The effect of cobalt on the reactants adsorption and activity of fused iron catalyst for ammonia synthesis

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Modern adsorption study facilities as well as scanning electron microscopy, X-ray diffraction, Mössbauer spectroscopy and X-ray fluorescence spectroscopy were used to investigate the effect of cobalt on the adsorption of nitrogen, hydrogen and ammonia on the surface of cobalt modified iron fused catalysts. Adsorption studies were carried out at the temperature range specific for ammonia synthesis (385°C). Activity tests were carried out under 10 MPa in the 350–450°C temperature range. Investigations were performed on the traditional multipromoted iron catalyst and on the series of catalysts prepared with addition of cobalt. Introduction of cobalt changed considerably the sample behaviour during activation and ammonia synthesis. Addition of cobalt promoted the iron catalyst for ammonia synthesis. The most active sample was that containing approximately 5.5 wt% Co. Cobalt changed the adsorption behaviour of the catalyst. Chemisorption of nitrogen is much higher for "cobalt" catalysts. Growth of nitrogen chemisorption and decrease of ammonia adsorption resulted in the growth of catalytic activity of "cobalt" catalysts in ammonia synthesis.

Keywords: ammonia synthesis; fused iron–cobalt catalyst; adsorption of reactants on ammonia synthesis catalyst

1. Introduction

The status of the present-day ammonia synthesis catalyst is the product of research spanning almost the century. One of the key problems in this subject is the mechanism of adsorption and reaction on the catalyst surface. In the late 30's it was concluded, that the nitrogen molecules enter into some sort of adsorptive or chemical combination with the iron atoms in the catalyst surface and thereby become capable of reacting with gaseous or adsorbed hydrogen to form ammonia [1]. On the other hand, adsorption of hydrogen has been found not to affect the synthesis rate. The adsorption of hydrogen on the most active areas of catalytic metals involves such a small activation energy, that the process is rapid at temperatures as low as −100°C [2]. The fundamental studies of Emmet and Brunauer showed non-uniformity of the ammonia catalyst surface. Their conclusion: "The portions of the surface adsorbing the nitrogen more quickly are those for which a small activation energy is required" [3] is very close to nowadays presented theories on the structure sensitivity and the effect of the actually exposed iron surface [4].

An industrial iron catalyst for ammonia synthesis has been in commercial use since the 1920's. It is usually obtained by fusing natural (or synthetic) magnetite with small amounts of additives (promoters), such as potassium, aluminium and calcium oxides. Then, the catalyst is reduced in hydrogen, or more often in synthesis gas [5]. The promoters constitute only a few percent of the catalyst mass. However, after reduction, they cover more than half of the iron surface [6,7].

The catalyst prepared in such a way is active at higher temperatures. Unfortunately, the equilibrium concentration of ammonia strongly depends on temperature and pressure. Accordingly, all novel catalysts should be active at lower temperatures.

As mentioned above, the catalytically active component in those systems is mostly iron. The other metal described as interesting in ammonia synthesis is cobalt. As Shcheglov and co-workers have found [8], cobalt, following iron, is the second most active metal in ammonia synthesis. On the other hand, the results of Rambeau et al. [9] indicate low activity of cobalt powder in ammonia synthesis. Although cobalt alone is not a perfect catalyst ammonia synthesis, its alloys with iron have been reported on as promising in this process.

Morozov et al. [10] studied Fe–Co alloy catalysts of various compositions. The most active sample was that with high cobalt content. Artukh et al. [11] prepared a series of doubly promoted iron–cobalt alloy catalysts. A sample containing 15% Co proved some three times more active than that without cobalt. The specific activity of the samples was strongly dependent on the catalyst composition. Taylor and colleagues [12,13] studied a Fe–Co alloy catalyst with 3% alumina added to stabilize the structure. The best catalytic properties have been shown by a sample containing 95% Fe and 5% Co. Recently, two works were published dealing with the effect of cobalt on the properties of iron supported on magnesium hydroxycarbonate [14] and alumina [15]. An interesting effect of cobalt on the sample structure was found.

More recently, results of studies of fused iron–cobalt catalysts have been published [16,17]. Addition of cobalt changes considerably the activity of the catalyst sample. It has been shown that this effect is the result of a change of the catalyst surface morphology. The catalyst surface changes as an effect of inclusion of cobalt in the magnetite crystallic lattice and (especially) in the wüstite crystallic lattice [16]. Nonstoichiometry of wüstite, as calculated from Mössbauer data, equals 0.16 and 0.22 (analogous nonstoichiometry for magnetite 0.008 and 0.44), respectively. The new catalyst morphology causes the change of reduction behaviour of the samples. The typical iron fused catalyst changes its mass faster during reduction. On the other hand, however, the change of the surface of the catalysts during activation, as measured in situ by the thermal desorption method, was faster for the "cobalt catalysts". BET surface was higher for the typical iron catalyst. In ref. [17]

the faceting of the catalyst surface was postulated to describe the difference between activity and low temperature (77 K) nitrogen adsorption. The more active the catalyst the less nitrogen it adsorbs. In low temperature adsorption experiments the total nitrogen adsorption on the catalyst surface is measured. For the reaction kinetics the amount of nitrogen molecules chemisorbed at synthesis condition is decisive. In this study the effect of cobalt on the adsorption/chemisorption properties as measured in the ammonia synthesis temperature range is presented.

