3/h [STP], 300 mg Ru + BN mass of the catalyst sample), the NH_3 content in the outlet stream (x_2) was determined. Consequently, the integral reaction rate corresponding to the ($0-x_2$) interval could be calculated. Two samples, those of the highest activity, were additionally tested at high NH_3 content in the gas, i.e. the reaction rates corresponding to 8.5% NH_3 in the stream (400 °C, 63 bar) or to 10% NH_3 (400 °C, 90 bar) were determined through the small increments ($x_2 - x_1$) in the concentration of ammonia that was formed on the catalyst layer due to the reaction. The detailed description of the NH_3 synthesis rate measurements at high ammonia concentrations can be found elsewhere [43,58–60].

2.4. Characterisation studies of the supports and catalysts

The supports were examined both by XRD and XPS methods, the catalysts were characterised by XRD and chemisorption. The X-ray photoelectron spectra (XPS) of the supports were acquired in an ESCAI-AB-210 spectrometer with AlKct (1456.6 eV) irradiation source. During the experiment, the pressure in the spectrometer chamber was approximately 5×10^{-9} mbar. Samples were pressed into pellets before use. Survey spectra were recorded in the binding energy range of 0–1400 eV with the step of 0.75 eV. High-resolution scans for the B 1s, N 1s, C 1s, O 1s, Al 2p were recorded with the 0.05 eV step and dwell time of 100 ms. The analyser pass energy was set as 20 eV. A take-off angle of 90° was used in all XPS studies. Curve fitting was performed using the ECLIPSE v. 3.1 data system software. This software describes each component of the complex envelope as a Gaussian–Lorentzian sum function; a constant 0.3 G/L ratio was used. The background was fitted using a nonlinear model function proportional to the integral of elastically scattered electrons (Shirley background). As an internal standard, the biggest peak of C 1s was used with BE = 284.5 eV. XPS studies allowed setting the contamination level (particularly B_2O_3 content) in the BN materials used.

The XRD measurements were carried out in the Siemens D5000 diffractometer using Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å), scintillation detector and DiffracPlus Software. To determine structural differences among boron nitrides used as well as differences among the supported Ru catalysts, the collected diffraction patterns were analysed employing a peak fitting routine to the Pearson VII functions (Program Peakfit [61]). The average crystallite sizes of both BN materials and ruthenium particles deposited on BN were calculated from line broadening. In the case of Ru catalysts, the pattern of the support was subtracted from that of the catalyst, to extract the broad and weak Ru reflections partially overlapping with the reflections of the BN substrate.

The chemisorption studies of the Ru/BN catalysts were carried out in the fully automated instrument – Peak 4 (Technical University of \Lódź) equipped with a computer-controlled reactor and TC detector. Prior to measurements, the samples (fresh or previously tested in ammonia synthesis) were reduced (rereduced) in a Hz Stream at 550 °C for 12 h. Subsequently, the samples were cooled in H_2 to 400 °C and flushed with a He stream to remove hydrogen from the ruthenium surface, followed by cooling in helium. Both oxygen and carbon monoxide were introduced by the pulse method into the He stream at 0 °C (O_2) or 20 °C (CO). The stoichiometries of O:Ru_s = 1:1 and CO:Ru_s = 0.6:1 were assumed to calculate the number of surface ruthenium atoms and fraction exposed [62,63]. The average crystallite sizes were calculated from the formula proposed by Borodziński and Bonarowska [64].

3. Results

3.1. Characterisation studies

Figure 1 shows, as an example, the survey XPS scan (figure 1a) and high-resolution spectrum in the scope of the O 1s line (figure 1b), both obtained for the same BN sample. The chemical composition of the BN materials is presented in Table 1. The data collected in table 1 demonstrate that all of the samples contain impurities, mainly carbon (C 1s signal) and oxygen (O 1s), the latter element being bound to boron (B_2O_3). The oxygen content in the commercial BNS specimen (about 7 at.%) is almost twice higher than that in HCV (3.8%). The overheating of the starting nitrides in ammonia leads to the lowering of the oxygen content, the effect being significantly stronger in the case of BNS. This means that boron oxide was partly converted to boron nitride when heating in NH_3. The BN phase formed during the BNS pretreatment is finely dispersed as evidenced by the significantly higher BET surface area of the modified support (270 m^2/g) compared to that of the fresh one (190 m^2/g).

