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Ammonia Synthesis over the Carbon-Based Iron Catalyst Promoted with Potassium

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Catalytic ammonia synthesis is one of the largest energy consuming processes of chemical industry [1,2] – more than 1% of the global energy consumption is used for the NH_3 production [2]. Efforts have been made, therefore, to improve the process [3,4] and to work out a new catalyst that would be significantly more active than the conventional, triply promoted magnetite. Jacobsen has reported recently [2] that ternary nitrides Fe_3Mo_3N, Co_3Mo_3N and Ni_2Mo_3N exhibit high catalytic activities in NH_3 synthesis, especialy when doped with caesium. Attention should be paid, however, to the catalysts deposited on carbon [3–11]. The carbon-based Ru system promoted with caesium and barium was commercialized in the last decade by the Kellog Company and more recently by Kellog Brown and Root [3,4]. This paper shows that graphitized carbon may also be used as a support for the preparation of highly active iron catalysts, promoted with the alkali. The studies demonstrate that the ammonia partial pressure dependencies of the reaction rate for K-Fe/C are close at high conversions to that for the industrial fused iron catalyst. However, the catalytic properties of small iron particles deposited on carbon are strongly dependent on the particle size, *i.e.* higher dispersion results in a higher activity, expressed as the turnover frequency (TOF) of NH_3 synthesis.

Two Fe/C systems of different iron contents were prepared, both supported on the same carbon material: a commercial active carbon (Norit R O 08) was first heated at 1900°C in a helium atmosphere. Then the material was gasified partly in flowing carbon dioxide at about 840°C up to 34% mass loss, followed by cooling in an argon stream [12]. In consequence, a graphitized carbon support of high surface area (S_{BET} = 440 m^2/g) was obtained. Iron nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) – a precursor of the active phase – was introduced onto the surface of the support by the multistage impregnation method (incipient wetness technique), followed by calcining in air at 220°C to convert Fe nitrate into oxide (Fe_2O_3). The samples were then reduced in hydrogen at 400°C for 24 h and passivated. The contents of iron in the resultant specimens were 24% (symbol Fe24/C) and 5.7% (symbol Fe5.7/C), respectively. Both Fe/C systems

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were impregnated with an alcoholic solution of potassium hydroxide up to K^+: C = 0.07 mol:mol, the former system (Fe24/C) was impregnated also with an aqueous solution of potassium nitrate (K^+ : C = 0.07). The dispersion of iron in the promoted catalysts was determined by the hydrogen chemisorption method, the details of the experimental procedure were described in [10]. Prior to the chemisorption measurements, the samples were rereduced in flowing hydrogen at 450°C for 24 h. The activity measurements of the NH_3 synthesis were carried out in a flow gradientless microreactor [13,14], operating with a stoichiometric $H_2 – N_2 – NH_3$ mixture of controlled ammonia content (0–10% NH_3). Both the effect of the gas composition on the activity and the effect of total pressure (4–90 bar) were examined. The studies of the reaction rate *vs* NH_3 content in the gas were performed at constant temperature of 400°C and under constant pressure of 90 bar or 63 bar, respectively. The preliminary reduction of the samples was performed *in situ* under the same conditions as those in the chemisorption experiments, *i.e.* at 450°C for 24 h.

Table 1 presents the chemisorption data, expressed as (i) the H_2 uptake, (ii) the fraction of Fe surface atoms accessible to hydrogen (FE – fraction exposed) and (iii) the average crystallite size of the metal (d_{Fe}); the latter parameter being calculated from the equation proposed by Borodziński and Bonarowska [15]. As seen from Table 1, the dispersion of iron particles depends upon the metal loading and, what is surprising, upon the kind of the potassium precursor: KNO_3-Fe/C shows lower dispersion than KOH-Fe/C, both derived from the same Fe24/C precursor.

Table 1. Chemisorption data for the K-promoted iron catalysts supported on carbon.