2. Experimental

2.1. SAMPLE PREPARATION

Catalysts were prepared in the laboratory plant (approximately 10 kg of catalyst per charge) in a similar way as described in ref. [18]. All samples were fused from the same starting material divided into four parts (without or with addition of different quantities of Co_3O_4).

2.2. APPARATUS

Phase compositions of the samples were investigated using an X-ray diffractometer (XRD) HZG-4 (Carl Zeiss Jena, Germany) with a cobalt tube (Co Kα radiation) and a scanning rate of 1° per minute.

Sample compositions were determined using an X-ray fluorescence spectrometer VRA30 equipped with a Cr tube, LiF(200) and PE crystals, and flow and scintillation detectors. Working parameters of the tube during measurements were 50 kV and 35 mA. The powdered samples were pressed into 14 mm internal diameter brass rings, yielding tablets approximately 5 mm thick. Conventional calibration procedure was used [19].

Kinetic measurements were conducted in the equipment described earlier [14] using an isothermal tubular reactor. The stoichiometric hydrogen–nitrogen mixture was obtained by ammonia dissociation under atmospheric pressure. The gas was purified from H_2O, CO and CO_2 over silica gel and molecular sieves. After compressing, the gas was passed over beds of an activated carbon, a palladium catalyst and drying agent to remove compressor oil and traces of oxygen compounds. The such prepared gas was fed into the reactor. Kinetic measurements were carried out under the pressure 10 MPa. All catalyst samples with particle radius 1.2–1.7 mm were reduced before the kinetic test according to the time schedule described in ref. [16]. The kinetic test was carried out at different temperatures in the order 450, 400, 350°C. Space velocity during reduction and kinetic measurements was 100000 h^{-1}.

Scanning electron microscopic (SEM) observations of the samples in oxidized

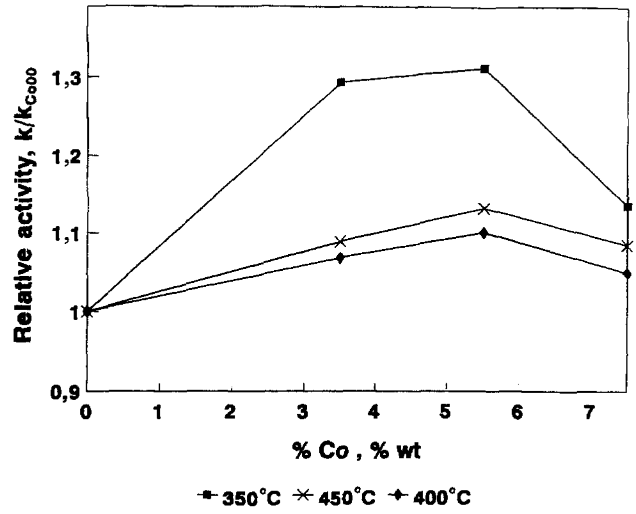

Fig. 1. Effect of sample composition on the catalysts activity.

state were carried out using a Jeol 1200EX microscope with scanning adapter. Samples were polished and etched with a (1 : 10) solution of hydrochloric acid.

The samples for the Mössbauer spectroscopic study were comminuted and pelletized. Observations were carried out at room temperature. ^{57}Co in chromium matrix (^{57}Co/Cr) served as the source. After taking the spectrum of an unreduced sample, the catalyst was reduced in situ for studying the reduced form by Mössbauer spectroscopy (after cooling under deoxygenated nitrogen). Isometric shift values are given in relation to α-Fe. Spectra have been computer fitted and Mössbauer parameters have been calculated.

Adsorption isotherms at low temperature (77 K) were taken on an ASAP 2000M V.2.00 apparatus, and adsorption isotherms at elevated temperatures on ASAP 2000C V2.00 (Micrometrics Instrument Corporation, USA). The measurements on both instruments were carried out according to the concept: first establishing the adsorption equilibrium then measure.

