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New efficient catalyst for ammonia synthesis: barium-promoted cobalt on carbon

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Barium-promoted cobalt catalysts supported on carbon exhibit higher ammonia activities at synthesis temperatures than the commercial, multipromoted iron catalyst and also a lower ammonia inhibition.

Without ammonia produced in the industrial process only 60% of the current global population could be nourished.[1] Ammonia synthesis over commercial, multipromoted iron-based catalysts is strongly inhibited by the reaction product leading to significantly decreased reaction rates at higher NH_3 concentrations.[2] About a decade ago, a promoted ruthenium catalyst supported on graphitized carbon[3] was introduced as an alternative ammonia catalyst in the Kellogg Advanced Ammonia Process (KAAP).[4] However, high catalyst costs combined with further disadvantages such as methanization of the carbon support at industrially preferred reaction conditions have stimulated the search for alternative, low-cost catalyst materials with high activities and a low NH_3 inhibition.[5] Recently, it has been shown that it is possible to rationalize the activities of known unpromoted and promoted ammonia synthesis catalysts through density functional theory calculations and microkinetic modelling.[6] From these investigations it appears that improved ammonia synthesis catalysts should result either from alloys or from the use of more efficient promoters. Previously, it has been found that cobalt-based catalysts exhibit low activity in ammonia synthesis.[7] Here, we report how very high activities can be achieved by promoting cobalt catalysts with barium. Interestingly, there are no previous reports on the use of barium as a promoter for cobalt-based ammonia synthesis catalysts, although barium has been found to be a useful promoter for ruthenium catalysts.[3–5]

Vulcan XC-72 (174 $m^2\ g^{-1}$, cleaned by heating in $N_2:H_2$ = 9:1 at 1373 K for 48 h) was used as the carbon support material. $Co(NO_3)_2$ and $Ba(O_2CCH_3)_2$ were added separately by incipient wetness impregnation. The impregnated material was dried at 333 K for 6 h and then at 393 K for 18 h after each addition. The Co content determined by AAS was 8 wt% and the Ba:Co atomic ratio (optimised through a series of experiments) was 0.87. The catalyst precursor was pressed into tablets, crushed and sieved to particles of size 0.35–0.71 mm. This material was transferred into a glass-lined stainless steel micro reactor (i.d. = 3 mm) and activated with a stoichiometric $N_2:H_2$ mixture at 1.3 bar. It was found to be essential that the barium-promoted Co catalyst was activated at high pressures (10 bar) and at low flows (total flow of 40 ml min^{-1} (STP)) to obtain the highest possible catalytic activities. The published data for the commercial catalyst (KM1) consisting of 94% Fe, 2.8% CaO, 2.5% Al_2O_3 and 0.6% K_2O was used for comparison.[8] Activity measurements were performed at temperatures between 320–440 °C, at pressures between 2–50 bar and at total flow rates between 40–267 ml min^{-1} (STP) , and by using different $N_2:H_2$ ratios. Power law kinetics is applied to determine the apparent activation energies (E_A) as well as the apparent reaction orders α, β and γ in rate eqn. (1):

$$r_{NH_3} = k\exp(-E_A/RT)p_{NH_3}^{\alpha}p_{N_2}^{\beta}p_{H_2}^{\gamma} \qquad (1)$$

X-Ray powder diffraction (XRPD) data were recorded on samples in sealed capillaries (sample was passivated with *ca.* 0.1% O_2 in Ar at 20 °C prior to the measurements) using a Huber G670 diffractometer at MAX-lab synchrotron in Lund (λ = 1.4788 Å).[9] *In situ* XRPD was performed as described previously.[9]

The catalytic activities of the Ba–Co/C catalyst are shown in Fig. 1 at various temperatures and NH_3 outlet concentrations. By comparing these data with results obtained from the commercial catalyst KM1,[8] three conclusions can be drawn: (1) at a pressure of 10 bar, equal NH_3 outlet concentrations and temperatures higher than 400 °C, the Ba–Co/C catalyst shows higher activity than KM1, *e.g.*, at 440 °C the activity per mass of catalyst is almost twice as high for the Co catalyst,[10] (2) the activity of the Ba–Co/C catalyst increases more rapidly with increasing temperature than that of KM1, and (3) at temperatures between 320 and 400 °C, the measured activities for the Co catalyst do not decline as rapidly with increasing NH_3 outlet concentrations as is observed for KM1. The calculated α-coefficients (Ba–Co/C; KM1: 320 °C: −0.81; −1.48, 360 °C: −0.82; −1.57, 400 °C: −1.07; −1.53) are significantly less negative for the Co-catalysts. The α-coefficients cannot be compared in a meaningful way at T = 440 °C because the equilibrium concentration ($c(NH_2)$ = 2.3%) is almost reached under these conditions and influences the reaction rate strongly. Therefore, eqn. (1) should only be used at relatively low conversions.