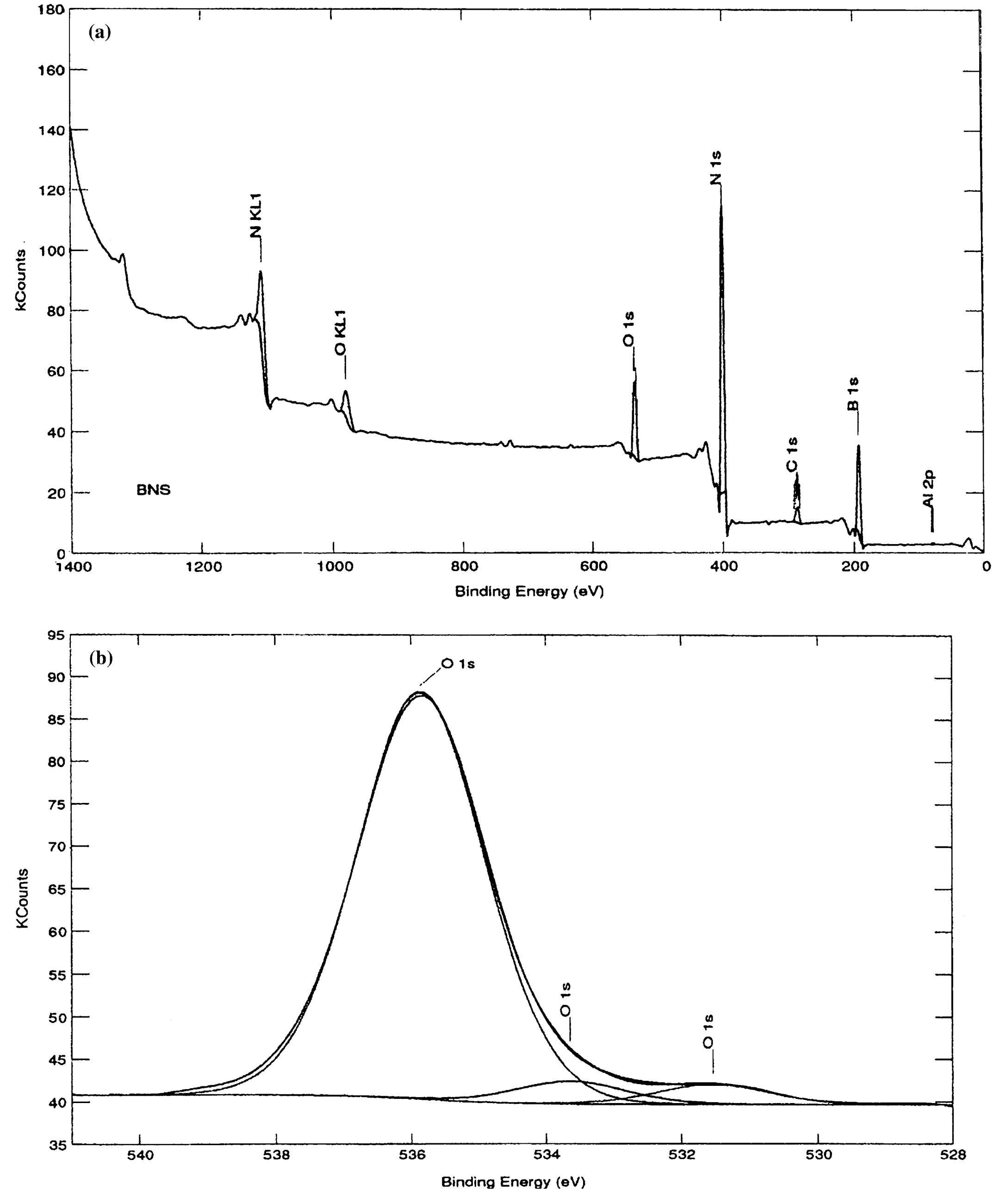

Figure 1. Survey XPS scan (a) and high-resolution spectrum in the scope of O 1s line (b) for the BNS support.

Table 1

Elemental composition of the BN materials, as determined by the XPS method [at.%]

Boron nitride	O 1s	C 1s	Al 2p	B 1s	N 1s
BNS	7.02	4.15	0.78	45.92	42.13
$\mathrm{BNS_{NH3}}$	3.51	2.48	0.78	47.65	45.58
HCV	3.84	1.50	0.45	48.81	45.40
$\mathrm{HCV_{NH3}}$	2.70	1.29	0.45	49.43	46.13

Figure 2 presents the XRD patterns of the four BN supports. Hexagonal boron nitride proved to be the only detectable phase in all of the materials. There are, however, some differences in the shape of individual patterns. The left-side asymmetry of the BN (0 0 2) signal in the patterns corresponding to the BNS and $\mathrm{BNS_{NH3}}$ specimens results most likely from the bi-modal distribution of the crystallite size. According to such an interpretation, the overall (0 0 2) peak is composed of two, slightly shifted peaks that correspond to small (2.8 nm, $2\theta = 25.59$) and to large (17 nm, $2\theta = 26.67$) crystallites. In contrast, a symmetric and rather narrow (0 0 2) signal is observed for the HCV and $\mathrm{HCV_{NH_3}}$ samples. The average crystallite size of 17 nm results from the (0 0 2) line broadening both for the fresh specimen (HCV) and for that modified with ammonia ($\mathrm{HCV_{NH_3}}$). The right-side asymmetry of the (1 0 1) signal well seen in each pattern evidences that the BN materials exhibit a turbostratic structure.

