

Ammonia synthesis with barium-promoted iron–cobalt alloys supported on carbon

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Abstract

Iron–cobalt alloys supported on carbon were investigated as ammonia synthesis catalysts. Barium was found to have a promoting effect for Fe with an optimum atomic ratio Ba/Fe of 0.35. At this Ba loading, a local maximum for the NH₃ synthesis activity was found at 4 wt% Co by varying the Fe/Co ratio. Samples containing only Co and no Fe, however, yielded by far the most active catalysts (7.0 μmol (NH₃) g⁻¹ s⁻¹, 673 K, 10 bar). Barium was a very efficient promoter for Co, increasing the NH₃ synthesis activity by more than two orders of magnitude compared to the unpromoted Co samples, while it was not as effective for Fe. Power-law kinetic investigation revealed that, compared to the commercial Fe-based NH₃ catalyst, the Ba–Co/C samples showed a lower inhibition by NH₃ and were more active under ordinary ammonia synthesis conditions.

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1. Introduction

During the past century, ammonia has been produced almost exclusively by the Haber–Bosch process. In this process, the multipromoted iron catalyst has been installed in all industrial facilities [1,2]. Although this catalyst has many virtues, such as high activity, a long lifespan, and relatively low cost, its overall activity is strongly influenced by the decreasing reaction rates at high NH₃ concentrations. Because of their strong interaction with iron, adsorbed nitrogen species are the most abundant intermediates on the catalyst surface under industrially relevant reaction conditions. This is the reason for the ubiquitous product inhibition in NH₃ synthesis [3,4]. Consequently, sufficient reaction rates can be obtained only at elevated temperatures around 650–800 K, which for thermodynamic reasons makes it necessary to work at high pressures, typically above ca. 140 bar [5].

Large catalyst volumes and expensive reactor materials that can withstand these relatively harsh conditions have to be applied, leaving some room for improvement of the overall economy of the established NH₃ process.

Several attempts were undertaken in the past decades to develop NH₃ synthesis catalysts with lower NH₃ inhibition and higher activities. A significantly lower inhibition by NH₃ was observed for Ru catalysts supported on graphitized carbon [1,6–9]. Some years ago, a cesium and barium co-promoted Ru catalyst was introduced industrially in the Kellogg advanced ammonia process [10–13]. This Ru/C catalyst is about one order of magnitude more active but also at least 100 times as expensive as the conventional Fe catalyst [14]. The high affinity toward H₂, combined with the possibility of support methanization, especially at temperatures above 730 K, is an additional disadvantage of the Ru/C catalyst [15]. Although MgO [7], MgAl₂O₄ [16], and BN [17,18] were presented very recently as alternatives for the carbon-support material, the long-term economic success of the Ru catalyst system seems to be debatable and very dependent on the Ru price as well as catalyst reclaim costs.

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Elements close to the maximum of the volcano curve for ammonia synthesis (Fe, Ru, Co) have all been shown to exhibit an intermediate binding energy to nitrogen [1,19]. It turns out that the nitrogen binding energy to the catalyst surface is linearly correlated with the activation energy for N_2 dissociation for both unpromoted [19] and promoted catalysts [20]. For elements at the right-hand side of the volcano curve a reduced binding energy is found whereas a higher nitrogen binding energy is found for elements at the left-hand side of the volcano curve. It appears that improved ammonia synthesis catalysts can only be found by alloying and/or by use of improved promoters. Cobalt is located at the right-hand side of the volcano curve and so far only low catalytic activities have been reported for cobalt catalysts [1,21–23]. Iron, on the other hand, is located at the left-hand side of the volcano curve. From the recently introduced interpolation concept [24] it thus appears that an improved catalyst could be achieved by alloying Fe and Co since they are located on each side of the volcano curve. Indeed, Taylor and coworkers [25] and recently also Kaleńczuk [26] showed that fused Fe–Co catalysts with ca. 3–6 wt% Co have slightly higher activities than the corresponding Fe catalysts in NH_3 synthesis. Contrarily, a maximum in activity was found at 20 wt% Co for an Al_2O_3 -supported catalyst [27]. Changes in the NH_3 inhibition or apparent activation energy with increasing cobalt content for supported catalysts have not been reported for the FeCo Al_2O_3 -supported catalysts, and results have generally been published only for low cobalt content. Kinetic investigation by Kaleńczuk [26] on a fused FeCo catalyst showed no change in the apparent activation energy, which was attributed to a segregation and enrichment of Fe on the catalyst surface in the FeCo system, which is otherwise completely miscible.

The target of this work is to investigate the potential of the Fe–Co system as ammonia synthesis catalysts and to obtain a more detailed insight into the reaction kinetics. Barium was selected as the promoter in these investigations since it has previously been demonstrated that Ba is an excellent promoter and provides resistance to methanization (of carbon supports) for Ru-based catalysts [1,6–9] and there have been no reports on carbon-supported barium-promoted Fe/CO alloy catalysts. There are only very few reports on Ba promotions in the Fe/Co system—one report on the NH_3 synthesis using fused FeCo catalysts promoted with $BaAlO_4$ and $BaZrO_3$ [28] as well as one report on clean and Ba-promoted Fe surfaces in N_2 adsorption studies [29].

