Effect of K, Cs and Ba on the kinetics of NH_3 synthesis over carbon-based ruthenium catalysts

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The kinetics of NH_3 synthesis over carbon-based ruthenium catalysts promoted with barium or alkali was studied. Both the ammonia partial pressure dependencies of the reaction rates ($T = 400\,^\circ C$, $p = 63$ bar, $H_2 : N_2 = 3 : 1$) and the pressure variations of the activity ($T = 370\,^\circ C$, $p = 4$–63 bar, $H_2 : N_2 = 3 : 1$) were found to be different for Ba and for the alkali (K, Cs). Ba–Ru/C proved to be more sensitive to the NH_3 content and to the total pressure. The rate of synthesis over the alkali-promoted catalysts is, in turn, much stronger influenced by the ruthenium dispersion. TOFs of NH_3 synthesis for the promoted samples at 370 °C and 4 bar (Ba 0.085 1/s, Cs 0.05 1/s, K 0.035 1/s) are significantly higher than that for the Ru(0001) basal plane (0.0085 1/s results from the literature data at 370 °C, 2 bar). The most active Ru/C samples (Ba or Cs) exceed significantly the fused iron catalyst, especially at high conversions.

Keywords: ammonia synthesis, kinetics, ruthenium catalysts, promotional effect

1. Introduction

Both iron and ruthenium exhibit high activity in ammonia synthesis. Iron catalysts manufactured by fusion of magnetite with small amounts of promoters (K_2O, Al_2O_3, CaO) have been commonly used in industrial plants and have been studied intensively for over 80 years.

The history of ruthenium as a catalyst for NH_3 synthesis is much shorter. The first papers in this field were published by Aika and his group, who studied numerous Ru catalysts deposited on various inorganic supports or carbon [1–11] and promoted with alkali metals or their oxides, alkaline earth metal oxides and lanthanide oxides. Muhler's group studied intensively the caesium-promoted Ru/MgO catalytic system [12–14], which proved to be very promising for industrial application. Haldor Topsøe Company developed its own Ru catalyst supported on magnesia–alumina spinel ($MgO{\cdot}Al_2O_3$) [15]. The advantage of this support is that Cs does not cause any sintering of Ru particles [15], an effect being observed in the case of MgO itself [6].

Primary attention should be paid, however, to the Ru catalysts supported on carbon. Such a catalyst was worked out by the BP, Engelhard and Kellog's group [16] and it was successfuly used in the Kellog advanced ammonia process (KAAP). The first commercial application of the KAAP catalyst (Kitimat, 1992) was, in fact, a retrofit to increase the capacity of an existing plant [17,18]. The next two applications (Los Angeles 1996 and Brisbane 1997) were also as revamps to increase capacity [17,18]. More recently (1998), however, Kellog Brown and Root built up two fully new plants in Trinidad, both of high capacity (1850 t/d) and of low pressure (91 bar). The overall ammonia production based on the KAAP technology (five operating plants) exceeds 6800 t/d at present, which is still much lower than the overall capacity of conventional, iron-based installations. Nevertheless, the trend to replace partly iron with ruthenium seems to be rather obvious.

Unfortunately, neither the chemical composition, nor the preparation procedure of the KAAP catalyst have been disclosed so far to the public domain. It is only known from the BP patents [19,20] and from Tennison [16] that carbon treated preliminarily at extremely high temperature of around 2000 °C was used as a support (so called high surface area graphite) and that alkali and barium promote strongly the synthesis of ammonia.