Catalyst	K:Fe [mol:mol]	H_2 uptake [μmol/g_{C+Fe}]	FE	d_{Fe} [nm]
KOH-Fe5.7/C	4.4	54.2	0.106	12.7
KOH-Fe24/C	1.0	120.5	0.056	24
KNO_3-Fe24/C	1.0	73.5	0.034	39.6

The kinetic relationships for the catalysts studied in the NH_3 synthesis are presented in Figs. 1–3. Fig. 1 illustrates the effect of the total pressure on the activity of the unpromoted Fe24/C sample and of that promoted with potassium hydroxide (KOH-Fe24/C). In both cases, the activities increase monotonously when the pressure is elevated. However, the promotional effect of potassium becomes more pronouced at higher pressures (see Fig. 1). This agrees well with the data obtained for the fused iron catalysts – the presence of potassium in such systems proved to be especially advantageous at high pressures [16] and at high conversions [13].

Fig. 2 shows the kinetic characteristics of the K-promoted Fe/C catalysts, *i.e.* the dependencies of the reaction rates *vs* ammonia content in the gas, the experiments being performed under 90 bar. Since the reaction rates are strongly dependent upon ammonia concentration, a ln - ln scale was used in Fig. 2 to distinguish between the curves over the whole range of NH_3 contents. As it results from Fig. 2, all the three K-Fe/C specimens exhibit similar characteristics as far as concerns the shape of the curves: an about 20-fold drop in the reaction rates is observed for instance in all the

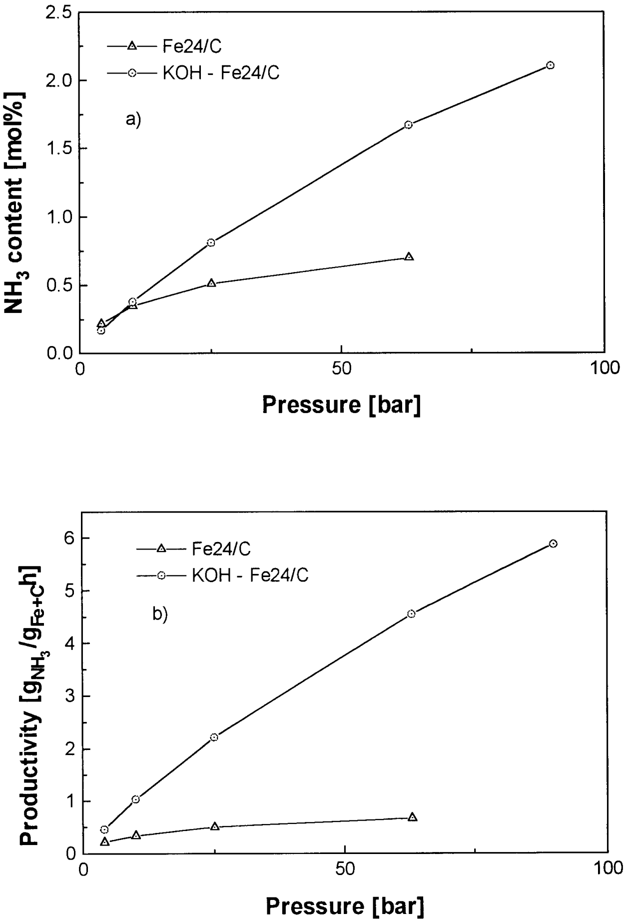

Figure 1. Effect of total pressure on the activity of the carbon-based iron catalysts: a) NH_3 concentration in the outlet gas *vs* pressure (gas entering the reactor was free from NH_3); b) productivity *vs* pressure: Δ – Fe24/C; T = 400°C; S.V. = $50 \cdot 10^3$ 1/h; O – KOH-Fe24/C; T = 400°C; S.V. = $140 \cdot 10^3$ 1/h.