Table 1
Compositions of samples studied

Sample code	Iron oxides (wt%)	K_2O (wt%)	CaO (wt%)	Al_2O_3 (wt%)	SiO_2 (wt%)	Co_3O_4 (wt%)
Co00	93.50	0.60	2.80	2.80	0.30	0.00
Co35	90.55	0.58	2.99	2.63	0.29	2.96
Co55	88.36	0.55	2.47	2.40	0.25	5.97
Co75	86.17	0.49	2.42	2.35	0.25	8.32
crystal used for analysis	LiF	LiF	LiF	PE	PE	LiF

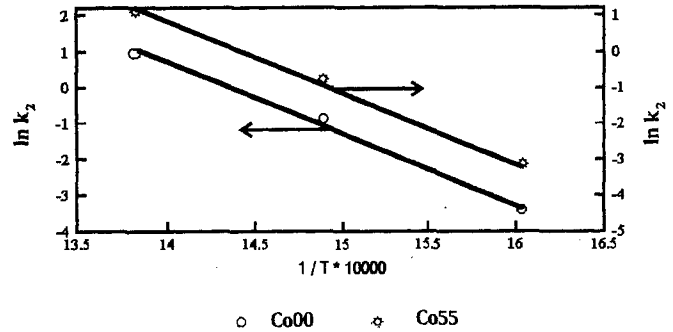

Fig. 2. Arrhenius plots for the samples Co55 and Co00 (activity, k_2, in kg NH_3 kg_{cat}^{-1} h^{-1} $atm^{0.5}$).

3. Results

Results of measurements and observations are presented in figs. 1–13 and tables 1 and 2.

Fig. 1 presents the effect of sample composition (as shown in table 1) on the activity in ammonia synthesis. The rate constant in the Temkin equation was calculated from the tubular reactor model assuming isothermal plug flow and was taken as an activity measure. Activities of the samples are presented in relation to the activity of the sample prepared in the same way but containing no cobalt. Fig. 2 presents Arrhenius plots for the samples of the Co55 and Co00 catalysts. As it follows from the results in fig. 2 ammonia synthesis on both samples can be characterized by the same activation energy.

The diffraction patterns for the samples studied are depicted in fig. 3. Figs. 4 and 5 present the SEM photographs of the surface of the sample that is most active in ammonia synthesis (Co55) and the sample containing no cobalt.

Mössbauer spectra are presented in figs. 6 and 7, while table 2 includes Mössbauer parameters.

Fig. 8 presents the adsorption isotherms of nitrogen at liquid nitrogen temperature for the sample Co55 and the sample without cobalt (Co00). Fig. 9 presents

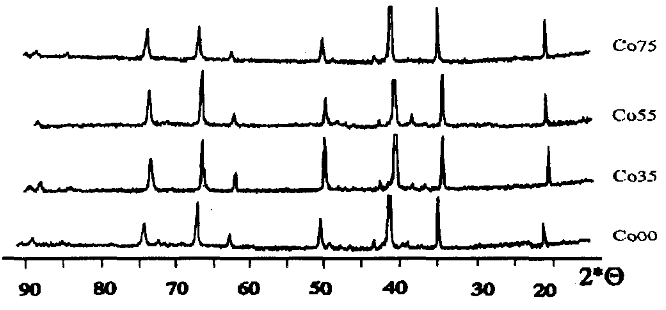

Fig. 3. Diffraction patterns for the samples studied.

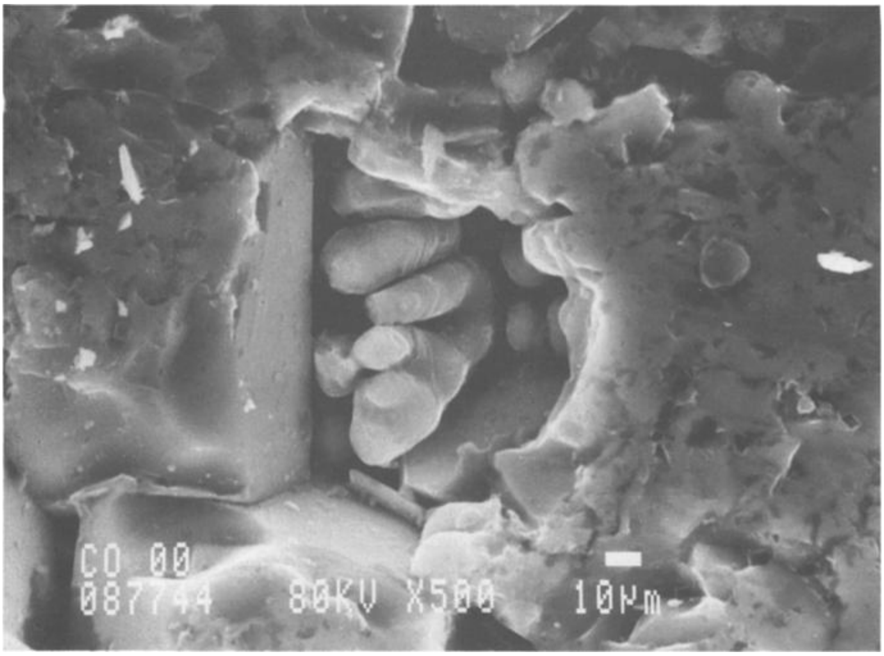

Fig. 4. SEM photograph of the surface of the Co00 catalyst (no cobalt) in oxidized state.