The high activity of the promoted ruthenium catalysts supported on the thermally modified carbon has been confirmed by the results of our own high-pressure NH_3 synthesis studies [21–24] and, recently, by the studies of Forni et al. [25,26]. Both groups demonstrated that potassium, caesium and barium might be used as effective promoters. There is doubt, however, as to the effect of individual promoters. According to our studies, the Ba–Ru/C system proved to be more than twice as active as the system promoted with potassium [23], the latter being slightly less active than that promoted with caesium [22]: $Ba \gg Cs > K$. In contrast, the rank obtained by Forni et al. [25,26] was ordered as follows: $Cs > Ba \gg K$. The above discrepancy cannot be easily explained due to the differences in the methods of activity evaluation and the differences in the tests parameters. Hence, the purpose of our present work was to study in detail the effect of potassium, caesium and barium on the kinetics of NH_3 synthesis. The term kinetics includes both the influence of NH_3 content in the gas phase on the reaction rate and the influence of total pressure on the

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catalyst activity. To get a closer insight into the role of the three promoters and aiming at better understanding of the promoted Ru/C systems the effect of ruthenium dispersion has also been investigated. For comparison, an industrial fused iron catalyst of high quality has been studied.

2. Experimental

2.1. Catalysts

Two carbon materials (C **I** and C **II**) were used as supports of the Ru catalysts, both obtained from the same, commercially available, raw active carbon (Norit RO 08). Carbon **I** was prepared by a single-step, high-temperature treatment (1900 °C) of the commercial product in a helium atmosphere [27]. Carbon **II** was obtained from carbon **I** by its subsequent partial gasification in flowing CO_2 up to about 20% loss of mass followed by cooling in argon. The prepared supports exhibited similar graphite-like structure, as evidenced by XRD, differing with their texture, i.e., the BET surface areas (66 and 330 m^2/g) and mercury porosimetry areas (60 and 110 m^2/g, respectively, for C **I** and C **II**).

Deposition of a ruthenium precursor onto the surface of the supports was performed by the impregnation from acetone solutions of $RuCl_3 \cdot 0.5H_2O$. After drying in air (90 °C, 24 h) the samples were reduced in hydrogen and passivated. The contents of the metal in both the unpromoted Ru/C materials were the same, equal to 9.1 wt%. However, due to the difference in the carbons texture, the dispersions of ruthenium were significantly different: the measurements of oxygen chemisorption performed at 273 K according to the procedure described previously [24] have shown that fractions of Ru atoms exposed (FE_{O_2}), i.e., the number of surface metal atoms referred to the total number of metal atoms, were equal to 0.215 and 0.62 for Ru/C **I** and Ru/C **II**, respectively, when assuming the same $O:Ru = 1.1:1$ stoichiometry [28,29].

The promoters (K, Cs, Ba) were introduced by impregnation from aqueous solutions of their salts (nitrates) followed by drying in air and crushing, to obtain a 0.2–0.6 mm fraction used subsequently in the kinetic studies of NH_3 synthesis. Since oxygen overestimates the dispersion of ruthenium (FE) in the presence of alkali [23], all the promoted samples were characterised by hydrogen chemisorption, according to the procedure described elsewhere [24]. The chemical composition and fraction exposed (FE_{H_2}) of the prepared catalysts are collected in table 1.

2.2. Kinetic measurements of NH_3 synthesis

The experiments were carried out in a multichannel differential flow reactor operating with a high-purity stoichiometric H_2–N_2–NH_3 mixture (>99.99995%) of controlled ammonia content. The high purity of the gas is essential for the correctness of the measurements, since both iron [30,31] and promoted ruthenium [16] are sensitive to oxygen-containing contaminants. According to Fastrup [30], the deactivation of a fused iron catalyst is appreciable even at 450 °C when the concentration of oxygen is as low as 1.6 ppm.

Table 1
Characteristics of the promoted ruthenium catalysts supported on carbons.

Sample	Ru in Ru + C (wt%)	Promoter/ruthenium (mol/mol)	FE_{O_2} [a]	FE_{H_2}
K–Ru/C	9.1	2.6	0.215	0.20
Cs–Ru/C	9.1	1.5	0.215	0.21
Ba–Ru/C	9.1	0.43	0.215	0.24
K–Ru/C	9.1	3.5	0.62	0.39
Cs–Ru/C	9.1	2.9	0.62	0.48
Ba–Ru/C	9.1	0.7	0.62	0.44

[a] As determined for the unpromoted Ru/C catalysts.