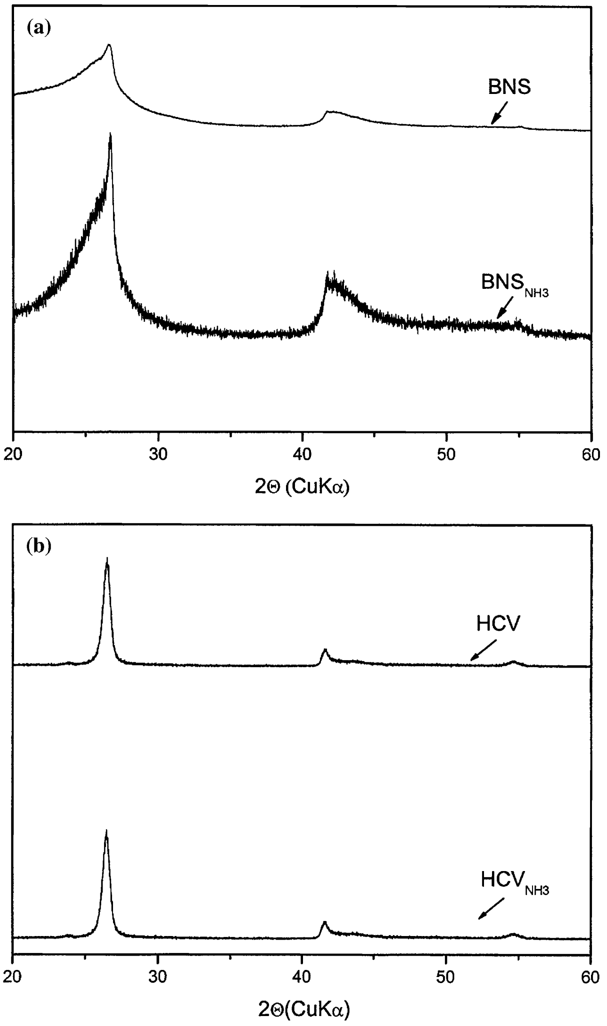

Figure 2. XRD patterns of the boron nitride supports; (a) BNS, $\mathrm{BNS_{NH_3}}$; (b) HCV, $\mathrm{HCV_{NH_3}}$.

Figure 3 shows, as an example, the XRD pattern obtained for one of the unpromoted Ru/BN catalysts. The Lorentzian-shape of the Ru maxima observed for each of the specimens (samples of 4.3 wt% Ru were examined) suggests either a very wide distribution of ruthenium crystallites or considerable strain. Both effects can substantially shift the estimate of an average size-up in the former and down in the latter case, respectively [65]. The size parameters of ruthenium crystallites (d_{XRD}) determined for all of the Ru4.3/BN samples from the integral width of the 1 0 1 Ru peak (for the Lorentzian-shape, the integral width is considered to be a better measure of broadening than the full width at half maximum) are listed in table 2. As it is seen, there are no essential differences among the average sizes of the ruthenium crystallites deposited on the BN supports used. It should be remembered, however, that the absolute values of d_{XRD} (6–7 nm, see table 2) may be uncertain and they should be treated comparatively only.

The chemisorption studies performed with the same group of the unpromoted Ru/BN samples have revealed, in turn, (table 2) that the systems prepared from HCV and $\mathrm{HCV_{NH_3}}$ expose considerably higher dispersions than the specimens derived from BNS and $\mathrm{BNS_{NH_3}}$, although the surface areas of the latter supports are significantly larger than those of the former ones. In spite of the differences, both XRD and chemisorption

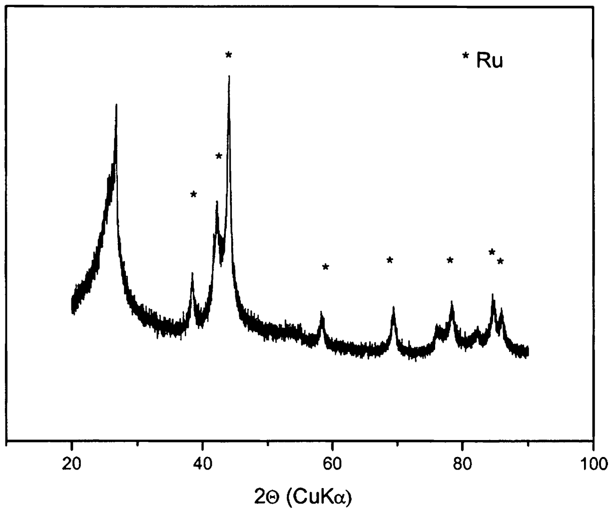

Figure 3. XRD pattern of the unpromoted Ru4.3/BNS catalyst.

Table 2
Dispersion of ruthenium in the unpromoted Ru/BN catalysts

Sample	d_{XRD} [nm]	Fe_{O_2}	D_{O_2} [nm]	FE_{CO}	D_{CO_2} [nm]
Ru4.3/BNS	7.4	0.12	11.2	0.14	9.6
Ru4.3/BNS_{NH_3}	6.2	0.16	8.4	–	–
Ru4.3/HCV	7.4	0.40	2.7	0.47	2.2
Ru4.3/HCV_{NH_3}	7.2	0.39	2.8	0.43	2.5
Ru4.3/HCV_{NH_3}[a]	–	0.37	3.0	0.41	2.6

[a] After the NH_3 synthesis test.

indicate that the preheating of the supports in ammonia does not influence the resultant Ru dispersions.

3.2. Activity of the catalysts in NH_3 synthesis

3.2.1. Effect of the reduction procedure

Preliminary studies of the Ba-promoted Ru catalysts deposited on the BNS substrate have shown that the samples reduced under mild, rather typical for ruthenium, conditions, i.e. at temperatures of 470–500 °C (H_2:N_2 = 3:1, 24–48 h) exhibit very low reaction rates. Hence, the effect of the activation procedure has been studied in detail.

