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Research Note

Carbon-supported cobalt catalyst for ammonia synthesis: Effect of preparation procedure

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Abstract

Supported cobalt catalysts were synthesised, characterised (by H_2 TPD, XRD, TEM), and tested in ammonia synthesis at 9.0 MPa (400–470 °C; H_2:$N_2 = 3$:1). Partly graphitised carbon of high surface area (840 m^2/g), cobalt nitrate, and barium nitrate were used as a support, a precursor of the active phase, and a promoter precursor, respectively. Both cobalt dispersion in the Ba-doped catalyst and, to a greater extent, catalytic properties of the promoted Co surfaces (TOF) proved to be dependent on the unpromoted material pretreatment (reduction in H_2, subsequent calcination in air). The kinetic studies of NH_3 synthesis have shown explicitly that Ba-promoted cobalt on carbon is very active and less inhibited by the ammonia product than the commercial magnetite-based material.

Keywords: Ammonia synthesis; Cobalt catalyst; Barium promoter; Catalyst preparation; Cobalt dispersion; Hydrogen chemisorption

1. Introduction

Activated carbons modified through a high-temperature route (around 2000 °C) have been found to be excellent supports for the ruthenium catalysts designated for ammonia synthesis [1,2]. The Ru/C systems promoted with barium and/or alkali proved to be significantly more active [3–8] than conventional iron commonly used in ammonia plants. Although various supported ruthenium catalysts were shown to be very active as well [9–12], doubt remains as to whether the high cost of the noble metal is counterbalanced by its advantageous catalytic properties [13]. Consequently, efforts have been made to work out a new system [14–16] that is more effective than the iron-based ones, especially at high conversions, and also is considerably cheaper than those based on ruthenium.

Recent low-pressure NH_3 synthesis studies of Hagen et al. [13,17] have shown that barium-promoted cobalt on carbon is a promising candidate for the industrial applications. This communication is also addressed to the Ba–Co/carbon systems. The purpose of our work was to study the effect of the preparation procedure on the cobalt dispersion and catalytic properties of the Ba–Co/C catalysts in ammonia synthesis. In contrast to those earlier studies [13,17], high-surface area graphitised carbon was used as a support for the active phase, and NH_3 synthesis tests were performed under an industrially relevant pressure of 9.0 MPa to explore the practical potential of these new materials. The dispersion of cobalt was characterised by the hydrogen chemisorption (H_2 TPD) and XRD methods. Some TEM experiments have also been performed.

2. Experimental

2.1. Support and catalysts

The carbon support was obtained from commercial activated carbon RO 08 (extrusions of 0.8 mm diameter; Norit), according to the following two-step modification procedure [3]: (1) heating at 1900 °C in helium for 1 h and (2) subsequent

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Table 1
Chemical composition of the Co/C catalysts promoted with barium

Catalyst symbol	Cobalt loading[a] (wt%)	Barium loading (mmol/g_{Co+C})
Ba–Co/C	10.1	0.84
Ba–Co_{R+P}/C	10.3	0.92
Ba–Co_{R+P+C}/C	10.7	0.73

[a] In relation to the mass of the unpromoted material.

treatment in a CO_2 stream at about 850 °C up to 23.8% mass loss. The graphitised material thus prepared ($S_{BET} = 840\ m^2/g$) was impregnated with an alcoholic solution of cobalt nitrate [$Co(NO_3)_2{\cdot}6H_2O$], followed by drying and calcining in air at 220 °C for 24 h to decompose the salt (sample marked as Co/C). Subsequently, the calcined sample was reduced in flowing hydrogen at 350 °C for 24 h, followed by the passivation step (symbol Co_{R+P}/C). Then the passivated material was calcined (reoxidised) again in air at 220 °C for 24 h (Co_{R+P+C}/C). For Ba-promoted catalysts, all three precursors (Co/C, Co_{R+P}/C and Co_{R+P+C}/C) were impregnated with aqueous solutions of barium nitrate at 90 °C and dried in air at 110 °C. The chemical compositions of the resulting catalysts are presented in Table 1.