Optionally, the reactor tubes of 4.5 mm in internal diameter and 7.2 mm in diameter were applied in the measurements, depending on the activity of the catalysts tested. Each of the tubes was equipped with a separate thermocouple (0.5 mm in diameter) moveable along the catalyst layer that allowed an axial temperature profile to be taken and a mean level of temperature to be determined. In fact, the temperature gradients inside the catalytic beds proved to be rather negligibly small. Typically, they were lower than 2–3 °C. The concentration of ammonia in the outlet and inlet gas streams was determined interferometrically [22,32]. The rate of NH_3 synthesis was calculated from a mass balance for a differential catalyst layer, according to the equation [21,23,24]

$$r = \frac{x_2 - x_1}{(1 + x_1)(1 + x_2)m} \frac{17.03}{22.08} V_0,$$

where r is the reaction rate ($g_{NH_3}/g_{C+Ru}\,h$), x_1 and x_2 are the contents of NH_3 (molar fractions) in the inlet and outlet gas streams, respectively, V_0 is the flow rate of the gas (H_2, N_2) (dm^3(STP)/h) and m is the mass of the sample (g).

Prior to the kinetic measurements the samples were stabilised in a flowing $H_2 : N_2 = 3:1$ mixture under atmospheric pressure according to the following temperature program: slow heating to 400 °C (8 h) and maintaining at 400 °C for 16 h, heating to 430 °C (K–Ru/C and Cs–Ru/C) or 460 °C (Ba–Ru/C) and keeping this temperature for further 16 h. Then, the temperature was lowered, the gas was compressed and the measurement procedure was started.

The studies of the reaction rate vs. NH_3 content in the gas phase were performed under constant pressure of 63 bar and at constant temperature of 400 °C. The content of NH_3 in the gas entering the measuring reactor (x_1) was altered in the range 0.00–7.5%.

The effect of the total pressure on the catalysts activity was measured typically, i.e., an ammonia-free gas mixture ($x_1 = 0$) entered the reactor and the concentration of NH_3 in the outlet gas was determined. The studies were performed at low temperature of 370 °C and high space velocities (SV), to avoid any significant equilibrium limitations that could occur under a low pressure and at higher temperature. In consequence, the activities corresponding to the low conversions were determined.

3. Results

Figure 1 illustrates the pressure variations of NH$_3$ synthesis activity for the three promoters (K, Cs, Ba), the experiments being limited to the systems of lower dispersion ($\mathrm{FE}_{\mathrm{O}_2} = 0.215$). Both, the concentration of ammonia in the outlet gas (figure 1(a)) and the mean reaction rate (so called productivity) (figure 1(b)) are presented vs. total pressure for each sample. The difference in the catalytic behaviour of the Ba-promoted sample from one side and those of the alkali-promoted samples, from the other side, is well seen. The productivity of the former decreases successively when the pressure is lowered. In contrast, caesium and potassium keep their activities nearly constant vs. pressure. The following promotional effects of $\mathrm{Ba : Cs : K} = 7.5 : 1.25 : 1.0$ were found at the highest pressure of 63 bar and $2.75 : 1.45 : 1.0$, respectively, at the lowest pressure of 4 bar. Correspondingly, the TOF values of synthesis at 370 °C, based on the hydrogen chemisorption data were as follows: 0.25 (Ba), 0.05 (Cs) and 0.04 1/s (K) at 63 bar and 0.085 (Ba), 0.05 (Cs) and 0.035 1/s (K) at 4 bar.