Two different activation procedures A or B were applied. According to the A procedure, the samples were pretreated in an ammonia free (H_2:N_2 = 3:1) gas stream under 1 bar using the following temperature programme: (1) heating to 520 °C and maintaining at this temperature for 24 h, (2) further stabilisation at 520 °C for 168 h, (3) heating to 550 °C and maintaining at 550 °C for 48 h, (4) heating to 600 °C and maintaining at 600 °C for 24 h. After each isothermal step, the gas was compressed to 63 bar and the activity measurement was performed, i.e. the NH_3 content in the effluent gas was monitored under standard conditions of the flow rate (63 dm^3 [STP]/h) and temperature (520 °C).

The activation procedure B was more complex than A. First, the samples were heated to 550 °C in a NH_3 rich (10%) stoichiometric $H_2 + N_2$ mixture flowing under the pressure of 90 bar and maintained under such conditions for 5 h. Then, the pressure was reduced to the atmospheric one and the activation was continued at 550 °C for further 16 h in a flowing 0.5% NH_3 + H_2:N_2 (H_2:N_2 = 3:1) stream. Subsequently, the gas was compressed to 63 bar, and the activity was measured at 520 °C. To check the stability of the catalysts, the whole procedure, consisted of high pressure treatment (550 °C, $p = 90$ bar, 10% NH_3) followed by that of low pressure (0.5% NH_3 + H_2:N_2 (H_2:N_2 = 3:1)), was repeated and the activation was determined again.

The results obtained for the Ba0.5–Ru9/BNS sample doped with barium nitrate (Ba precursor) are presented in figure 4 (procedure A) and in figure 5 (procedure B), the activity being expressed as an integral NH_3 synthesis rate corresponding to the ($0-x_2$) interval. It is clearly seen in figure 4 that the stabilisation of the system in a pure H_2:N_2 = 3:1 mixture flowing under atmospheric pressure (procedure A) is very slow – an enhancement in the reaction rate was observed after each isothermal step. The high pressure reduction with an ammonia rich stream (procedure B, figure 5) leads, first of all, to a significantly higher level of activity as compared to A (higher integral rate of ammonia synthesis). However, an advantageous effect of the additional reduction step is rather small. Analogous relationships were found for the Ru9/BNS samples doped with barium nitrite, barium acetate or hydroxide – the activity of each system increased systematically versus time on stream (procedure A) and procedure B was always more effective than A. There are, however, some differences among the Ba precursors used (see figure 6), especially when the reduction was performed according to procedure A. Namely, barium nitrate was less effective than the other precursors.

3.2.2. Effect of the BN support modification with ammonia

The catalysts of low ruthenium loading (4.3 wt%) and of different Ba loadings were studied in the NH_3 synthesis to distinguish between raw supports (BNS, HCV) and those modified with ammonia (BNS_{NH_3}, HCV_{NH_3}). All of the samples were doped with barium nitrite (Ba:Ru = 1:1 or Ba:Ru = 3:1 molar ratios) and all

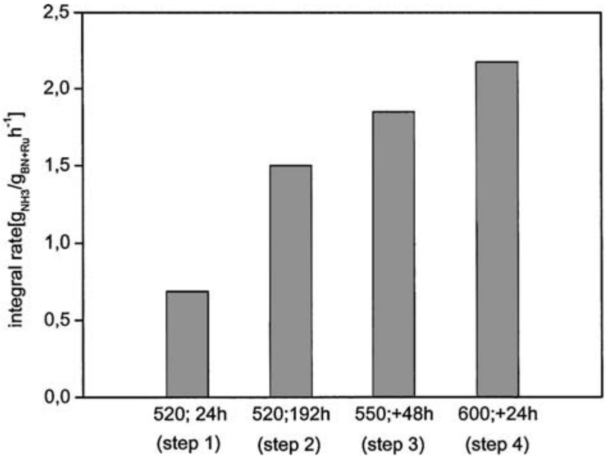

Figure 4. Integral rate of NH_3 synthesis after subsequent activation steps performed with an ammonia free H_2:N_2 = 3:1 stream at 1 bar pressure (procedure A). Activity was measured at 520 °C and 63 bar, $V_{H_2+N_2}$ = 63 dm^3 [STP]/h; sample Ba0.5–Ru9/BNS (0.3 g Ru + BN).

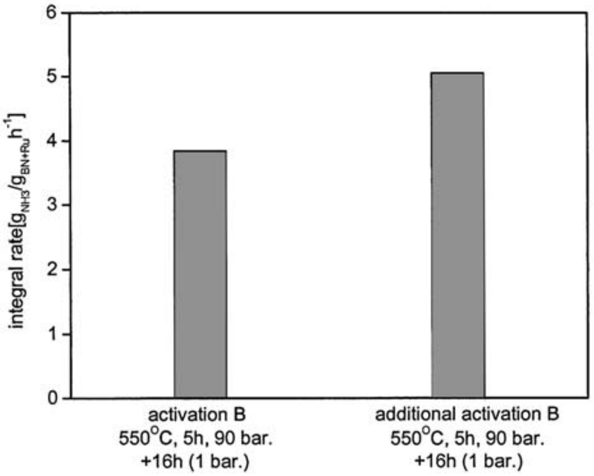

Figure 5. Integral rate of NH_3 synthesis after an activation performed according to procedure B (90 bar, 10% NH_3, 550 °C (5 h) + 1 bar, 0.5% NH_3, 550 °C (16 h)) and after an additional activation B. Activity was measured at 520 °C and 63 bar, $V_{H_2+N_2}$ = 63 dm^3 [STP]/h; sample Ba0.5–Ru9/BNS (0.3 g Ru + BNS).