2. Experimental

2.1. Catalyst preparation

The active carbon support material (Vulcan XC-72; $174\text{ m}^2/\text{g}$) is cleaned by heating in formier gas ($N_2:H_2 = 9:1$) at 1373 K for 48 h. This procedure ensures the removal of any heteroatoms and is absolutely necessary to obtain

reproducible and active supported metal catalysts [30]. The obtained carbon material is impregnated by incipient wetness impregnation (IWI) [31] with a solution containing $Fe(NO_3)_3$ and $Co(NO_3)_2$ salts and dried at 333 K for 6 h and at 393 K for 18 h. All samples are prepared to have a mass ratio of (Fe + Co metal)/carbon = 0.1. The barium promoter is subsequently introduced by IWI as $Ba(OOCCH_3)_2$. The catalyst precursor is dried again, pressed into tablets, and crushed to a sieve fraction of 0.35–0.71 mm. The obtained material is placed in the test reactor and activated with a stoichiometric (1:3) $N_2:H_2$ mixture at 1.3 bar as described below.

The following standard activation procedure is optimized for the Ba–Fe/C catalysts and then applied to all catalysts (total flow: 267 N ml min^{-1}): (i) heating from 298 to 573 K with 300 K h^{-1} ; (ii) holding for 1 h; (iii) heating from 573 to 793 K with 20 K h^{-1} ; (iv) holding for 5 h; (v) cooling from 793 to 713 K with 100 K h^{-1} ; (vi) start of measurements. For the last 60 min in step (iv) as well as in step (v) the pressure is increased to 10 bar and the total flow reduced to 40 N ml min^{-1} in order to bring the reduction process to completion. The unpromoted samples, which are reduced under significantly milder conditions than the Ba-promoted samples, are activated only up to a temperature of 723 K to avoid methanization of the support, especially in the case of Co-rich samples. The commercial catalyst (KM1) consisting of 94% Fe, 2.8% CaO, 2.5% Al_2O_3 , and 0.6% K_2O is used for comparison [32]. The published data on the activity measurements for this catalyst can be reproduced to within 5% using the present equipment.

2.2. Activity measurements

The experimental setup for the activity measurements consists of a glass-lined stainless steel microreactor (i.d. = 3 mm) placed in a vertically arranged, steel-lined oven with two independently heated zones to ensure a satisfactory temperature profile. The catalyst is held within the reaction tube by plugs of quartz wool. H_2 , N_2 , and He (99.9999% each) are passed over a guard reactor (25 g of an activated commercial catalyst (KM1), at room temperature) to ensure the purity of the used gases before the test reactor is entered. A mass spectrometer (Baltzer QMG 421) is used to analyze the reaction components and is repeatedly calibrated with a certified ammonia gas (2% NH_3 in N_2). An NDIR detector (Fisher–Rosemount, NGA 2000; detection range: 0–800 ppm) is applied for the unpromoted Co catalyst to obtain reliable results for very low NH_3 concentrations. The gas lines between the test reactor and the detection unit are heated to about 380 K to prevent adsorption of ammonia onto the walls.

Activity measurements are performed in the temperature range of 593–713 K, a pressure range of 5–20 bar, and with total flows of 40 – 267 N ml min^{-1} of a stoichiometric (1:3) $N_2:H_2$ mixture. Two series of activity measurements conducted with 300 and 600 mg of catalyst, respectively, are

performed to ensure the reproducibility of the results and to ensure the absence of heat and mass-transfer limitations. During the measurements of the activity as a function of the H_2 (N_2) content in the synthesis gas, a constant total flow of $120 \text{ N ml min}^{-1}$ and a constant N_2 flow of 40 N ml min^{-1} ($H_2 = 20 \text{ N ml min}^{-1}$) are maintained while varying the H_2 flow from 0 to 80 N ml min^{-1} ($N_2: 0\text{--}100 \text{ N ml min}^{-1}$) and balancing the total flow with He.

2.3. Catalyst characterization

In both the temperature-programmed desorption (TPD) of N_2 and the temperature-programmed surface reaction with H_2 (TPSR), the catalyst is pretreated (823 K , 10 bar , total flow 50 N ml min^{-1}) with a stoichiometric (1:3) $N_2:H_2$ mixture and then pure N_2 gas for 1 h each. The catalyst is cooled to and kept at 540 K in N_2 (50 N ml min^{-1}) for ca. 12 h. In the TPSR case, the system is cooled under N_2 to room temperature. Subsequently, the gases are changed to He (TPD) or H_2 (TPSR, 50 N ml min^{-1} each), respectively, by repeated evacuation and flushing of all gas lines before the reactor. After the catalyst is flushed for ca. 1 h, the temperature is raised with 5 K min^{-1} to 550 K and kept there for at least 30 min.

Temperature-programmed reduction (TPR) is performed by using a 5% H_2 in Ar mixture, heating the samples with 5 K min^{-1} from 298 to 923 K , and holding at this temperature for 30 min. The water formed in the reduction process is condensed in a cryogenic trap before the thermoconductivity detector. XRD measurements were performed on a Philips analytical X-ray PC-APD system using Cu anodes ($\alpha_1 = 1.5406 \text{ \AA}$, $\alpha_2 = 1.5444 \text{ \AA}$, $2\theta = 5\text{--}50^\circ$, step size 0.02°).

3. Results and discussion

3.1. X-ray powder diffraction

Crystal sizes were evaluated from X-ray powder diffraction (XRPD) patterns (see Fig. 1) of unpromoted, reduced samples using the Debye–Scherrer equation. The results show that average crystal sizes around 20 nm are observed both in samples with Fe content from 5 to 50% (all have bcc structures) as well as in the samples with Co content of 95 and 100% (most likely mixture of hcp Co of fcc Co).