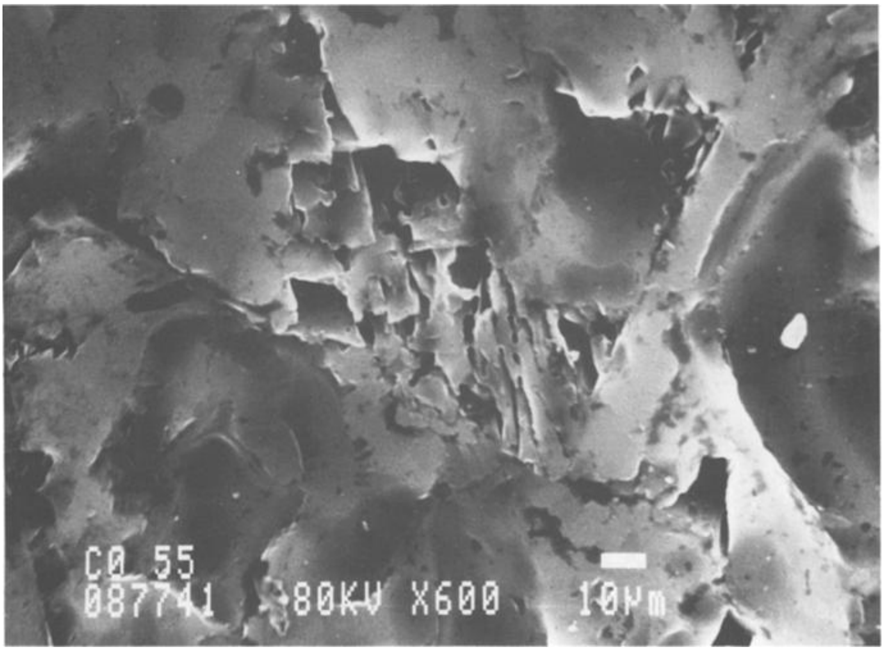

Fig. 5. SEM photograph of the surface of the most active sample (Co55) in ammonia synthesis in oxidized state.

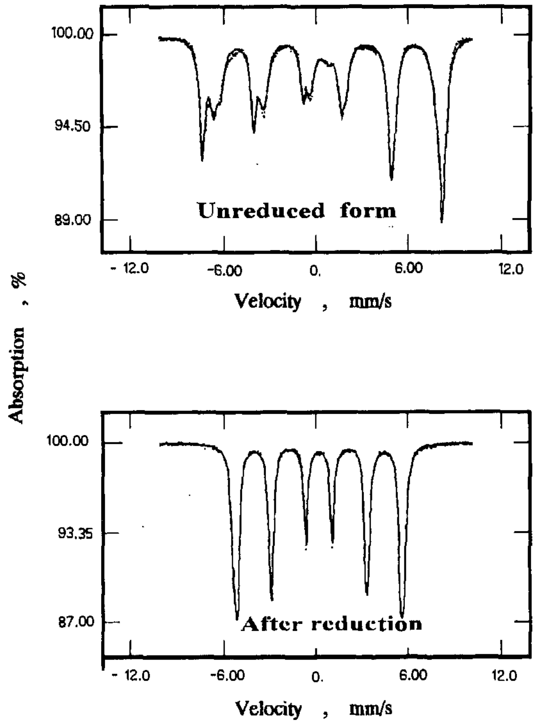

Fig. 6. Mössbauer spectra for the sample Co00 after computer fitting.

the adsorption isotherms of nitrogen for the above mentioned samples as measured in situ at the ammonia synthesis temperature (in this case 385°C). Adsorption isotherms for the case of hydrogen measured at 385°C are shown in fig. 10, while fig. 11 presents adsorption isotherms of ammonia measured at 100°C. Chemisorption of nitrogen and hydrogen are presented in figs. 12 and 13, respectively. Chemisorptions have been calculated as the difference between the first and the second adsorption run after sample outgassing. Sample outgassing was carried out by evacuating at 385°C under vacuum to the zero desorption rate.

4. Discussion

The diffraction patterns (fig. 3) show that all the samples under study possess a similar phase composition in oxidized state. Addition of cobalt changes, however, the catalyst surface morphology. The images of the surfaces of the samples are different.