were reduced according to the more advantageous procedure B. The kinetic tests were performed at a low temperature of 400 °C to avoid thermodynamic limitations that might occur at elevated temperatures if any of the samples were very active. The results are collected in table 3. Both ammonia contents in the outlet gas streams (x_2) and integral reactions rates corresponding to the (0–x_2) regions are listed in the table.

Generally, the catalysts of a lower Ba content (Ba:Ru = 1:1) are more active than those of a higher Ba content (3:1) results from the data presented in table 3, the difference being particularly large for the system based on the BNS support. It is also seen that ruthenium carbonyl is a more advantageous precursor of the active phase than nitroso nitrosyl. Attention should first of all be paid, however, to the differences between the samples derived from raw nitrides and those derived from nitrides preheated in ammonia. The integral reaction rates over the Ba–Ru/BNS_{NH_3} catalysts are about twice higher (Ba:Ru = 1:1) or even three times higher (Ba:Ru = 3:1) than the rates obtained for the samples based on starting nitride BNS, respectively. In the case of the HCV material, the preheating in ammonia results in a smaller but still noticeable (60%) activity enhancement. The above comparison shows clearly that the preliminary annealing of the BN supports in an ammonia stream is advantageous for the catalytic properties of the Ba-promoted systems in NH_3 synthesis, the effect being dependent, however, on the choice of the starting material used.

3.2.3. The BN supports versus graphitised carbon

The authoritative comparison of the ruthenium catalysts supported on boron nitride with the systems derived from graphitised carbon should be based on the rates determined under strictly the same, well defined conditions of pressure, temperature and ammonia concentration, in an gas mixture. The NH_3 synthesis rates determined under such conditions (400 °C, 63 bar, 8.5% NH_3 in H_2:N_2 = 3:1 and 400 °C, 90 bar, 10% NH_3, H_2:N_2 = 3:1) for the most active Ba–Ru/BN catalysts prepared in this study (Ba1–Ru4.3/HCV_{NH_3} and Ba1–Ru4.3/HCV) and for the catalysts supported on carbon (previously examined in our laboratory [43,45]) are collected in table 4. Since the ruthenium loadings in the systems were different, the comparison is based on the reaction rates referred to the Ru mass and, additionally, on the rates expressed in terms of TOF that are illustrative for the catalytic properties of Ru surfaces in the systems under consideration.

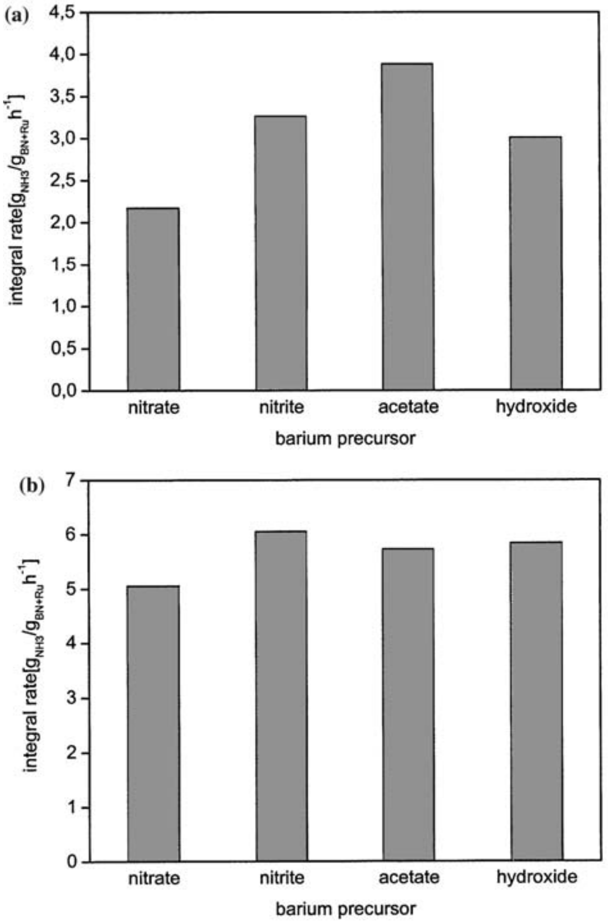

Figure 6. Activity of the Ba0.5–Ru9/BNS catalysts doped with various Ba precursors; (a) after full (4-step) activation A, (b) after activation B; activity was measured at 520 °C and 63 bar; $V_{H_2+N_2}$ = 63 dm^3 [STP]/h.

As one may notice (see table 4), carbon is a significantly more effective substrate for ruthenium than boron nitride. The surface activities (TOF) of Ba–Ru/C are by several times higher than those of Ba–Ru/BN both at 63 and 90 bar. The supremacy of the former catalyst is even more pronounced when the reaction rates referred to the active metal mass are compared.