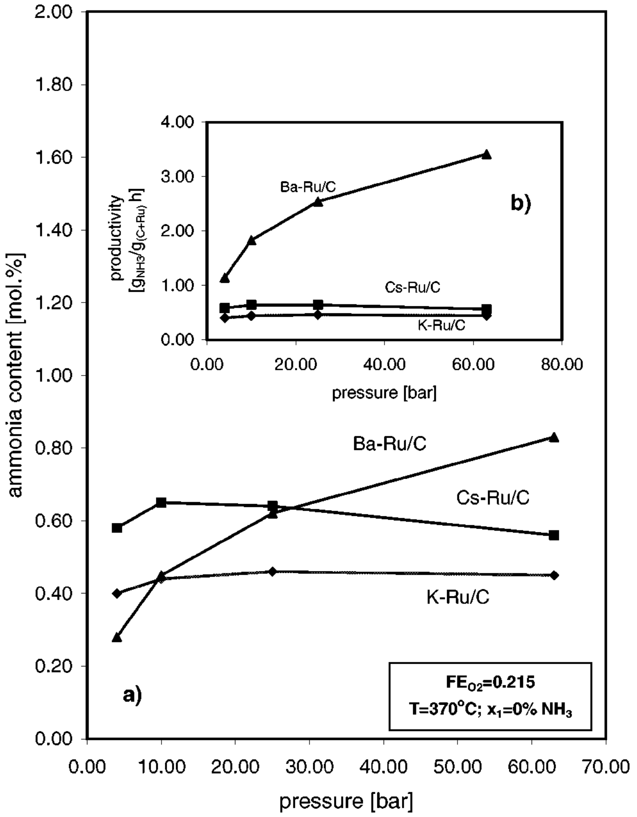

Figure 1. Effect of total pressure on the activity of the three promoted ruthenium catalysts (K–Ru/C, Cs–Ru/C and Ba–Ru/C) of low dispersion ($\mathrm{FE}_{\mathrm{O}_2} = 0.215$), $x_1 = 0$, $T = 370\,^\circ\mathrm{C}$, SV = 65 000 1/h for K and Cs, SV = 260 000 1/h for Ba–Ru/C. (a) Pressure variations of the NH$_3$ content in the effluent gas mixture and (b) productivity vs. pressure.

Figure 2(a) presents the ammonia partial pressure dependencies obtained for all the three promoted catalysts prepared from the Ru/C material of lower dispersion ($\mathrm{FE}_{\mathrm{O}_2} = 0.215$). As it is seen, the rate of the reaction over the Ba–Ru/C catalyst is much higher than that over Cs–Ru/C throughout the whole range of ammonia concentration in the gas (0–8%), the latter being only slightly higher than that over K–Ru/C. It is also seen that the Ba-containing system is more sensitive to the changes in ammonia content than the two other ones (K–Ru/C and Cs–Ru/C): about four-fold drop in the rate of synthesis is observed for Ba–Ru/C and only two-fold, or even lower, in the case of K–Ru/C and Cs–Ru/C when changing the concentration of ammonia from 1 to 8%. In consequence, a relative effect of barium, i.e., the effect referred to potassium (Ba/K) decreases significantly vs. NH$_3$ concentration (figure 2(b)) from the value of about 6.5 at 1% NH$_3$ to the value of about 2.5 at 8% NH$_3$, whereas the relative effect of caesium (Cs/K) remains almost constant, equal to about 1.3–1.4 only (see figure 2(b)) through the whole range of NH$_3$ content. It is worth of notice that the ratio of rates over Ba- and K-promoted samples (about 2.5 at 8% NH$_3$) agrees perfectly with the ratio reported previously [23] for similarly prepared specimens, the activity of which was measured under the same conditions of 400 °C and 8% NH$_3$.

Figure 3(a) shows the NH$_3$ partial pressure dependencies for the catalysts derived from the Ru/C precursor of higher dispersion ($\mathrm{FE}_{\mathrm{O}_2} = 0.62$). Qualitatively, the obtained relationships seem to be similar to those presented above: am-