2.2. *Characterisation and activity studies*

The H_2 TPD experiments were performed in a fully automated PEAK-4 instrument, according to a procedure described previously [4]. The outline is as follows: On reduction in a 80:20 hydrogen–argon stream at 500 °C (20 h), the Ba–Co/C sample (0.2 g) was flushed with argon at 500 °C and cooled in Ar to 150 °C. Then the Ar stream was replaced with that of hydrogen, followed by cooling in H_2 to 0 °C. Finally, the sample was heated (15 °C/min) in a flow of argon (40 ml/min) and the concentration of hydrogen in the outlet stream was monitored (H_2 TPD). The amount of preadsorbed hydrogen was determined by integrating the TPD response. The XRD experiments were performed on a Siemens D5000 instrument. The average size of cobalt crystallites was determined from line broadening, using the integral width of Co reflections. The TEM images were recorded with a Philips CM20 Super Twin microscope, which provides a 0.25-nm resolution at 200 kV.

Activity measurements of NH_3 synthesis were carried out in a flow reactor supplied with a stoichiometric $H_2 + N_2$ mixture of controlled ammonia concentration (x_1). Under steady-state conditions of temperature (400–470 °C), pressure (9.0 MPa), gas flow rate (65 Ndm^3/h), and x_1 (typically about 7.5%), the increment in NH_3 content ($x_2 - x_1$) due to the reaction over a small catalyst layer (usually 0.45 g) was determined. Consequently, the NH_3 synthesis rates corresponding to the mean values of $x = (x_1 + x_2)/2$ can be calculated; the details of such calculations can be found elsewhere [18].

3. Results and discussion

TEM studies performed with one of the samples (Ba–Co_{R+P}/C) previously tested in NH_3 synthesis reveal (Fig. 1) that the specimen is heterogeneous. Large crystallites of metallic cobalt covered with amorphous layers are accompanied by significantly smaller (4–10 nm), poorly organised, and poorly visible particles, most likely of cobalt oxide formed from fine Co crystallites on contact of the postreaction material with air. Because of the significant heterogeneity, a detailed analysis of the particle size distribution could not be performed.

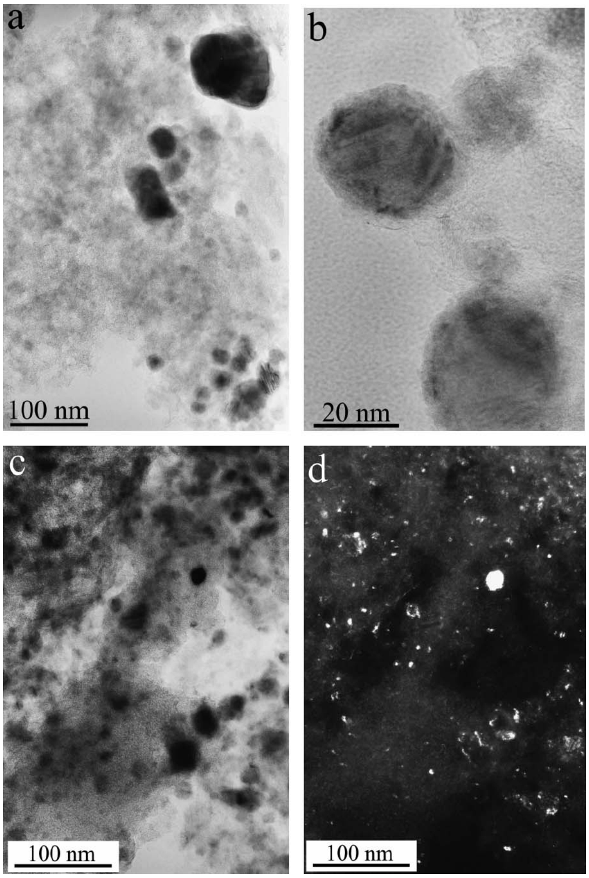

Fig. 1. TEM micrographs of Ba–Co_{R+P}/C catalyst after exposure to air; (a) general view showing broad Co particle size distribution; (b) high-resolution image depicting surface oxidation of Co particles; (c) and (d) a pair of bright and dark field images of the catalyst sample revealing a complex nature of Co particles seen in BF images.