As it follows from SEM photographs of the catalyst samples in oxidized state (figs. 4 and 5) the morphology of the catalyst Co55 differs considerably from the morphology of the catalyst containing no cobalt (sample Co00). The image of the surface of the cobalt promoted catalyst (fig. 4) shows that on the surface mainly

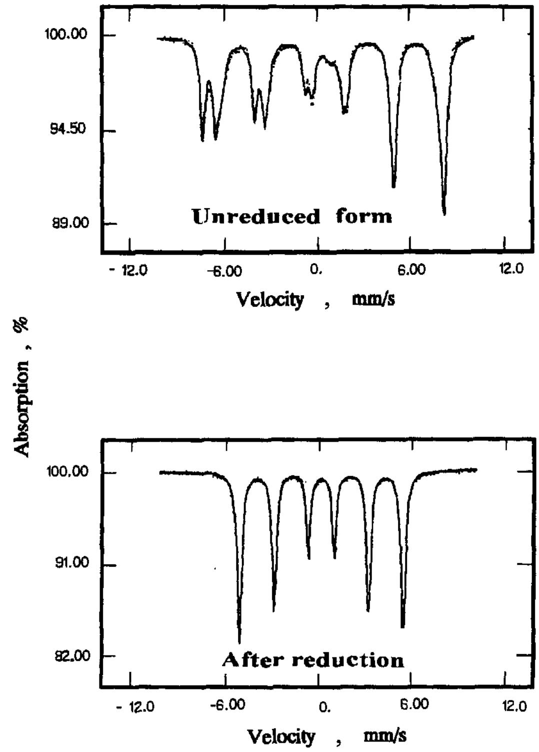

Fig. 7. Mössbauer spectra for the sample Co55 after computer fitting.

large crystallites with particle radius of approximately 0.1 mm are present. Between the large particles some inclusions in dendritic shape are observed. In the photograph no inclusions of other phases in the intercrystallic space are visible. This latter finding is probably connected with the fact that other phases (in ammonia synthesis catalyst structural promoters for instance) are rinsed out during the etching. The image of the surface of the cobalt free catalyst, fig. 5, is different from that described above. Beside the large crystallites, with a size comparable to that of the catalyst with cobalt, small particles in the intercrystallic space are present. They are about ten times smaller in radius with a characteristic oval shape. These inclusions may be wüstite particles. The content of wüstite in cobalt promoted catalyst is lower than in an iron catalyst. This results from disturbance of crystallisation caused by the competition of cobalt and iron atoms.

SEM pictures describe changes of the surface morphology of catalyst precursors in macroscale. Sample reduction resulted in microscale, however.

This is confirmed by Mössbauer spectroscopy observations. The Mössbauer spectrum of the sample Co00 (without cobalt) presented in fig. 6A is typical for iron fused catalysts with magnetite as a main component. Visible broadening of the component line from the atoms in octaedric position (there are two types of iron sites in the magnetite lattice, the tetrahedral sites A, and the octahedral sites B, of

Table 2
Mössbauer parameters for spectra presented in figs. 6 and 7 (investigations at room temperature) [a]

Component	*H* (kOe)	IS (mm/s)	*Γ* (mm/s)	Contribution (%)
sample Co00				
unreduced form				
FeO		0.77(3)	0.76(4)	5(1)
Fe_3O_4 A	484.1(1)	0.28(1)	0.19(1)	33(1)
Fe_3O_4 B	448.0(5)	0.64(1)	0.27(2)	62(2)
after reduction				
Fe	329.8(2)	0.00(1)	0.17(1)	100
sample Co55				
unreduced form				
FeO		0.65(5)	0.50(2)	4(1)
Fe_3O_4 A	483.7(1)	0.27(1)	0.21(1)	41(1)
Fe_3O_4 B	461.0(2)	0.66(1)	0.31(2)	55(2)
after reduction				
Fe	330.9	0.01(1)	0.14(1)	36.8(4)
Fe–Co	344.1(6)	0.01(1)	0.19(2)	63.2(7)

[a] *H*, magnetic field; IS, isomer shift; *Γ*, intensity half-width.

which the former are occupied by Fe^{3+} ions and the latter by Fe^{2+} and Fe^{3+} ions) is evidence for the promoter atoms being built in the vacancies of this sublattice. For the fitting of this spectrum, the wüstite parameters according to the literature values were taken, which gives the possibility for evaluation of the wüstite quantity.

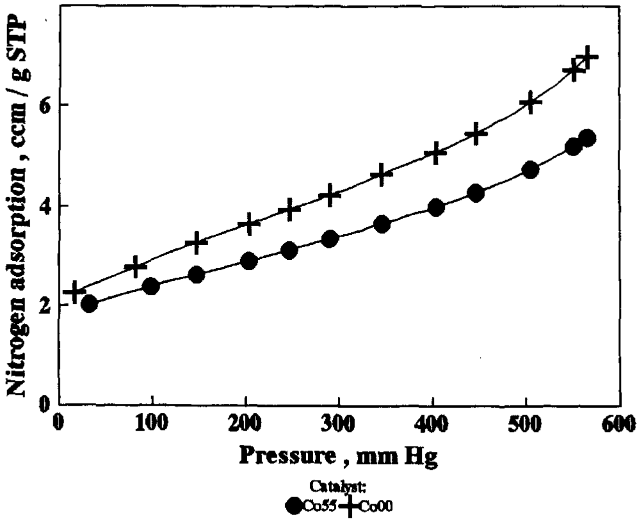

Fig. 8. Adsorption of nitrogen on the Co00 and Co55 samples at –196°C.