As reported very recently [23], XRPD patterns obtained from slightly passivated, Ba-promoted samples using synchrotron radiation revealed that Co can only be detected in its cubic form (fcc). This was supported by in situ XRPD measurements performed under NH_3 synthesis conditions. $BaCO_3$ was detected also by in situ XRPD, and the formation of carbonates was confirmed by XPS.

3.2. Ba-promotion studies

Promotion can strongly affect the performance of a catalyst. Therefore, optimization of the promoter content is necessary to explore the full potential of a given catalytic system. The catalytic activity of the barium-promoted iron catalyst supported on carbon shows a maximum upon increasing the Ba/Fe ratio. The optimum is found around an atomic Ba/Fe ratio of 0.35 (see Fig. 2). It can be seen from Fig. 2 that a slight change in the promoter content, resulting from minimal batch-to-batch variations during the catalyst preparation, does not have a significant influence on the activity of the catalyst. The optimum content of the Ba promoter found for the Fe catalyst is applied also for all other Fe–Co catalysts with different Fe/Co ratios. The promotion of Fe and Co with other electropositive elements as well as

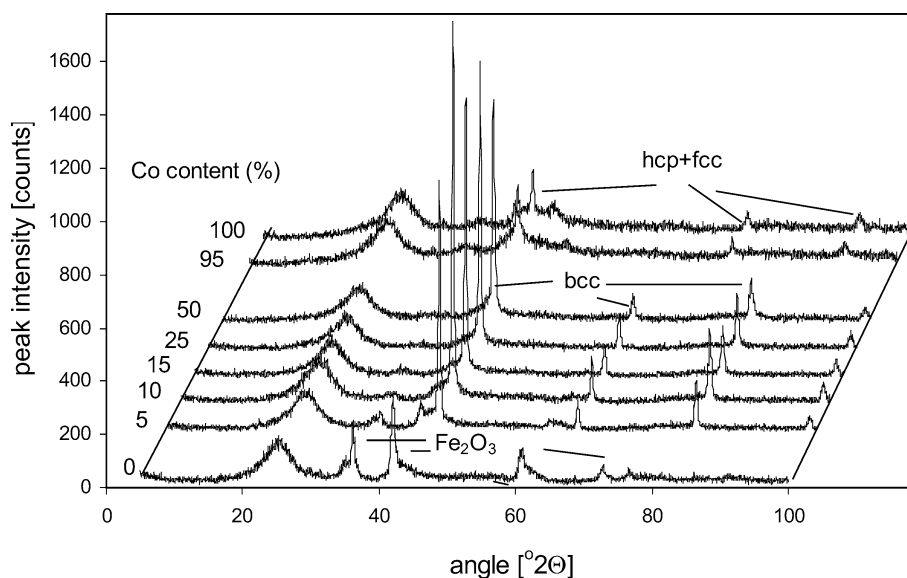


Fig. 1. Powder XRD of unpromoted, reduced, and passivated FeCo samples on active carbon substrates. Please note that the sample containing Fe only is completely reoxidized in air after the passivation procedure.

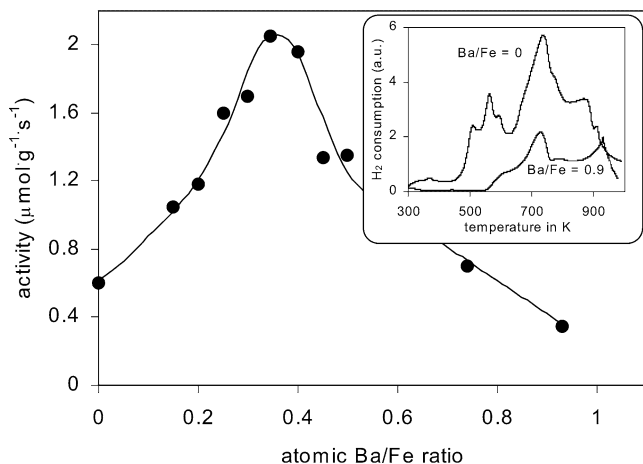


Fig. 2. Activities for carbon-supported Fe catalysts with varying atomic Ba to Fe ratios ($T = 673$ K, $p = 10$ bar, $H_2:N_2 = 3:1$, NH_3 outlet concentration = 0.75%, 600 mg catalyst). TPR profiles for an unpromoted (Ba/Fe = 0) and a strongly promoted sample (Ba/Fe = 0.94).

copromotion with more elements and variation of the Ba/Co ratio will be the subject of further investigations.

The overall activity decreases significantly at Ba-promoter content above atomic Ba/Fe ratios of ca. 0.4. It is discussed throughout the literature [33] that promoter species, e.g., Ba–O coadsorbates, are located at the surface of Fe and Ru in NH_3 synthesis catalysts. This leads not only to a promotion of the catalyst, but also to an increased blocking of the active sites on the surface of the transition metal. Thus, at high promoter concentrations very few active sites are accessible. Furthermore, higher temperatures are necessary to complete the reduction of Fe in Ba-promoted samples [33,34]. This is underscored by TPR results for carbon-supported Fe samples with and without a Ba promoter (see inset in Fig. 2). While the reduction of the unpromoted sample runs to completion within the TPR experiment, the H_2 consumption for the sample with a high atomic Ba/Fe ratio of 0.9 reaches only ca. 50% of the theoretical value within the TPR cycle using a gas containing 5% H_2 at atmospheric pressure. Therefore, appropriate temperatures, as well as sufficient reaction times in combination with high partial pressures of H_2 (and possibly NH_3) must be applied to run the activation process to completion. The importance of applying relatively high reduction temperatures was previously reported, e.g., for the system $KOH-FeCo/\gamma-Al_2O_3$ [27] and also for Ba-promoted Ru catalysts [7,14].