The measurements of NH_3 outlet concentrations with varying $H_2/(H_2 + N_2)$ ratios is shown in Fig. 2. The optimum ratio decreases from the nearly stoichiometric value (0.75) at 440 °C

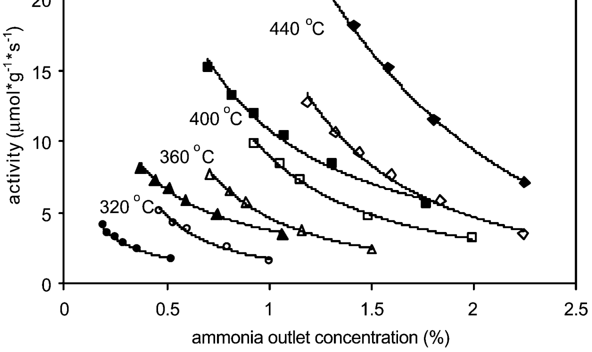

Fig. 1 Catalytic activities per mass of catalyst of Ba-promoted and carbon-supported Co catalyst (filled symbols, 100 mg) and the commercial, multipromoted Fe-catalyst (KM1, open symbols, 200 mg) at 10 bar, $N_2:H_2$ = 1:3 and temperatures of 320 °C (circles), 360 °C (triangles), 400 °C (squares) and 440 °C (diamonds).

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(0.66) to *ca.* 0.4 at a temperature of 320 °C (see dashed line in Fig. 2). Likewise, the γ-coefficients obtained from independent experiments decrease from +2.1 (440 °C) to +0.7 (320 °C). The obvious conclusion is that the catalyst surface is covered with increasing amounts of hydrogen at lower temperatures, leaving less active sites available for dissociation of dinitrogen—the rate limiting step in ammonia synthesis. The blocking of the surface by hydrogen is even more pronounced for Ru-based catalysts, where negative γ-coefficients are often observed.[3] The β-coefficients obtained at different temperatures are between 0.8 and 0.9 suggesting that the dissociation of N_2 at the surface is the rate limiting step in the ammonia synthesis on Ba–Co/C.

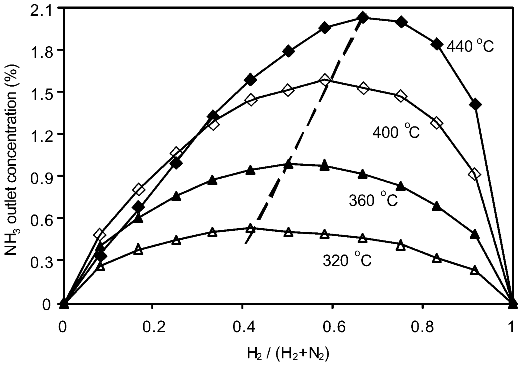

Fig. 2 NH_3 outlet concentrations at different temperatures and varying H_2:N_2 ratios (Ba–Co/C, 10 bar, 220 mg, total flow = 120 ml min^{-1} (STP)).

Carbon-supported nickel catalysts are also strongly promoted by addition of Ba. The NH_3 outlet concentration increases nearly three orders of magnitude, from about 10 ppm to 0.8% for the promoted sample (atomic ratio Ba:Ni = 0.8:1) under the same reaction conditions (300 mg sample of 10% Ni/C, 440 °C, 10 bar, N_2:H_2 = 1:3, 40 ml min^{-1} (STP) total flow). As expected, the apparent activation energy is relatively high (150 kJ mol^{-1}, see also Table 1 and Fig. 3) and the α-coefficient is close to zero ($\alpha = -0.2$ in the temperature range of 360–440 °C) indicating a weaker bonding of nitrogen species to the Ni surface compared to Fe and Co. Although the overall activity of Ni is significantly lower compared to the Ba–Co/C sample, to our knowledge this is the first example where Ni has been efficiently promoted as a catalyst for NH_3 synthesis.[11]

Table 1 Selected properties of NH_3 synthesis catalysts

Catalyst	Activity[a]/ μmol g^{-1} s^{-1}	E_A/ kJ mol^{-1}	α	β	γ
Co/C	0.20	149	−0.3	+0.8	−0.4
$Ba_{0.8}Co_{1.0}$/C	12.0	103	−1.1	+0.9	+1.5
Ni/C	0.0014[b]	n.m.[c]	±0.0	n.m.	n.m.
$Ba_{0.8}Ni_{1.0}$/C	0.31	150	−0.2	+0.9	−0.2
Fe (KM1)	7.36	70	−1.5	+0.9	+2.2

[a] Activities determined for T = 400 °C, 10 bar and a total flow of 160 ml min^{-1} (STP), N_2:H_2 = 1:3. [b] Ni/C: 440 °C. [c] n.m.—not measured, reaction rates too low.

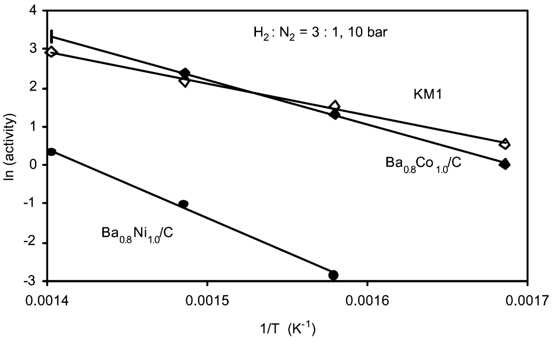

Fig. 3 Arrhenius plot of selected catalysts.