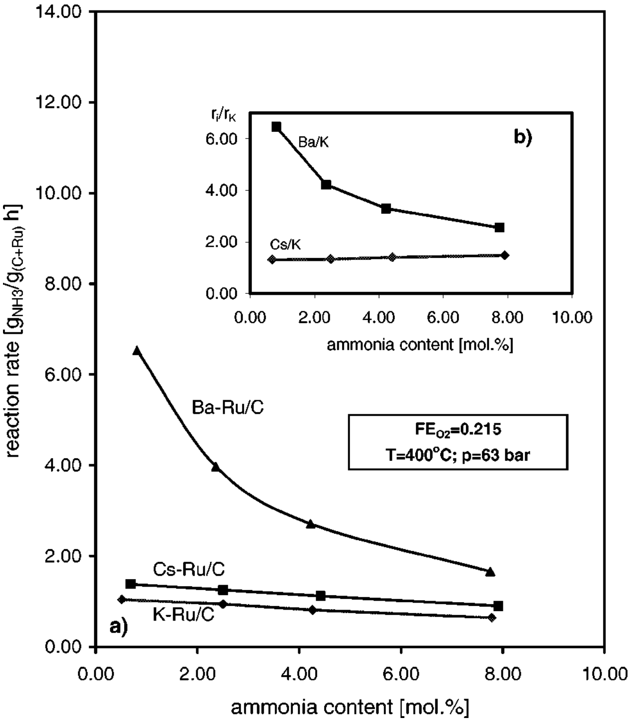

Figure 2. Ammonia content variations of the activity for the Ru/C catalysts of low dispersion ($\mathrm{FE}_{\mathrm{O}_2} = 0.215$), $T = 400\,^\circ\mathrm{C}$, $p = 63.0$ bar. (a) Reaction rate vs. NH$_3$ content in the gas and (b) the relative rate over Ba–Ru/C and Cs–Ru/C referred to K–Ru/C vs. NH$_3$ content.

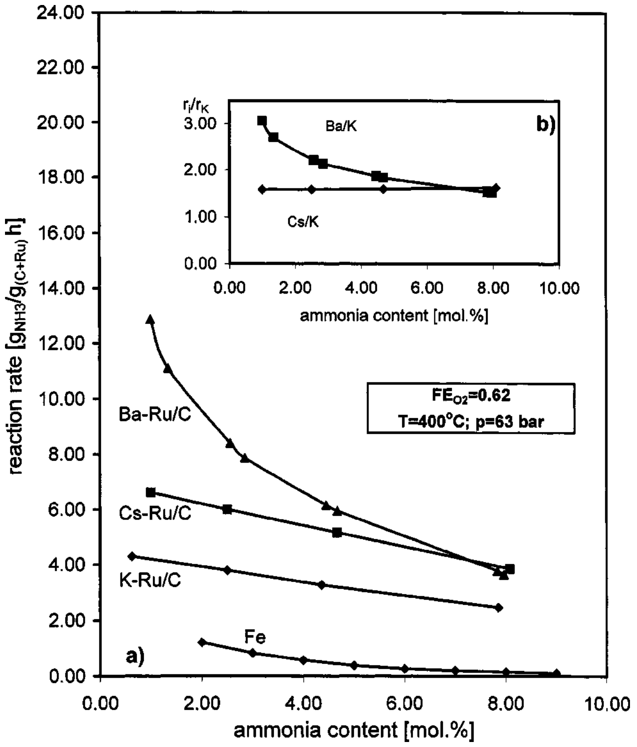

Figure 3. Ammonia content variations of the activity for the Ru/C catalysts of high dispersion ($FE_{O_2} = 0.62$) and for the fused iron catalyst (trace Fe), $T = 400\,^\circ C$, $p = 63.0$ bar. (a) Reaction rate vs. NH_3 content in the gas and (b) the relative rate over Ba–Ru/C and Cs–Ru/C referred to K–Ru/C vs. NH_3 content.

monia influences the rate of synthesis over Ba–Ru/C much stronger than the rate over both Cs– and K–Ru/C. There are, however, essential quantitative differences. Firstly, barium is considerably superior to caesium in the range of small ammonia concentrations only. At about 7–7.5% NH_3 the rates of synthesis are equal to each other, and above that value Cs is more effective than Ba results from the trend of the curves shown in figure 3 (a) and (b). Secondly, the difference between Cs and K (about 60%, see figure 3(b)) is higher than that observed for the corresponding samples of lower dispersion (about 30–40%, see figure 2(b)).

