Wustite based iron-cobalt catalyst for ammonia synthesis

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ABSTRACT

By way of melting, iron and iron-cobalt wustite based catalysts promoted with oxides of calcium, aluminium, and potassium were obtained. Measurements of the activity in the ammonia synthesis reaction at pressure of 10 MPa were conducted. A positive effect of cobalt addition into the wustite structure of the iron catalyst on increasing in the catalyst catalytic activity in the ammonia synthesis reaction, lowering a temperature, at which catalysts achieved the maximum reduction rate, decreasing values of the apparent activation energy of obtained catalysts, and increasing resistance to the overheating process was observed. All the results were compared with the results obtained for the industrial magnetite-based iron catalyst.

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1. Introduction

The invention of the fused iron catalyst for the ammonia synthesis laid the foundations for the development of currently known heterogeneous catalysis. For more than 90 years, history of researches on improving properties of the iron catalyst failed to achieve a breakthrough progress. A precursor of a conventional magnetite-based iron catalyst is mainly composed of iron oxide Fe_3O_4 and metal oxides acting as promoters of which most commonly used are oxides of aluminium, calcium, and potassium (Al_2O_3, CaO, and K_2O). The composition and the type of promoters were main variables in studies on the activity of the catalysts in the ammonia synthesis reaction [1] for long time. The issue of the selection of iron ions Fe^{2+}/Fe^{3+} ratio was not undertaken in conjunction with the assumptions of classical volcano shape curve describing the dependence of catalytic activity from the mentioned earlier ratio described as R. According to this curve, catalysts with R-value close to 0.5, corresponding to the ratio of iron ions in natural magnetite, achieve optimal activity.

A breakthrough in this matter was Liu's and co-workers work [2–6], in which wustite based iron catalyst was used for the ammonia synthesis. According to the Chinese researchers, an increase in the value of the R ratio does not only affect an increase in the content of iron on the second oxidation degree but mainly on the change in a phase composition of resulting catalyst precursors. Above a certain limiting R value, the structure of wustite catalyst is formed only

by $Fe_{1-x}O$ phase. This issue led Liu to studies on the effect of catalyst precursors phase composition on the activity in the ammonia synthesis reaction what was illustrated with a new camel's hump type activity curve. Chinese scientists' results met great interest of researchers dealing with the iron catalysts for the ammonia synthesis [7–9].

Another catalyst that showed high activity in the ammonia synthesis reaction is a magnetite based iron-cobalt catalyst. In 1967 Artyukh [10] studied fused an iron-cobalt catalyst. Its activity in the ammonia decomposition reaction was found to be three times higher than for a pure iron catalyst at temperatures below 400 °C what caught the attention of other researchers. In the 1980s the British company ICI launched a low-pressure installation ICI-AMV, which used a new iron catalyst with an addition of cobalt ICI-74-1 [11]. Researchers from the University of Fuzhou in China [12] successfully developed a Fe-Co A201 catalyst in 1985. In 1995 the same team introduced into the iron-cobalt catalyst rare earth oxides, reducing a content of cobalt oxide, and released a new A202 catalyst. Currently, iron catalysts containing cobalt are widely used in industrial plants in China.

In a study by Kaleńczuk [13], it has been shown that the catalytic activity of iron-cobalt catalyst promoted with potassium changes with the cobalt content and reaches a maximum in the vicinity of 5.5% by weight of cobalt, what largely agrees with the results of Hagen et al. [14], according to which the maximum activity of Fe-Co catalyst promoted with barium and supported on carbon carrier was achieved for 4 wt.% of cobalt.

The aim of the studies was to combine the aspects of cobalt addition and the type of catalyst precursor and to define the conditions

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of the activation process. The activity of wustite based iron-cobalt catalysts in the ammonia synthesis reaction was also determined.

2. Experimental

2.1. Preparation of catalyst precursors

Precursors of examined iron catalysts were prepared by fusing in a laboratory resistance furnace [15]. A batch consisted of magnetite ore and promoters: calcium oxide, aluminium oxide, potassium nitrate, and iron. Precursors of iron-cobalt catalysts were prepared in the same way but reagent mixture was enriched with cobalt oxide.