3.3. Activity measurements

To compare the two sets of activity measurements obtained with different amounts of catalysts, the mass-based activities are shown for the same NH_3 outlet concentration of 0.75% in Fig. 3. The substitution of Fe by only a few percent of Co significantly increases the activity of the catalysts. At a pressure of 10 bar, an activity maximum is found at a Co content of ca. 4 wt% for temperatures ranging from

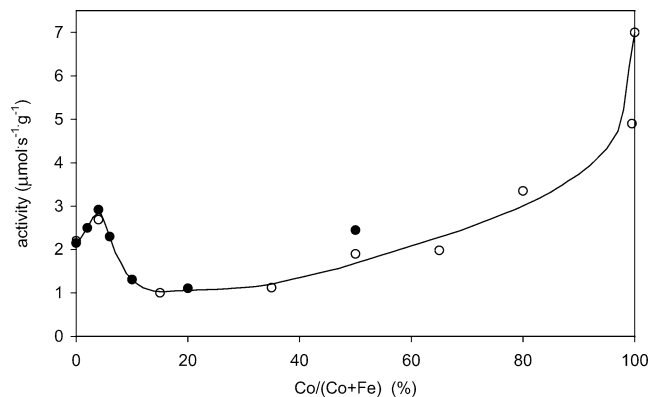


Fig. 3. Effect of the Co concentration on the activities of Ba-promoted Fe samples at $T = 673$ K, $p = 10$ bar, $H_2:N_2 = 3:1$, NH_3 outlet concentration = 0.75%. Masses of the catalysts: 600 mg (closed circles) or 300 mg (open circles), respectively.

593 to 713 K. This is well in agreement with the reported optima for K-promoted fused Fe–Co alloys [26]. The difference from the reported optimum of $Co/(Fe + Co) = 0.2$ for alumina-supported alloys [27] remains ambiguous but it was suggested that an alumina-induced segregation of Fe and Co occurred and therefore a higher surface concentration of Fe resulted for these oxide-supported samples. This segregation process was not further explained; however, possible explanations could include a strong interaction of Co with alumina (spinell-type structures, “Thenards blue”) before the reduction process and a known stronger Fe–N binding energy compared to that of Co–N [1,23].

An increase in the Co concentration to ca. 20 wt% of the transition metal content results in a sharp decrease of the NH_3 synthesis activity. However, to our surprise, the ammonia production is very much enhanced, if the Co content is increased to 50% and above. The highest activities ($7.0 \mu mol g^{-1} s^{-1}$) are obtained for the sample containing 100% Co. The NH_3 formation rate of these samples is very sensitive to traces of Fe; the addition of 0.5% Fe to pure Co samples reduces the activity by ca. 30% to $4.9 \mu mol g^{-1} s^{-1}$. We suggest that this is explained by the stronger interaction of Fe than of Co with nitrogen resulting in an enrichment of Fe on the surface of the transition metal crystals. These findings are quite different from results obtained by Kaleńczuk [27], who measured a drastic drop to almost negligible activities for a K-promoted, alumina-supported sample with ca. 80% Co.

Although the reason for the surprisingly high activities of the Ba-promoted, carbon-supported Co catalysts has not yet been explained, clearly in NH_3 synthesis, barium is a very efficient but hitherto unexplored promoter for carbon-supported Co catalysts. Compared to the unpromoted sample, the activity increases ($T = 633-673$ K, 10 bar, total flows of 80–267 $N ml min^{-1}$) by a factor of ca. 300–500. This factor is much higher compared to that of the Ba-promoted Fe catalyst (ca. 2–4) or Ru (ca. 10–20 [14]) on carbon. Based on the XRPD results it can be assumed that the increased activity of Co-rich samples is not the

result of significantly increased surface areas for these alloy compositions. In the following we shall present a plausible explanation of the observed activity curve, which we will ascribe to two factors. The first factor is that of alloying. According to the interpolation concept, a CoFe alloy has a nitrogen binding energy, which is intermediate between that of Co (which is too low) and Fe (which is too high) [24]. Consequently, a higher activity is achieved with the alloy. The optimal Co content is dependent on the test conditions as demonstrated by our concept of optimal catalyst curves [35]. The higher the ammonia partial pressure the higher the optimal cobalt content.

The second factor is that of promotion. It is clear that Ba is a significantly better promoter for metals at the right-hand side of the volcano curve than for metals at the left-hand side, whereas the opposite is true for alkali metal promoters. Thus, the local maximum results from the optimal binding energy of a Fe/Co alloy promoted with Ba (which is not the optimal promoter for this system), whereas the maximum activity at high Co content results from the efficient promotion of Co by Ba.

3.4. Kinetic studies

Compared to Fe, nitrogen species should not be bound so strongly to Co. Therefore, the inhibition of the NH_3 synthesis rate by the product NH_3 itself should be less pronounced. To explore this in more detail, the experimental data were evaluated by applying simple power-law kinetics (see Eq. (1) in [36])

$$r_{\text{NH}_3} = k p_{\text{NH}_3}^\alpha p_{\text{N}_2}^\beta p_{\text{H}_2}^\gamma, \quad (1)$$

leading to

$$r_{\text{NH}_3} = k_1 p_{\text{NH}_3}^\alpha, \quad (2)$$

assuming constant partial pressures of N_2 and H_2 . Integration of Eq. (2) over time and by substitution of time with the quotient of catalyst volume and total flow (F) leads to

$$\ln p_{\text{NH}_3} = \frac{1}{(1-\alpha)} \ln \frac{1}{F} + C \text{ (constant)}, \quad (3)$$

where the exponential factor α for the NH_3 partial pressure can be obtained by plotting $\ln(p_{\text{NH}_3})$ versus $\ln(1/F)$.