Table 3
Effect of the support on the activity of the Ba-promoted Ru4.3/BN catalysts (barium nitrite was used as the Ba precursor)

Sample	Ba:Ru [mol/mol]	x_2 [mol%]	Integral reaction rate [$g_{NH_3}/g_{BN} + Ru\ h^{-1}$]
Ba1–Ru4.3/BNS	1:1	0.21	0.36
Ba3–Ru4.3/BNS	3:1	0.12	0.20
Ba1–Ru4.3/BNS$_{NH_3}$	1:1	0.44	0.75
Ba3–Ru4.3/BNS$_{NH_3}$	3:1	0.31	0.52
Ba1–Ru4.3/HCV	1:1	0.51	0.86
Ba3–Ru4.3/HCV	3:1	0.39	0.67
Ba1–Ru4.3/HCV$_{NH_3}$	1:1	0.87	1.30
Ba1–Ru4.3/HCV[a]	1:1	0.29	0.49

Activity was measured at 400 °C and 63 bar. The samples (0.3 g Ru + BN) were reduced according to procedure B (90 bar, 10% NH_3 550 °C (5 h) + 1 bar, 0.5% NH_3 550 °C (16 h).

[a] Ruthenium nitroso nitrosyl was used as the Ru precursor instead of $Ru_3(CO)_{12}$.

Hence, the results of comparison seem to remain in a strong disagreement with the data of Jacobsen [56], who claims that the Ba–Ru/BN catalysts are even more active than the carbon-based ones. The reason for the discrepancy will be discussed in the next chapter.

4. Discussion

A slow stabilisation of the Ba-promoted ruthenium catalysts during the high temperature activation in a hydrogen–nitrogen mixture (procedure A) as well as an advantageous effect of the ammonia presence in the gas (procedure B) seem to be specific features of the Ba–Ru/BN catalysts prepared. Studies of the barium-doped Ru catalysts deposited on graphitised carbon [66] or magnesia [21] demonstrate that the samples reach their steady-state level of the reaction rate after a short time of reduction (24–48 h) at 470 and 520 °C, respectively. A prolonged activation at 520 °C, or above, may even lead to an activity decline due to the sintering of ruthenium particles [40]. Hence, a systematic increase in activity observed for the Ba–Ru/BN specimens heated in a pure $H_2 + N_2$ mixture at 550–600 °C (see figure 4), can be justified neither by the slow reduction of the ruthenium surface nor by slow decomposition of the barium precursors and should be ascribed to the changes in the BNS substrate when operating or, more precisely, to the systematic decrease of the boron oxide content in the support. We suggest that B_2O_3 present in the substrate material (BNS contains about 7 at% oxygen, see table 1) acts as a deactivating agent for the system. During the low pressure stabilisation of the Ba–Ru/BNS samples at elevated temperatures, B_2O_3 reacts slowly with ammonia that is formed on the Ru surface due to the NH_3 synthesis. In consequence, the B_2O_3 content decreases slowly, thus resulting in an activity increase. The reaction between B_2Q_3 and NH_3 ($B_2O_3 + 2NH_3 = 2BN + 3H_2O$) is significantly faster and an activity enhancement is more pronounced when the reduction is performed with an ammonia rich stream at high pressure (procedure B). Under such conditions, the NH_3 partial pressure is by several orders of magnitude higher than that under atmospheric pressure, even if the gas mixture reaches an equilibrium state when flowing through the sample.

A concept of the catalyst poisoning by B_2Q_3 finds a strong support in the NH_3 synthesis studies performed with samples derived from the BN materials preheated in ammonia. Higher reaction rates observed for the catalysts based on the preliminarily modified supports compared to those for the systems based on starting nitrides, respectively, should be attributed to the lower B_2O_3 contents in the former substrate materials. Clearly, in the case of HCV, the drop in an oxygen content due to the pretreatment with ammonia is relatively small and a small increase in activity is observed. If, however, the oxygen content is reduced significantly (BNS$_{NH_3}$ versus BNS), a significantly higher (2–3-fold) increase in the integral NH_3 synthesis rate results (see table 3).

Table 4
Rates of ammonia synthesis over the Ba–Ru/BN and Ba–Ru/C catalysts at high ammonia contents in the $H_2:N_2 = 3:1$ mixture

Catalyst	400 °C, 63 bar, 8.5% NH_3		400 °C, 90 bar, 10% NH_3		References
	r [$g_{NH_3}/g_{Ru}\ h^{-1}$]	TOF_{O_2} [1/s]	r [$g_{NH_3}/g_{Ru}\ h^{-1}$]	TOF_{O_2} [1/s]	
Ba1–Ru4.3/HCV	3.1	0.013	3.6	0.015	Present study
Ba1–Ru4.3/HCV$_{NH_3}$	4.8	0.020	5.5	0.023	Present study
Ba–Ru9.1/carbon	36.2	0.096	–	–	[44]
Ba–Ru9.1/carbon	–	–	38	0.104	[45]

According to the above observation, the activity of Ba–Ru/BN catalysts in NH_3 synthesis should be the higher, the lower the oxygen content (B_2O_3) in starting boron nitride was, Consequently, a very pure oxygen-free BN support would be necessary to prepare a very active Ba–Ru/BN system, possibly as active as that described by Jacobsen [56]. Since Jacobsen did not specify the purity of the BN support used in his studies [56] and we were not able to reduce the oxygen content in the starting boron nitrides more significantly (to the best of our knowledge, boron nitrides of high surface areas and of low oxygen content are still commercially unavailable), further studies are necessary to explain whether a low oxygen content in the BN material is the main criterion for active Ba–Ru/BN catalysts preparation.