Table 2
Dispersion of cobalt in the Co/C catalysts doped with barium

Catalyst symbol	H_2 uptake (μmol/g_{C+Co})	FE[a]	d_H[a] (nm)	d_{XRD}[b] (nm)
Ba–Co/C	110	0.13	9.7	14.5
Ba–Co_{R+P}/C	77	0.09	14	18.7
Ba–Co_{R+P+C}/C	135	0.15	8.4	13

[a] H:Co_s = 1:1 stoichiometry [22] and formula proposed by Borodziński and Bonarowska [23] were used for calculation FE and d_H, respectively.
[b] Post-reaction samples were studied.

The results of chemisorption experiments (H_2 TPD), collected in Table 2, indicate that the reduction of the calcined Co/C material before impregnation with barium nitrate is disadvantageous for the resultant catalyst (or, more precisely, for its dispersion). The value of the fraction exposed (FE, defined as the number of surface cobalt atoms referred to the total num-

Table 3
Rates of ammonia synthesis over the three carbon-based cobalt catalysts at 470 °C and at 8% NH_3 in the gas phase; $p = 9.0$ MPa

Catalyst symbol	Reaction rate ($g_{NH_3}/(g_{Co+C}\ h)$)	TOF (s^{-1})
Ba–Co/C	1.69	0.125
Ba–Co_{R+P}/C	0.32	0.034
Ba–Co_{R+P+C}/C	2.17	0.13

ber of Co atoms) decreases from 0.13 for Ba–Co/C to about 0.09 for Ba–Co_{R+P}/C. In contrast, additional calcination of the reduced and passivated specimen leads, after promotion, to increased cobalt dispersion; the FE of the Ba–Co_{R+P+C}/C sample (0.15) is significantly (almost twice) higher than that of Ba–Co_{R+P}/C (0.09). Average crystallite diameters calculated from the H_2 chemisorption data (d_H) are slightly lower than those estimated from XRD (see Table 2, d_{XRD}). But the agreement seems to be surprisingly good when taking into account that the latter experiments (XRD) were performed ex situ and that very small Co particles remain undetected due to oxidation on exposure to air. As a result, the mean crystallite sizes (d_{XRD}) can be overestimated.

Redispersion of Co particles induced by reduction–oxidation pretreatment was observed previously both for the model systems Co/silica [19], Co/carbon [20], and real Co/SiO_2 catalyst [21]. This phenomenon was ascribed to splitting of the faulted oxidised particles during subsequent reduction in hydrogen [21].

Rates of ammonia synthesis determined at 470 °C and at 8% NH_3 in the gas phase are listed in Table 3. The table also reports the corresponding turnover frequencies (TOFs) obtained by combination of the kinetic and H_2 chemisorption data. A sequence of the weight-based reaction rates established at 470 °C (Ba–Co_{R+P+C}/C $>$ Ba–Co/C $\gg$ Ba–Co_{R+P}/C) remained unchanged when the temperature changed to 430 or 400 °C (not presented). The apparent energies of activation determined at low temperatures ($E_{400–430}$) proved to be almost identical (about 90 kJ/mol). Over the range of 430–470 °C (8% NH_3), the apparent activation energies were smaller (about 55 kJ/mol), thus showing the thermodynamic limitations to be essential at higher temperatures (at 470 °C, 9.0 MPa, and H_2:$N_2 = 3:1$, the equilibrium NH_3 content is about 12.5%).

The comparison of the surface-based activities expressed in terms of TOF indicates clearly (see Table 3) that the catalytic properties of the promoted cobalt surfaces are dependent on the preparation procedure. Whereas the samples calcined before barium deposition (i.e., Ba–Co/C and Ba–Co_{R+P+C}/C) expose similar TOF values (0.125 s^{-1} and 0.13 s^{-1}, respectively), the third material (Ba–Co_{R+P}/C) is considerably less active (in terms of TOF), by a factor of 3.5–4. The reasons for the difference are unclear. Either the morphologies of the cobalt particles formed during the final reduction in an NH_3 synthesis reactor are different (structure sensitivity effect) or, alternatively, the promotional effects of barium are different (the unpromoted systems were shown to be almost inactive [13]). According to the former concept, the morphology of the Ba-doped Co crystallites operating under ammonia synthesis conditions would be dependent on the form of the cobalt precursor. (Cobalt oxide in the calcined Co/C and Co_{R+P+C}/C samples is expected to be more crystallised than that in Co_{R+P}/C—small amorphous particles or amorphous layers covering the Co cores.) According to the latter, the Co precursor form would control the distribution of barium between the active metal surface and carbon surface and, possibly, the chemical form of the promoter when operating. It is impossible to distinguish between the two options from the available data. Extensive studies of the catalysts derived from cobalt acetate (in progress) should give a more decisive response.