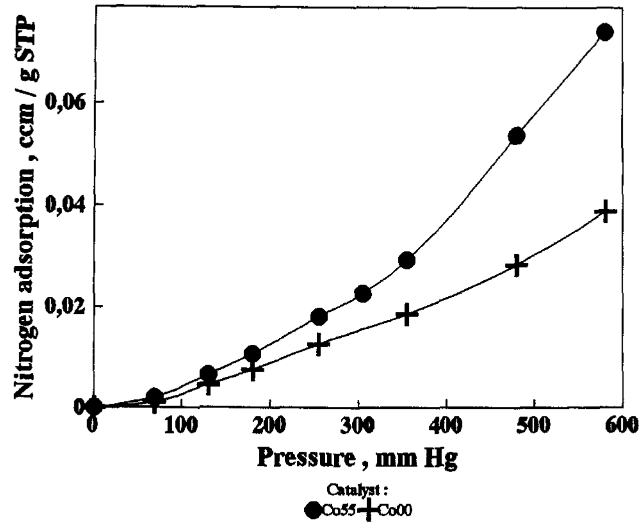

Fig. 9. Adsorption of nitrogen on the Co00 and Co55 samples at 385°C.

The FeO content is 5 ± 1%. Better fitting was observed by assuming the magnetic field distribution for the site B of magnetite. The weighted average of this field was calculated as 448 kOe, the minimum and maximum values were estimated as 426 and 454 kOe (respectively).

The spectrum for the Co55 catalyst (most active in ammonia synthesis) presented in fig. 7A is similar to that for the Co00 sample. Difference is visible for the ratio of intensity of lines corresponding to the magnetite sublattices. The quantity

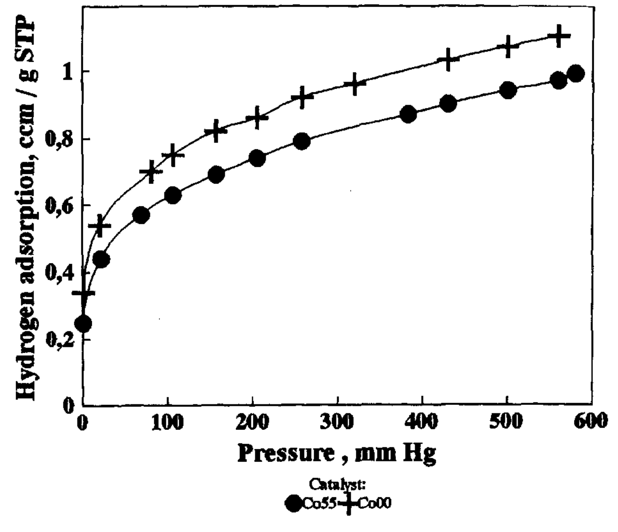

Fig. 10. Adsorption of hydrogen on the Co00 and Co55 samples at 385°C.

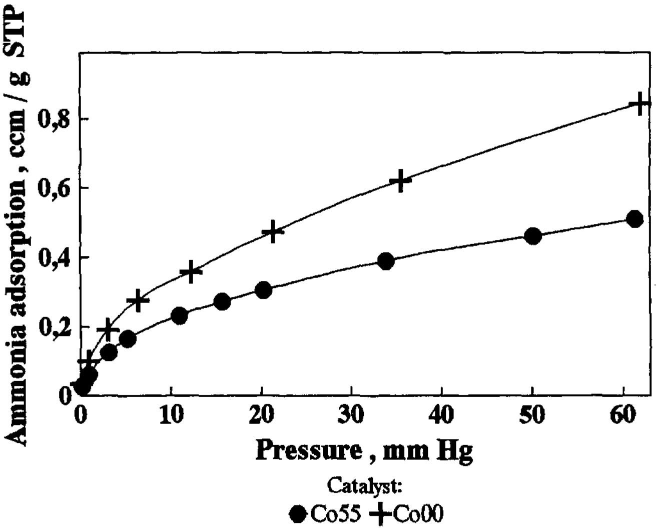

Fig. 11. Adsorption of ammonia on the Co00 and Co55 samples at 100°C.

of wüstite in this sample is slightly lower than in the sample Co00 (4 ± 1%). Noticeable is the broadening of site B lines in relation to site A lines, which confirms inclusion of impurities (effect of promoters as for Co00 sample increased by cobalt) in sublattice B. Significantly high asymmetry of the shape of the site B line additionally showed an asymmetric distribution of the magnetic field.