The deactivating mechanism of B_2O_3 is a separate question. To elucidate the problem, a reference should be given to the paper of Hansen *et al.* [34], who have shown that the barium promoter in the supported ruthenium catalysts is distributed both on the metal surface and on the support surface. More specifically, the promoter location and, consequently, its promoting effect are controlled by the relative affinities of barium for the support and for ruthenium, respectively [34]. Generalisation of the above observation leads to the conclusion that boron oxide may also be localised partly on the BN surface and partly on the metal surface when operating under ammonia synthesis conditions. Hence, the ruthenium crystallites would be covered by the (Ba + O) adlayer and, additionally, by the B_2O_3 species that interact with BaO, thus suppressing the promotional effect from barium.

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References

[1] C.J.H. Jacobsen, Chem. Commun. (2000) 1057.

[2] K. Tamaru, in: *Catalytic Ammonia Synthesis. Fundamentals and Practice*, J.R. Jennings (eds.), (Plenum Press, New York, 1991) ch. 1.

[3] R. Kojima and K. Aika, Appl. Catal. A: Gen. 215 (2001) 149.

[4] R. Kojima and K. Aika, Appl. Catal. A: Gen. 218 (2001) 121.

[5] R. Kojima and K. Aika, Appl. Catal. A: Gen. 219 (2001) 157.

[6] S. Hagen, R. Barfod, R. Fehrmann, C.J.H. Jacobsen H.T. Teunissen and I. Chorkendorff, J. Catal. 214 (2003) 327.

[7] S. Hagen, R. Barfod, R. Fehrmann, C.J.H. Jacobsen, H.T. Teunissen, K. Stahl and I. Chorkendorff, Chem. Commun. (2002) 1206.

[8] A. Jedynak, D. Szmigiel, W. Raróg, J. Zieliński, J. Pielaszek P. Dłużewski and Z. Kowalczyk, Catal. Lett. 81 (2002) 213.

[9] A. Jedynak, Z. Kowalczyk, D. Szmigiel and J. Zieliński, Pol. J. Chem. 75 (2001) 1801.

[10] R. Kojima, H. Enomoto, M. Muhler and K. Aika, Appl. Catal. A: Gen. 246 (2003) 311.

[11] R. Schlogl, Angew. Chem. Int. Ed. 42(18) (2003) 2004.

[12] I. Jasinska, K. Lubkowski and W. Arabczyk, Przem. Chem. 82 (2003) 230.

[13] M.J. Figurski, W. Arabczyk, Z. Lendzion-Bielun and S. Lenart, Appl. Catal. A: Gen. 266 (2004) 11.

[14] M.J. Figurski, W. Arabczyk, Z. Lendzion-Bielun, R.J. Kalenczuk and S. Lenart, Appl. Catal. A: Gen. 247 (2003) 9.

[15] N. Pernicone, E. Ferrero, I. Rossetti, L. Forni, P. Canton P. Riello, G. Fagherazzi, M. Signoretto and F. Pinna, Appl. Catal. A: Gen. 251 (2003) 121.

[16] R.B. Strait, Nitrogen Methanol 238 (1999) 37.

[17] R.B. Strait and S.A. Knez, in: *International Conference Exhibition*, Caracas, 28 February – 2 March (1999).

[18] O. Hinrichsen, F. Rosowski, A. Hornung, M. Muhler and G. Ertl, J. Catal. 165 (1997) 33.

[19] F. Rosowski, A. Hornung, O. Hinrichsen, D. Herein, M. Muhler and G. Ertl, Appl. Catal A: Gen. 151 (1997) 443.

[20] H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, Angew. Chem. Int. Ed. 40(6) (2001) 1061.

[21] D. Szmigiel, H. Bielawa, M. Kurtz, O. Hinrichsen, M. Muhler, W. Raróg, S. Jodzis, Z. Kowalczyk, L. Znak and J. Zieliński, J. Catal. 205 (2002) 205.

[22] B.C. McClaine and R.J. Davis, J. Catal. 210 (2002) 387.

[23] S.E. Siporin and R.J. Davis, J. Catal. 222 (2004) 315.

[24] C. Zupanc, A. Hornung, O. Hinrichsen and M. Muhler, J. Catal. 209 (2002) 501.

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

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

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

[28] S. Wu, J.X. Chen, X.F. Zheng, H.S. Zeng, C.M. Zheng and N.J. Guan, Chem. Commun. (2003) 2488.

[29] P. Moggi, G. Predieri and A. Maione, Catal. Lett. 79 (2002) 7.

[30] P. Moggi, G. Predieri, G. Albanesi and S. Papadopulos, Appl. Catal. A: Gen. 53 (1989) L1.