The comparison of the data presented in figures 2 and 3 shows clearly that the promoter effect depends upon the ruthenium dispersion: the three-fold increase in the dispersion, as measured by O_2 chemisorption for the unpromoted Ru/C precursors, is accompanied by an about two-fold increase in the reaction rate over the Ba-promoted catalyst and by the much higher, about four-fold and five-fold increase in the rates over K–Ru/C and Cs–Ru/C, respectively, regardless of the ammonia concentration in the gas phase. The combination of the NH_3 synthesis rates and hydrogen chemisorption data obtained for the promoted catalysts demonstrates (table 2) that TOF of synthesis over Ba–Ru/C is roughly independent of the Ru dispersion. This is in full agreement with our previous results [24]. In contrast, the alkali-doped catalysts are sensitive to dispersion: both potassium and caesium promote small ruthenium particles more effectively than those of larger size (see table 2).

Table 2
TOF (1/s) of ammonia synthesis at $T = 400\,^\circ C$, $p = 63$ bar, $x_{NH_3} = 8\%$, based on the hydrogen chemisorption data.

Catalytic system	TOF (H_2)	
	$FE_{O_2} = 0.215$	$FE_{O_2} = 0.62$
K–Ru/C	0.060	0.115
Cs–Ru/C	0.075	0.145
Ba–Ru/C	0.125	0.145

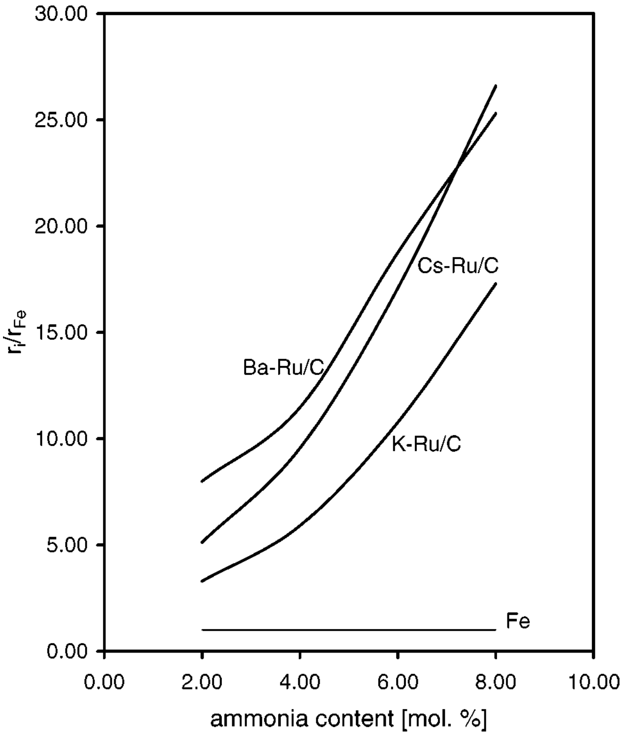

Figure 4. The ratio of reaction rates (as referred to mass unit) on the promoted Ru/C catalysts of high dispersion ($FE_{O_2} = 0.62$) and on the fused iron catalyst vs. ammonia content, $T = 400\,^\circ C$, $p = 63.0$ bar.

4. Discussion

First, it should be noticed that the Ru/C catalysts derived from the precursor of high dispersion ($FE_{O_2} = 0.62$) are significantly more active than the industrial fused iron catalyst used in the studies as a reference material (see figure 3). The beneficial effect of ruthenium is the higher, the higher the conversion is, as shown in figure 4. This remains in full agreement with the results of our previous kinetic studies [21] as well as with the industrial practice. It has been reported recently by Strait [17,18] that the KAAP radial-flow reactors installed in the Trinidad ammonia plants are equipped with four catalytic beds but only the first bed contains iron that operates at low conversions, the remaining three beds being filled with the KAAP Ru/C catalyst and operating at high conversions up to about 20% NH_3 in the gas.