cases when changing the NH_3 concentration from 1% to 9%. At high conversions, corresponding to 4–10% NH_3 in the gas, the kinetic characteristics of the K-Fe/C samples are very close to the characteristics of the fused iron catalyst (see Fig. 2), which was used in the studies as a reference material. The differences between the individual K-Fe/C catalysts concern the absolute levels of the activities only. A sequence of the reaction rates: KOH-Fe24/C > KOH-Fe5.7/C > KNO_3-Fe24/C does not agree, however, with a sequence of the Fe surface areas expressed in μmol H_2/g_{C+Fe} (column "H_2 uptake", see Table 1). This means that the catalytic properties of the iron surface are influenced by the dispersion of Fe particles. Fig. 3 shows the variations of the NH_3 synthesis rates, expressed as TOFs referred to the H_2 chemisorption *vs* the av-

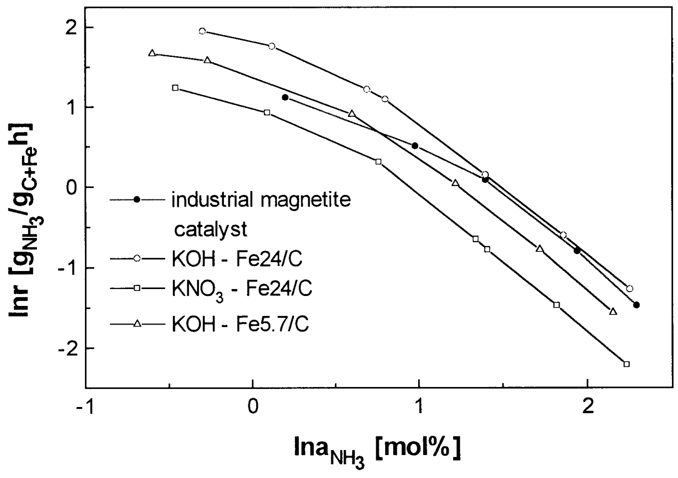

Figure 2. Rates of ammonia synthesis (r) over K-promoted Fe/C catalysts *vs* NH_3 content in the gas (ln – ln scale): T = 400°C; p = 90 bar: Δ – KOH-Fe5.7/C; O – KOH-Fe24/C; H – KNO_3-Fe24/C; ∇ – industrial magnetite catalyst.

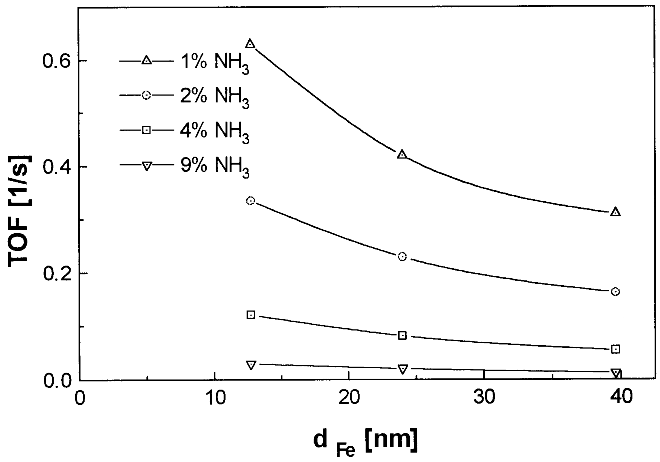

Figure 3. TOF values of NH_3 synthesis over K-Fe/C as a function of iron dispersion: T = 400°C; p = 90 bar; Δ – 1% NH_3, O – 2% NH_3, H – 4% NH_3, ∇ – 9% NH_3 in the gas mixture.

erage particle size of iron for 1%, 2%, 4% and 9% NH_3 in the gas mixture. It is clearly seen from Fig. 3 that the surface of small iron particles is more active in NH_3 synthesis than the surface of larger ones: TOFs for the crystallites of 13 nm (average size) are more than twice higher than those for the crystallites of 40 nm. The above observation is essential for the practice – a very active K-Fe/C catalyst requires iron to be finely dispersed: the effect of the activity enhancement would be double then, due to the increase of the iron surface (for constant Fe loading) and due to the increase in TOFs. Further studies are necessary, however, to explain the correlation between TOF of the NH_3 synthesis and iron dispersion on the molecular level.

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