In the temperature range of 593–673 K very similar α values are obtained with regression coefficients (R^2) usually higher than 0.995. The dependency on the NH_3 concentration of the total flow is shown for selected catalysts in Fig. 4. The Ba-promoted Co sample and the KM1 catalyst have nearly the same high NH_3 outlet concentration at low total flows while the NH_3 output is significantly lower for KM1 at high flows showing a stronger NH_3 inhibition for the commercial catalyst compared to the Co-based catalyst.

At higher temperatures, the measured NH_3 concentrations are too close to equilibrium (e.g., $c_{\text{eq}}(\text{NH}_3) = 2.3\%$ at 10 bar and 713 K), so the NH_3 decomposition reaction cannot be neglected anymore and it erroneously results in more

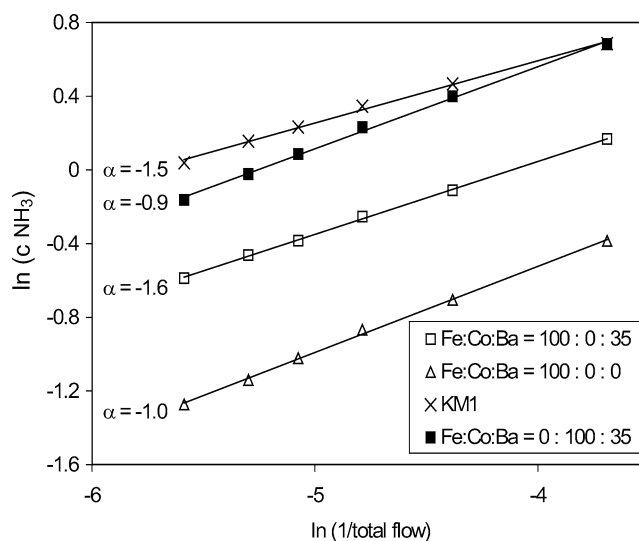


Fig. 4. Determination of the exponential factor α (NH_3 inhibition, slope = $1/(1-\alpha)$) at $T = 673$ K, $p = 10$ bar, $\text{H}_2:\text{N}_2 = 3:1$, FeCo catalysts: 300 mg, KM1: 200 mg.

negative α values. The same applies at lower temperatures, however, to a much lesser extent. Therefore, the shown α values are the average numbers from the α values obtained in the temperature range from 593 to 673 K (e.g., the following values are obtained for the Ba/Co catalyst: $\alpha_{593\text{K}} = -0.72$, $\alpha_{633\text{K}} = -0.86$, $\alpha_{673\text{K}} = -1.05$, $\alpha_{\text{av}} = -0.88$; but $\alpha_{713\text{K}} = -1.85$).

The correlation between the transition metal composition and the resulting NH_3 inhibition of the Ba-promoted FeCo catalysts is shown in Fig. 5 and compared to data in the literature for the commercial Fe catalyst and for selected Ru catalysts in Table 1. In summary, the α values increase (the inhibition by NH_3 decreases) with increasing Co content in the Fe/Co alloy. The Ba-promoted Fe catalyst shows the same NH_3 inhibition behavior (α values of -1.5 – -1.6) as the commercial catalyst KM1 (Figs. 4 and 5 and

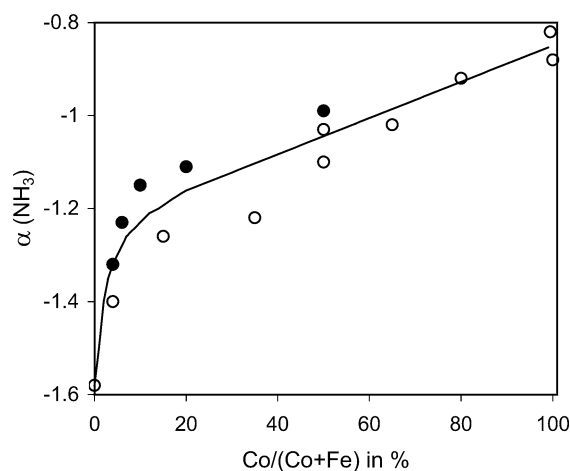


Fig. 5. NH_3 inhibition (α -values) for Ba-promoted catalysts; mass of the catalyst: 600 mg (closed circles) and 300 mg (open circles), $T = 633$ K, $p = 10$ bar, $\text{H}_2:\text{N}_2 = 3:1$.

Table 1

Comparison of reaction orders and apparent activation energies of a selection of unpromoted and promoted FeCo and Ru catalysts

Catalyst	p (bar)	T (K)	α (NH ₃) ^a	β (N ₂) ^a	γ (H ₂) ^a	E_A ^b (kJ mol ⁻¹)
Unprom. Fe/C	10	593–673	-1.0	0.9	1.5	143
Unprom. Co/C	10	593–673	-0.3	0.8	-0.4	149
Ba _{0.35} -Fe/C	10	593–673	-1.6	1.2	2.3	104
Ba _{0.35} -Fe ₅₀ Co ₅₀ /C	10	593–673	-1.1	0.9	1.8	104
Ba _{0.35} -Co/C	10	593–673	-0.9	0.9	1.2	102
Sr _{0.35} -Co/C	10	633–713	-0.8	1.0	0.9	110
Fe-cat. (KM1)	10	593–673	-1.5	0.9	2.2	70
Ru/MgO [7]	20	588–673	-0.6	0.8	-0.7	79
Cs-Ru/MgO [14]	20	533–648	-0.1	1.0	-1.2	106
Ba-Ru/MgO [7]	20	513–588	-0.6	0.8	-0.6	77

^a Average value in the given temperature range, except Ru-based catalysts.^b Calculated for a constant NH₃ outlet concentration.