After reduction in the nitrogen–hydrogen mixture at the temperature 773 K, the spectrum of the Co00 sample (fig. 6B) is characteristic for metallic iron. Typical

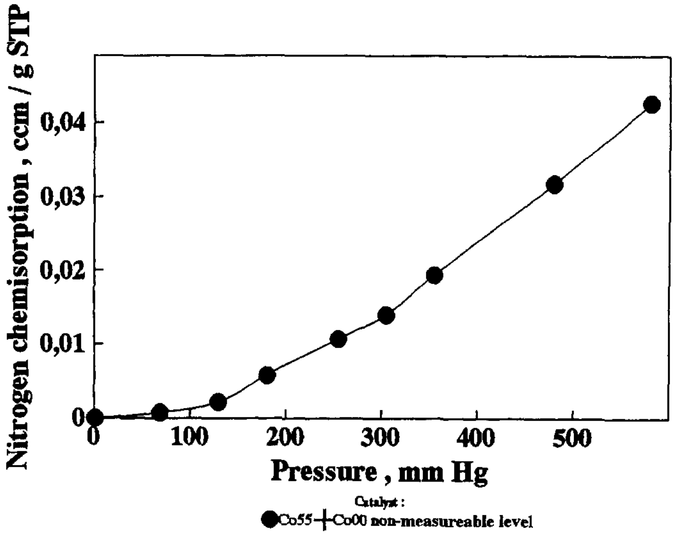

Fig. 12. Chemisorption of nitrogen on the Co00 and Co55 samples at 385°C.

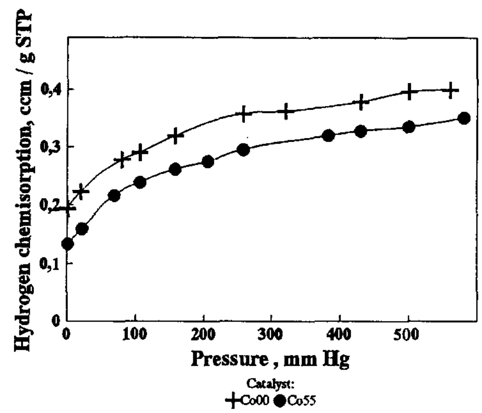

Fig. 13. Chemisorption of hydrogen on the Co00 and Co55 samples at 385°C.

magnetic splitting is observed. The magnetic field for the pure iron is 330 kOe. The slight broadening of the line is the effect of the presence of promoters, which disturb the surroundings of the iron atoms (typical intensity half-width for pure iron: $\Gamma = 0.15$ mm/s).

The spectrum of the Co55 catalyst after reduction (fig. 7B) is similar to that observed for the cobalt free catalyst. It is the sextet resulting from the magnetic splitting of iron. The visible broadening of lines (with the relation to the pure iron) and, after an analysis, the visible slight asymmetry suggest the presence of a second magnetic component with similar but slightly higher field value (fitting of this spectrum with the single sextet results in the higher value of the magnetic field). Probably it is evidence for the formation of an intermetallic iron–cobalt compound. This spectrum was fitted with two magnetic components, the first the pure iron, the other one the Fe–Co system compound. Phase diagram analysis for the Fe–Co system [20] in the same temperature range as used in the present study shows the possibility of formation of intermetallic compound Fe_3Co.

Reduction behaviour as a result of cobalt addition is followed by the change of adsorption properties of the "cobalt catalyst" sample. For the case of adsorption of gaseous nitrogen at the liquid nitrogen temperature on the surfaces of both "cobalt" and typical iron catalysts (samples Co55 and Co00, respectively) an unexpected result can be concluded. The sample which adsorbs more nitrogen (Co00) is less active in ammonia synthesis. That means that adsorption properties of the studied samples during measurement under low temperature adsorption conditions are very different from those at the ammonia synthesis temperature. The next adsorption measurements were then provided in situ at higher temperatures.

Adsorption of nitrogen at 385°C is presented in fig. 9. Adsorption of this component is higher on the surface of the more active catalyst sample (sample Co55 – "cobalt" catalyst). The opposite effect is observed for the case of hydrogen (fig. 10) and for the case of ammonia adsorption at 100°C (fig. 11). Chemisorption of nitrogen is much higher for the case of the "cobalt" catalyst (fig. 12).

Adsorption of nitrogen on the different faces of the single iron crystal showed [4] that the Fe(111) surface dissociatively chemisorbed nitrogen 20 times faster than the Fe(100) surface and 60 times faster than the Fe(110) surface. The addition of potassium reduced this effect. Single crystal experiments also have shown [21] the possibility of surface restructuring by aluminium oxide during water pretreatment. For the case of the much more complicated industrial iron catalyst (similar to the samples measured in this study) Strongin and Somorjai [4] suggest that interaction between promoters and iron results in formation of solid solutions which could prevent planes such as Fe(111) formed during reduction from converting to more thermodynamically stable planes, such as Fe(110) and Fe(100) surfaces. Results observed during the present work confirmed restructuring of the iron catalyst surface by cobalt addition as postulated in ref. [17]. Its action can be similar to the role of aluminium oxide – stabilization of active iron planes on the catalyst surface.