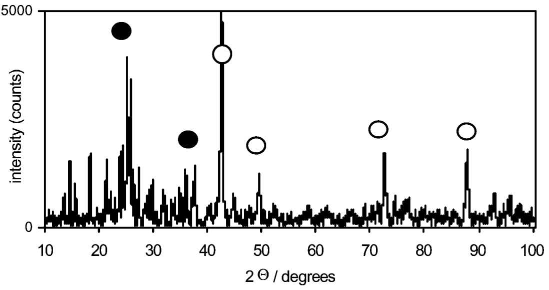

Fig. 4 X-Ray powder diffraction pattern of passivated Ba–Co/C (synchrotron radiation, λ = 1.4788 Å). Open circles: *fcc*-Co, closed circles: $BaCO_3$ (assigned from *in situ* XRPD).

XRPD patterns obtained at 25 °C from slightly passivated samples by use of synchrotron radiation (Fig. 4) as well as *in situ* XRPD measurements performed under NH_3 synthesis conditions reveal that Co can only be detected in its cubic form (*fcc*). $BaCO_3$, possibly formed by the thermal decomposition of $Ba(O_2CCH_3)_2$, is observed in the catalyst by *in situ* XRPD, but the presence of BaO on the surface as has recently been identified by *in situ* TEM on Ru catalysts[12] can neither be verified nor discounted. The presence of carbonates could also be confirmed by XPS (shoulder at 287 eV).

Previously, cobalt and nickel have received little interest as NH_3 synthesis catalyst. However, promotion with barium and using a carbon support results in catalysts that are surprisingly active for the NH_3 synthesis reaction. The NH_3 inhibition is lowered significantly compared to the commercial Fe-catalyst. Apparently, the primary role of barium is to lower the activation energy for dinitrogen dissociation.

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Notes and references

1 V. Smil, *Am. J. Agric. Econ.*, 2001, **83**, 790.

2 S. Dahl, J. Sehesterd, C. J. H. Jacobsen, E. Törnqvist and I. Chorkendorff, *J. Catal.*, 2000, **192**, 391.

3 H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, *Angew. Chem.*, 2001, **113**, 1096; H. Bielawa, O. Hinrichsen, A. Birkner and M. Muhler, *Angew. Chem., Int. Ed.*, 2001, **40**, 1056.

4 A. I. Foster, P. G. James, J. J. McCarroll and S. R. Tennison (British Petroleum), *US Pat.*, US-A 4163775, 1979; R. Strait, *Nitrogen Methanol*, 1999, **238**, 37.

5 Z. Kowalczyk, S. Jodzis, W. Rarog, J. Zielinski and J. Pielaszek, *Appl. Catal. A*, 1998, **173**, 153.

6 A. Logadottir, T. H. Rod, J. K. Nørskov, B. Hammer, S. Dahl and C. J. H. Jacobsen, *J. Catal.*, 2001, **197**, 229; C. J. H. Jacobsen, S. Dahl, A. Boisen, S. Bjerne, H. Topsøe, A. Logadottir and J. K. Nørskov, *J. Catal.*, 2002, **205**, 382.

7 O. V. Shcheglov, G. K. Boreskov and M. G. Slin'ko, *Dokl. Akad. Nauk SSSR*, 1955, **105**, 123; S. R. Logan and C. Kendall, *J. Chem. Soc., Faraday Trans.*, 1960, **56**, 144; G. Rambeau, A. Jorti and H. Amariglio, *J. Catal.*, 1985, **94**, 155.

8 J. Sehested, C. J. H. Jacobsen, E. Törnqvist, S. Rokni and P. Stoltze, *J. Catal.*, 1999, **188**, 83.

9 B. S. Clausen, G. Steffensen, B. Fabius, J. Villadsen, R. Freidenhans'l and H. Topsøe, *J. Catal.*, 1991, **132**, 524; Y. Cerenius, K. Ståhl,, L. A. Svensson, T. Ursby, Å. Oskarsson, J. Albertsson and A. Liljas, *J. Synchrotron Radiat.*, 2000, **7**, 203.

10 The Ba–Co/C catalyst shows higher activities per mass of catalyst than KM1 at pressures of 2–50 bar (T = 400 °C, H_2:N_2 = 3:1). A mass loss of 18.8% (TGA) during the course of the activation is not considered in the calculation of the activities (per mass of catalyst).

11 A. Mittasch, *Adv. Catal.*, 1950, **2**, 81; K. Aika and K. Tamaru, in *Ammonia—catalysis and manufacture*, ed. A. Nielsen, Springer Verlag, Berlin, 1995, p. 103.

12 T. W. Hansen, J. B. Wagner, P. L. Hansen, S. Dahl, H. Topsøe and C. J. H. Jacobsen, *Science*, 2001, **294**, 1508.