Table 1). On the other hand, the Ba-promoted Co catalyst comes close to the favorable low ammonia inhibition that was recently demonstrated for the Ba-promoted Ru/MgO catalyst (Table 1). The unpromoted Co sample shows nearly no inhibition by NH₃ ($\alpha = -0.3$).

The apparent activation energies (E_A) are obtained from Eq. (5) (r = reaction rate = activity) after k_1 is substituted in Eq. (2) by the term given in Eq. (4):

$$k_1 = k_0 \cdot e^{-E_A/RT}, \quad (4)$$

$$\ln r = -\frac{E_A}{R} \cdot \frac{1}{T} + d \text{ (constant)}. \quad (5)$$

The strong influence of the NH₃ pressure on the reaction rate makes it necessary to compare only those activities for each catalyst that are obtained at the same NH₃ outlet concentrations at different temperatures. Regression coefficients (R^2) of usually > 0.99 are obtained from the Arrhenius plots in the temperature region of 593–673 K.

The unpromoted Fe and Co catalysts have apparent activation energies of 143 and 149 kJ mol⁻¹, respectively. Addition of Ba results in a significant reduction of the E_A values for both Fe and Co catalysts (see Table 1). For the Ru/MgO catalyst, however, the apparent activation energy remains virtually unchanged when Ru is promoted with Ba (79 vs 77 kJ mol⁻¹, compare to Table 1). The E_A values in the range of ca. 90–110 kJ mol⁻¹ (see Fig. 6) for the Ba-promoted FeCo catalyst supported on active carbon are slightly higher than those reported for Ba-promoted Ru catalysts using carbon or BN as support [7,14,17]. The activation barrier is also significantly higher than that obtained for a KM1 reference sample (70 kJ mol⁻¹), which is in good agreement with the published data [37].

The differences in the E_A values for different FeCo samples are not very large and should not be overemphasized. It seems that the apparent activation energy goes through a slight minimum (see Fig. 6) decreasing from $E_A = 104$ kJ mol⁻¹ for the pure Fe samples to $E_A = 90$ kJ mol⁻¹ for Co content of 4–6%. This Co content corresponds also to the catalysts with the highest activities for the Fe-rich samples (see Fig. 3). Further substitution of Fe by Co causes an increase to values around $E_A = 100$ kJ mol⁻¹. It is, how-

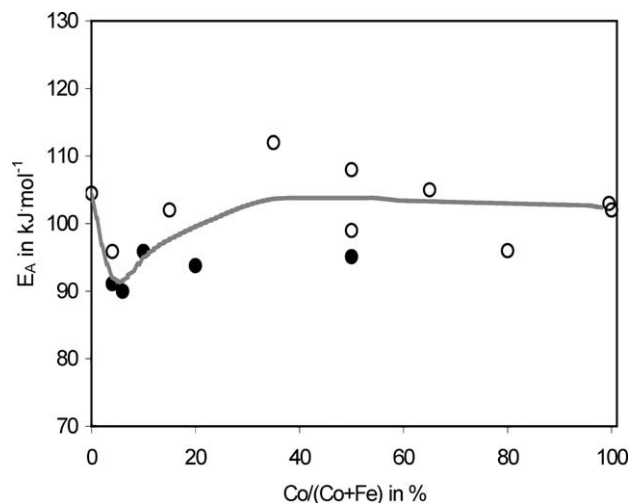


Fig. 6. Apparent activation energy with increasing Co content for Ba-promoted catalysts; mass of the catalyst: 600 mg (closed circles) and 300 mg (open circles), respectively; $p = 10$ bar, H₂:N₂ = 3:1, $T = 593$ –673 K.

ever, obvious that the drastic changes in the activities for the promoted FeCo samples are not a result of the slight differences in the apparent activation energy but rather results from higher intrinsic activities of the active sites.

From detailed kinetic investigations on fused Fe and supported Ru catalysts it was concluded that the dissociative adsorption of N₂ is the rate-limiting step in the NH₃ synthesis [38]. A value of $\beta = 1$ for the reaction order of N₂ is generally considered to be in accordance with this assumption. All FeCo-based catalysts listed in Table 1 exhibit β values between 0.8 and 1.0 (except the Ba-Fe/C catalyst with $\beta = 1.2$) under the chosen conditions. Therefore, it appears that the rate-limiting reaction step in NH₃ synthesis is the same for both the Ba-promoted FeCo catalysts investigated and for the commercial Fe- and Ru-based catalysts.