[31] B. Fastrup, Catal. Lett. 48 (1997) 111.

[32] C.J.H. Jacobsen, S. Dahl, P.L. Hansen, E. Tornqvist, L. Jansen, H. Topsoe, D.V. Prip, P.B. Moenshaug and I. Chorkendorff, J. Mol. Catal. A: Chem. 163 (2000) 19.

[33] S. Dahl, J. Sehested, C.J.H. Jacobsen, E. Tornqvist and I. Chorkendorff, J. Catal. 192 (2000) 391.

[34] T.W. Hansen, R.L. Hansen, S. Dahl and C.J.H. Jacobsen, Catal. Lett. 84 (2002) 7.

[35] S.E. Siporin, B.C. McClaine, S.L. Anderson and R.J. Davis, Catal. Lett. 81 (2002) 265.

[36] B.C. McClaine, S. Siporin and E.R.J. Davis, J. Phys. Chem. B 105 (2001) 7525.

[37] B.C. McClaine, T. Becue, C. Lock and R.J. Davis, J. Mol. Catal. A: Chem. 163 (2000) 105.

[38] B. McClaine and R.J.C. Davis, J. Catal. 211 (2002) 379.

[39] L. Forni, D. Molinari, I. Rossetti and N. Pernicone, Appl. Catal. A: Gen. 185 (1999) 269.

[40] I. Rossetti, N. Pernicone and L. Forni, Appl. Catal. A: Gen. 208 (2001) 271.

[41] I. Rossetti, N. Pernicone and L. Forni, Appl. Catal. A: Gen. 248 (2003) 97.

[42] Z. Kowalczyk, J. Sentek, S. Jodzis, E. Mizera, J. Góralski, T. Paryjczak and R. Diduszko, Catal. Lett. 45 (1997) 65.

[43] W. Raróg, Z. Kowalczyk, J. Sentek, D. Składanowski and J. Zieliński, Catal. Lett. 68 (2000) 163.

[44] W. Raróg, I. Lenarcik, Z. Kowalczyk, J. Sentak, M. Krukowski and J. Zieliński, Pol. J. Chem. 74 (2000) 1473.

[45] Z. Kowalczyk, M. Krukowski, W. Raróg-Pilecka, Szmigiel and J. Zieliński, Appl. Catal. A: Gen. 248 (2003) 67.

[46] Ch. Liang, Z. Wei, Q. Xin and C. Li, Appl. Catal. A: Gen. 208 (2001) 193.

[47] X.L. Zhenh, S.J. Zhang, J. Xu and K.M. KWei, Carbon 40 (2002) 2597.

[48] Ch. Liang, Z. Li, J. Qiu and C. Li, J. Catal. 211 (2002) 278.

[49] H.S. Zeng, K. Inazu and K. Aika, Appl. Catal. A: Gen. 219 (2001) 235.

[50] Z. Zhong and K. Aika, J. Catal. 173 (1998) 535.

[51] Z. Zhong and K. Aika, Inorg. Chem. Acta 280 (1998) 183.

[52] S.M. Yunusov, E.S. Kalyuzhnaya, B.L. Moroz, S.N. Agafonova, V.A. Likholobo and V.B. Shur, J. Mol. Catal. A: Chem. 165 (2001) 141.

[53] S.E. Siporin, R.J. Davis, W. Raróg-Pilecka, P. Szmigiel and Z. Kowalczyk, Catal. Lett. 93 (2004) 61.

[54] Z. Li, Ch. Liang, Z. Feng, P. Ying, D. Wang and C. Li, J. Mol. Catal. A: Chem. 211 (2004) 103.

[55] W.F. Han, B. Zhao, C. Huo and H.Z. Liu, Chin. J. Catal. 25 (2004) 194.

[56] C.J.H. Jacobsen, J. Catal. 200 (2001) 1.

[57] T.W. Hansen, J.B. Wagner, P.L. Hansen, S. Dahl, H. Topsoe and C.J.H. Jacobsen, Science 294 (2001) 1508.

[58] Z. Kowalczyk, Catal. Lett. 37 (1996) 173.

[59] Z. Kowalczyk, J. Sentek, S. Jodzis, R. Diduszko, A. Presz, A. Terzyk, Z. Kucharski and J. Suwalski, Carbon 34 (1996) 404.

[60] Z. Kowalczyk, S. Jodzjs, W. Raróg, J. Zieliński and J. Pielaszek, Appl. Catal. A: Gen. 173 (1998) 153.

[61] Jandel Scientific GmbH, *Peakfit, Version 3.11*, Jandel Scientific GmbH D-40699 Erkrath, Germany (1990).

[62] K.C. Taylor, J. Catal. 38 (1975) 229.

[63] N.E. Buyanova, A.P. Karnaukhov, N.G. Koroleva, I.D. Ratner and O.N. Černavska, Kinet. Katal. 13 (1972) 1533.

[64] A. Borodziński and M. Bonarowska, Langmuir 13 (1997) 5613.

[65] J.I. Langford, D. Louer and P. Scardi, J. Appl. Cryst. 33 (2000) 964.

[66] Z. Kowalczyk, S. Jodzis, W. Raróg, J. Zieliński, J. Pielaszek and A. Presz, Appl. Catal. A: Gen. 184 (1999) 95.