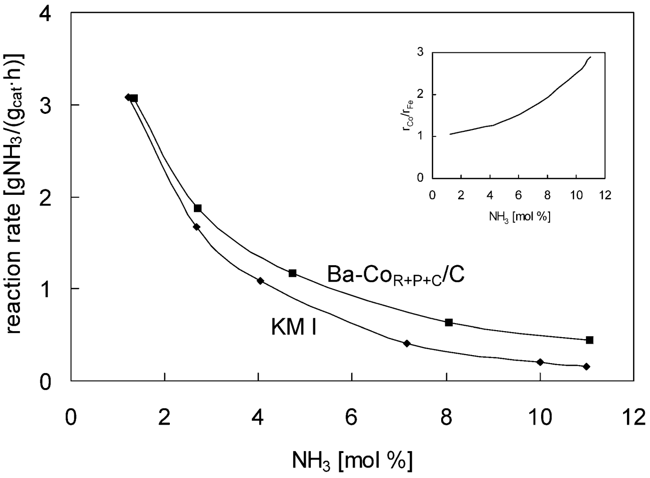

Fig. 2. Ammonia partial pressure dependencies of the NH_3 synthesis rates over the Ba–Co_{R+P+C}/C catalyst and triply promoted fused iron catalyst (KM I) at 400 °C (9.0 MPa) and (inside)—the ratio of the reaction rates (r_{Co}/r_{Fe}) vs. NH_3 content in the gas; the date for KM I were taken from [24].

The final part of the study is devoted to the application potential of the Ba–Co/C catalysts. Fig. 2 illustrates the effect of conversion expressed by ammonia content in the gas phase (x) on the NH_3 synthesis rate over the most effective cobalt catalyst (Ba–Co_{R+P+C}/C). For comparison, the data obtained previously [24] for the commercial, magnetite-based material (KMI, H. Topsoe) are also included. In both cases (Co and Fe), the reaction rates decrease with conversion. However, the cobalt catalyst is kinetically less sensitive to the changes in ammonia concentration (see Fig. 2). Although at low NH_3 content (1–2%), the two catalysts are almost equally active, at high NH_3 content (11%), the reaction rate is almost three times higher over the former system. The difference between Co and Fe will be significantly larger for still higher, but industrially important conversions (15–20% NH_3), as evidenced by the r_{Co}/r_{Fe} trend demonstrated in Fig. 2.

The foregoing comparison suggests that cobalt on carbon might be a substitute for expensive ruthenium rather than an alternative to iron. Clearly, the Ba–Co/carbon catalyst, after optimisation, may replace the ruthenium-based material, which operates effectively at high conversion in final catalytic beds in the large-scale reactors commercialised by Kellogg Brown and Root [1]. But close inspection of the kinetic data obtained for Ba–Co_{R+P+C}/C (in the present work) and those published previously [4] for the group of ruthenium catalysts (Ba–Ru/graphitised carbon) reveals that under comparable conditions (9.0 MPa, 400 °C, 11% NH_3 in H_2:N_2 = 3:1), the latter systems have higher reaction rates (in terms of the metal mass) than the former systems (23–40 $g_{NH_3}/(g_{Ru}\,h)$ [depending on the Ru dispersion [4]] vs. 4.5 $g_{NH_3}/(g_{Co}\,h)$ [in the present work]). The difference stems partly from the higher dispersion of ruthenium (FE_{Ru} varies from 0.9 for 3 wt% Ru to 0.5 for 20 wt% Ru [4] vs. $FE_{Co} = 0.15$ for 10 wt% Co in the present work) and partly from its more advantageous catalytic properties expressed as TOF of NH_3 synthesis (0.03–0.16 s^{-1} for Ru, depending on the crystallite size vs. 0.03 s^{-1} for Co). As is seen from the above comparisons, cobalt dispersion is a critical parameter of the Ba–Co/carbon system usefulness. Further experimental work, aiming at improving the Co dispersion (small particles, uniform particle size distribution) and possibly at optimising the Ba/Co ratio is necessary to take full advantage of the practical potential of the new materials.

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