It is seen that very different reaction orders of H₂ (γ) result from the different catalysts. The γ values for KM1 and for the Ba-promoted Fe catalyst are both around 2.3 (see Fig. 7 and Table 1) while the corresponding number for

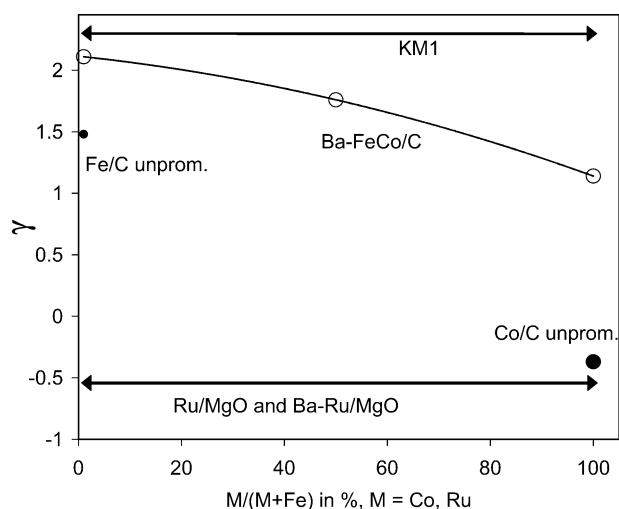


Fig. 7. The H_2 reaction order (γ) for various promoted and unpromoted transition metal catalysts. For experimental conditions see Table 1.

the unpromoted, carbon-supported Fe catalyst is somewhat lower at $\gamma = 1.5$. Although the γ value decreases for the promoted samples to $\gamma = 1.1$ – 1.3 with increasing Co content, it differs strongly from the negative values observed for Ru-based ($\gamma = -0.4$ – 0.7 [6–9,14]) or Re-based ($\gamma = -0.2$ – 0.7 [39]) catalysts. A negative γ value was only measured for the unpromoted, carbon-supported Co sample ($\gamma = -0.4$). Low or even negative γ values indicate a stronger interaction of hydrogen species relative to the interaction with nitrogen species for the surface of the catalyst.

Although the power-law kinetic approach is not based on an analysis of the single reaction steps of the generally accepted reaction model [1–3] it provides a convenient method for data treatment. To demonstrate the feasibility of the power-law approach, we compare the activities calculated on the basis of power-law expression with the activities measured in the experiments on three different catalysts (see Fig. 8). The regression coefficient for the complete data set of the three catalysts is $R^2 = 0.966$. Of course, the power-law kinetic model fails if activities are measured relatively close to the thermodynamic equilibrium, i.e., at elevated temperatures (for our conditions $T > 690$ K). Within its limitation, the chosen data treatment enables a comparison of the influences of the reactants and reaction conditions on the overall reaction rate. Thereby, this procedure gives a relatively reliable guidance for the further development of catalysts with better performance.

3.5. Temperature-programmed surface studies

The performance of an ammonia synthesis catalyst obviously depends on the number of sites (on the atomic level) that are able to catalyze the rate-determining step in the reaction sequence of the NH_3 formation. This number is, however, extremely difficult to specify, particularly since the de-

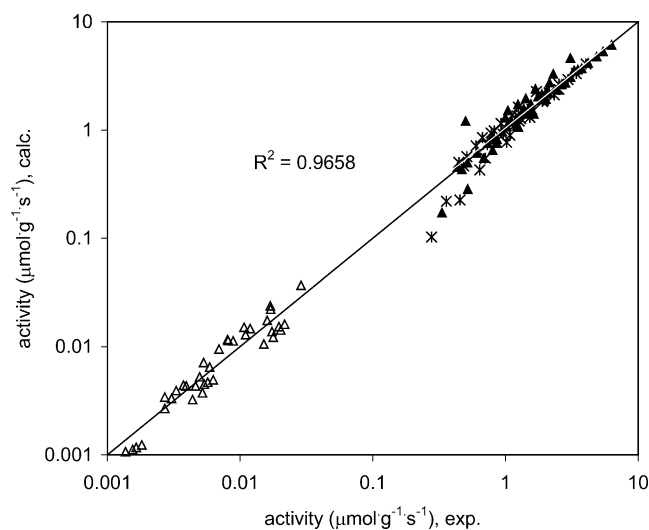


Fig. 8. Calculated versus experimental activities applying power-law kinetics (see Eq. (1) and data from Table 1); Co/C (unprom.): open triangles, Ba-Fe/C: crosses, Ba-Co/C: closed triangles.

tailed structure of the active sites of the promoted Fe-based catalysts is still under discussion. Although the number of active sites can probably in most cases be related to some fraction of the total surface area of the catalytically active element—in this case the transition metals Fe and Co—the activity of different planes of metals can vary by several orders of magnitude as it was recently demonstrated for Ru [40] and earlier for both Fe [41] and Re [42]. Furthermore, surfaces of metals can change their chemical composition (e.g., conversion to surface nitrides) or reconstruct under NH_3 synthesis conditions. Therefore, it is necessary to rely on surface measurements performed as close as possible to NH_3 synthesis conditions. We chose N_2 -TPD and N_2 -TPSR experiments of the catalysts (that were previously subjected to NH_3 synthesis) in order to evaluate the amount of N_2 that can adsorb onto the catalysts. Additionally, the methods provide a possibility to explore the conditions under which the nitrogen species are being desorbed in the form of molecular N_2 (TPD) or being converted to the reaction product NH_3 (TPSR).

N_2 -TPD on the Ba-promoted samples yields an amount of 0.1–0.15 $\mu\text{mol N}_2$ desorbed per mass of transition metal (see Table 2). This is about twice as high compared to KM1 indicating a higher metal surface area per mass of transition metal for the carbon-supported samples. However, no relation between the desorbed amount of N_2 as an indicator for the transition metal surface area and the activities of the samples can be established. The shape of the N_2 desorption trace (long tail) strongly indicates, however, that N_2 is not completely desorbed at temperatures up to 823 K.