Let us now discuss hydrogen adsorption/chemisorption data. Guess [21] demonstrated for the case of supported iron catalysts the small extent of adsorption of hydrogen molecules at room temperature and a considerable increase of hydrogen adsorption at the higher temperature of 200°C. The low content of hydrogen adsorption is attributed [21] to the stability of a monolayer of oxygen atoms on most of the crystallographic surfaces of iron. The only oxygen atoms which can be removed easily by hydrogen reduction are those adsorbed on the closely packed Fe(110) surface. This iron plane is pure in ammonia synthesis, so it should be concluded that a catalyst which chemisorbs more hydrogen will be less active in ammonia synthesis. Moreover, the ratio of the surface occupied by Fe(111) to the total iron surface atoms is, for such sample, less than for more active catalysts. In the case of the catalysts described during this study it can be postulated that (according to the hydrogen adsorption results) the Co55 catalyst surface offered more active adsorption sites than the Co00 (cobalt free) catalyst. This surface restructuring is probably an effect of cobalt addition.

Addition of cobalt caused the growth of chemisorption of nitrogen under ammonia synthesis conditions and decreased the adsorption of ammonia. "Cobalt" catalyst under reaction conditions adsorbed more nitrogen and more easily desorbed the products of catalytic reaction. This results in the growth of the catalytic activity observed during a kinetic test.

5. Conclusions

(1) Addition of cobalt produced the change of adsorption properties of fused iron catalyst for ammonia synthesis.

(2) Chemisorption of nitrogen is much higher for the case of "cobalt" catalyst. This is probably the effect of surface restructuring.

(3) Growth of nitrogen chemisorption and decrease of ammonia adsorption

resulted in the growth of catalytic activity of "cobalt" catalysts in ammonia synthesis.

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References

[1] Frankenburger, Ullmans, *Enzyklopädie der Technischen Chemie* (1928).
[2] H.S. Taylor, J. Am. Chem. Soc. 52 (1930) 5298.
[3] P.H. Emmet and S. Brunauer, J. Am. Chem. Soc. 56 (1934) 35.
[4] D.R. Strongin and G.A. Somorjai, *Catalytic Ammonia Synthesis, Fundamental and Practice*, ed. J.R. Jennings (Plenum Press, New York, 1991) p. 133.
[5] A. Nielsen, *An Investigation on Promoted Iron Catalyst for the Synthesis of Ammonia*, 3rd Ed. (Gjellerups, Copenhagen, 1968).
[6] A. Nielsen and H. Bahlbro, J. Am. Chem. Soc. 74 (1962) 953.
[7] D.C. Silverman and M. Boudart, J. Catal. 28 (1973) 477.
[8] O.V. Shcheglov, G.K. Boreskov and M.G. Slinko, Dokl. Akad. Nauk SSSR 105 (1955) 123.
[9] G. Rambeau, A. Jorti and H. Amariglio, J. Catal. 94 (1985) 155.
[10] N.M. Morozov, L.J. Luk'yanova and M.I. Temkin, Kinet. Katal. 6 (1965) 82.
[11] Yu.N. Artukh, M.T. Rusov and N.A. Boldyryeva, Kinet. Katal. 8 (1967) 1319.
[12] D.W. Taylor, P.J. Smith, D.A. Dowden, C. Kemball and D.A. Whan, Appl. Catal. 3 (1982) 161.
[13] P.J. Smith, D.W. Taylor, D.A. Dowden, C. Kemball and D. Taylor, Appl. Catal. 3 (1982) 303.
[14] R.J. Kaleńczuk, J. Chem. Tech. Biotechnol. 54 (1992) 349.
[15] R.J. Kaleńczuk, J. Chem. Tech. Biotechnol. 59 (1994) 73.
[16] R.J. Kaleńczuk, Appl. Catal. 112 (1994) 149.
[17] R.J. Kaleńczuk, J. Chem. Tech. Biotechnol., submitted.
[18] K. Kałucki, W. Arabczyk, R. Kaleńczuk, W. Morawski, U. Narkiewicz, B. Skowroński, A. Gołębiowski, Z. Janecki, Z. Śpiewak and S. Ludwiczak, Polish Patent 139580 (1986).
[19] H. Ehrhardt, ed., *Röntgenfluoresznzanalyse, Anwendung in Betriebslaboratorien* (VEB Deutscher Verlag für Grundstoffindustrie, Leipzig, 1981).
[20] L.M. Viting, Zh. Neorg. Khim. 2 (1957) 845.
[21] J.W. Gues, K.C. Waugh, in: *Catalytic Ammonia Synthesis, Fundamental and Practice*, ed. J.R. Jennings (Plenum Press, New York, 1991) p. 179.