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 syn-
thesis 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. Unfortu-
nately, the equilibrium concentration of ammonia strongly depends on tempera-
ture 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 sta-
bilize the structure. The best catalytic properties have been shown by a sample con-
taining 95% Fe and 5% Co. Recently, two works were published dealing with the
effect of cobalt on the properties of iron supported on magnesium hydroxycarbon-
ate [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 pub-
lished [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 sur-
face 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 sam-
ples. 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 activa-
tion, 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]