From the scientific point of view, the question about the role of individual promoters seems to be essential. The performed studies demonstrate that the kinetic characteristics of barium-promoted catalyst is qualitatively different from those of potassium or caesium, thus suggesting the role of alkali to be different than the role of barium. The alkali promotion is commonly assumed to proceed *via* electron transfer from the alkali to ruthenium [16]. The electron-rich surface of the metal would be then more active for the N_2 dissociative chemisorption, which is believed to be the rate-limiting step in the NH_3 synthesis. Such a concept requires the alkali to be in a reduced state when operating. Support for this comes from the chemisorption studies [23], which demonstrate that oxygen is consumed by both ruthenium and potassium when supported on carbon, as well as from the recent XPS investigations [33]. The location of the alkali metals is, however, unclear. Tennison [16] considers the following three possibilities: (1) alkali is located within the crystallites of ruthenium, possible as a complex with nitrogen, (2) is on the support, but in contact with ruthenium (the "hot ring" promotion), (3) is on the ruthenium surface at a concentration resulting from the heats of adsorption on the metal and support. A high catalytic sensitivity of the alkali-promoted samples toward the ruthenium dispersion, as shown in the present work, suggests the first possibility to be unlikely. It is impossible, however, to distinguish between the other two options from the available data and further studies are necessary to explain the problem.

In contrast to alkali, there is no evidence for barium (on Ru/C) to exist in a reduced state under ammonia synthesis conditions [33]. It is reasonable to assume, therefore, that Ba acts as a structural promoter [16] that modifies the local arrangement of Ru surface atoms, thus creating the sites of high activity. The above concept implies that ammonia synthesis over ruthenium is a structure sensitive reaction as in the case of iron [34]. Unfortunately no direct evidence based on the Ru singe crystal studies has been presented for this so far. A reference should be given, however, to the recent papers of Dahl et al. [35,36], who measured both the rate of nitrogen dissociation [35] and the rate of NH_3 synthesis [36] over the close-packed Ru(0001) basal plane. They have shown clearly, that the N_2 adsorption is totally dominated by the steps on the Ru(0001) surface [35], i.e., the adsorption rate at the steps is at least nine orders of magnitude higher than on the terraces at 500 K. This means, that the ammonia synthesis reaction should be extremely structure sensitive on ruthenium [35]. Furthermore, Dahl and co-workers [36] found TOF of NH_3 synthesis over the Ru(0001) surface at 400 °C (2 bar pressure, $H_2 : N_2 = 3 : 1$, low conversions) and the apparent energy of activation to be 2×10^{-2} 1/s and 101 kJ/mol, respectively, which gives the TOF value equal to 8.5×10^{-3} 1/s at 370 °C. Under comparable conditions (370 °C, 4 bar, low conversions) the barium-promoted Ru/carbon catalyst exhibits the much higher TOF of about 8.5×10^{-2} 1/s, as results from our present studies. Such a big difference (an order of magnitude) can be justified neither by the difference in pressure conditions (2 and 4 bar, respectively), nor by the effect of carbon support, since the unpromoted Ru/C materials are known to be almost inactive in NH_3 synthesis [22]. This leads to the conclusion that more open and more active planes (compared to Ru(0001) investigated in [35,36]) are formed in the presence of barium if barium acts indeed as a structural promoter. The detailed N_2 TPD studies and the kinetic studies of ammonia decomposition over the same Ba-, K- or Cs-promoted Ru/C catalysts, which are in progress, should give a more decisive answer as to the role of the three promoters.

5. Conclusions

- The promoted ruthenium/carbon catalysts of high dispersion are much more active than the conventional fused iron catalyst, the difference being especially pronounced at high conversions.
- The barium-promoted Ru/C system shows the kinetic characteristics to be different from those of alkali (K– or Cs–Ru/C), i.e., the former is more sensitive to the variations of ammonia concentration in the gas mixture and more sensitive to the variations in the total pressure. The reaction rate (referred to mass unit) over the alkali-promoted samples depends, in turn, on the ruthenium dispersion much stronger than the rate over Ba–Ru/C. Hence, the rank of the promoters is affected by both the Ru dispersion and the conditions of the activity measurements; caesium being, however, always more effective than potassium.
- In comparable conditions, all the promoted Ru/C catalysts exhibit much higher TOF values than over the close-packed Ru(0001) single crystal plane. It is suggested that barium acts as a structural promoter rather than an electronic one, the latter type of promotion being characteristic for the alkali only.

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