A significantly higher amount of N_2 (0.52 $\mu\text{mol g}^{-1}$), however, is desorbed from the unpromoted, carbon-supported Fe catalyst. A higher metal surface area in this case or, more likely, the fact that Ba largely covers the Fe surface of

Table 2

Comparison of activities, N₂-TPD, and N₂-TPSR results of a selection of unpromoted and promoted FeCo and Ru catalysts

Catalyst	Activity ^a ($\mu\text{mol g}^{-1} \text{s}^{-1}$)	N ₂ -TPD ($\mu\text{mol (N}_2\text{)}_2 \text{g}_{\text{cat.}}^{-1}$)	N ₂ -TPSR ($\mu\text{mol (NH}_3\text{)} \text{g}_{\text{cat.}}^{-1}$)
Unprom. Fe/C	2.1	0.52	2.79
Unprom. Co/C	0.022	0.15	0.076
Ba _{0.35} -Fe/C	4.0	0.14	1.12
Ba _{0.35} -Fe ₅₀ Co ₅₀ /C	3.8	0.11	1.00
Ba _{0.35} -Co/C	6.2	0.15	1.73
Sr _{0.35} -Co/C	1.4	n.m.	n.m.
Cs _{0.5} -Co/C	0.07	n.m.	n.m.
Fe-cat. (KM1)	10.5	0.068	0.178

^a Activities determined for $p = 10$ bar, $T = 673$ K, $F = 267$ ml min⁻¹, N₂:H₂ = 1:3, 300 mg of catalyst, $m_{\text{KM1}} = 200$ mg.

the promoted catalysts could account for these results [33]. Only 0.15 $\mu\text{mol g}^{-1}$ N₂, however, can be desorbed from the unpromoted, carbon-supported Co sample. The reason for this result could be the lower binding energy of cobalt to nitrogen species [1,19,20].

The amount of NH₃ formed by the interaction of nitrogen species with hydrogen gas ranges from 1.0–1.7 $\mu\text{mol g}^{-1}$ transition metal for the Ba-promoted samples. The results of the N₂-TPSR measurements show that the amount of nitrogen that is able to react with H₂ is significantly larger than the amount of nitrogen species that can be desorbed (N₂-TPD) from Ba-promoted and carbon-supported FeCo catalysts. The TPSR results correspond to four to six times the amount of nitrogen species compared to N₂-TPD for the Ba-promoted sample and a 2.7-fold amount for the unpromoted Fe/C catalyst. For the reference sample KM1, however, the amounts of surface nitrogen species determined by N₂-TPD and N₂-TPSR are corresponding quite well, if it is taken into account that some nitrogen species also cannot be desorbed from the surface of this catalyst [41]. Only relatively small amounts of NH₃ are formed in the N₂-TPSR experiment with the unpromoted Co sample. The majority of the nitrogen species desorbs in the form of molecular N₂ because of the very low NH₃ synthesis activity of this catalyst. This is a strong indication that the promotion with Ba drastically increases the number of active sites for Co possibly by (a) uncovering the surface of the cobalt crystal from carbon deposits as shown for Ru [43] and/or (b) controlling (creating) the concentration of the very active sites as suggested by Muhler and coworkers for Ba–Ru/MgO catalysts [44]. Elements other than barium do not promote cobalt that well. Cesium shows only a minor promoting effect (see Table 2) while strontium promotes Co/C reasonably well, reaching ca. 23% of the activity of an accordingly prepared Ba–Co/C catalyst (Table 2) with similar kinetic characteristics (Table 1). Obviously, earth alkali metal salts are much better promoters than alkali metal salts for Co/C catalyst in ammonia synthesis.

The reason for the large amount of nitrogen species detected in N₂-TPSR experiments compared to that seen in the

N₂-TPD is not clear. Under the NH₃ synthesis conditions, the interaction between the Ba promoter and the transition metals Fe and Co could result in an increased uptake of more strongly bonded nitrogen species. Possibilities could be the formation of new surface phases or the partly incorporation of N into interstitial positions of the transition metal lattice [45,46]. More detailed investigations are necessary to find the reason for the strong bonding of nitrogen species to the Ba-promoted surfaces of Fe/Co alloys.

4. Conclusions

It is demonstrated that Ba-promoted FeCo and especially the Ba-promoted Co catalysts have the potential of being an interesting alternative for NH₃ synthesis compared to the well-investigated Fe- and Ru-based systems [47]. As a promoter, barium enhances the NH₃ formation on FeCo catalysts and significantly decreases the apparent activation energy of the process. The barium promoter is especially effective for Co catalysts and increases the NH₃ production rates by more than two orders of magnitude compared to unpromoted samples. N₂-TPSR experiments indicate that Ba increases the number of active sites in carbon-supported Co catalysts drastically.

Activity measurements reveal that the NH₃ inhibition decreases significantly with increasing Co content reaching numbers ($\alpha = -0.7$ – -1.0 for 100% Co) that are similar to those of Ru-based catalysts. An inhibition of the NH₃ synthesis rate by hydrogen ($\gamma < 0$), similar to that reported for Ru-based catalysts, was only observed for the unpromoted Co catalyst. For Ba-promoted FeCo samples, only γ values larger than 1, showing a slight decrease with increasing Co contents, are measured.

Nitrogen adsorbs very strongly on Ba-promoted FeCo samples and can only partly be desorbed at temperatures up to 823 K. The dissociative adsorption of N₂ is most likely the rate-limiting step in NH₃ synthesis with Ba-promoted FeCo catalysts as indicated by an exponential factor of $\beta = 1$ for N₂.

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