The proportions of the individual components were selected to obtain predetermined promoters and cobalt amounts as well as a sufficient oxidation degree R (Fe^{2+}/Fe^{3+}) in catalyst precursors. The mixture of components was melted and poured out into a stainless steel container to solidify reagents and cool down at ambient temperature. The obtained catalyst precursors were crushed and sieved to obtain a fraction of 1.0–1.2 mm.

2.2. Characterization of catalysts

The phase composition of the obtained catalyst precursors was determined with the X-ray diffraction method on X'Pert Pro Philips apparatus. The radiation source was an X-ray tube with a copper anode emitting CuK_a radiation. To identify catalyst crystallographic phases the X'PertHighScore program was used.

Quantitative composition analyses of the catalyst precursors were performed by ICP-OES method using a Perkin Elmer spectrometer Optima 5300DV type. The molar ratio of iron ions Fe^{2+}/Fe^{3+} in the resulting samples expressed as a catalyst oxidation degree R, was determined with manganometric titration [16]. Before titration, catalysts were dissolved in hydrochloric acid in nitrogen atmosphere.

The reduction process of the catalyst precursors was tested with the aid of the temperature-programmed reduction (TPR) method on Autochem II 2920 Micromeritics apparatus. Samples were reduced with 10% H_2 in argon using a temperature ramp rate 10 °C/min to 1000 °C.

The activity of the obtained catalysts in the ammonia synthesis reaction was examined in a six-channel differential steel reactor equipped with an ammonia analyser and an interferometer for tracking changes in a concentration of the synthesised ammonia. Appropriate sample weights of catalyst fraction of dimensions 1.0–1.2 mm were tested. The synthesis gas was a purified mixture of hydrogen and nitrogen in a ratio of 3:1, obtained by catalytic decomposition of gaseous ammonia. The purity of the reaction mixture was ensured thanks to the use of a number of adsorbers and cleaning reactors added to the installation. The pressure of the synthesis generated by a membrane compressor was 10 MPa. Before the activity measurement, the catalysts were subjected to a reduction process with a mixture of nitrogen and hydrogen at atmospheric pressure according to the following temperature program: 250 °C, 1 h; 300 °C, 1 h; 350 °C, 3 h; 400 °C, 13 h; 450 °C, 24 h (after this step control activity measurement was performed at a temperature of 450 °C); 475 °C, 18 h (activity measurement at temperatures of 475, 450, and 400 °C); 500 °C, 15 h (activity measurement at temperatures of 500, 450 and 400 °C). The space velocity of reduction gas was about 20,000 h^{-1}.

The overheating resistance of the catalysts was examined using measurements of the activity at temperatures of 500, 450, and 400 °C after 18 h annealing of the catalysts at 600 °C in an atmosphere of synthesis gas. The activity of the catalysts is represented as the reaction rate constant k [g_{NH3} $MPa^{0.5}/g_{Cat}$ h], calculated

Table 1
The R value and the percentage composition of the wustite based iron and iron-cobalt catalyst precursors as well as the industrial magnetite-based catalyst precursor. The remaining mass is comprised of iron oxides.

Sample name	R	Oxide content [%]			
		Al_2O_3	CaO	K_2O	CoO
WARW-8	6.4	1.81	1.63	0.39	–
ZBRW-10	6.7	2.18	1.3	0.44	2.01
ZBRW-11	4.9	3.36	2.09	0.67	3.62
IND-Fe_3O_4	0.5	3.41	3.39	0.78	–

according to the Temkin-Pyzhev equation [17]. Results obtained for an industrial magnetite-based iron catalyst IND-Fe_3O_4, in tests conducted under the same conditions, were used as a reference point.

3. Results and discussion

Table 1 summarizes the quantitative composition and the oxidation degree R of the wustite based iron and iron-cobalt catalyst precursors obtained by melting as well as the industrial magnetite-based catalyst.

Fig. 1 shows diffraction patterns of the prepared catalyst precursors. Reflections corresponding to the wustite phase according to the JCPSD 00-006-0615 card are visible in the diffraction pattern. Small reflections visible on magnification in the vicinity of the angle 2Θ~45° marked with (●) may correspond to the maximum reflections both for Fe phase (JCPSD 00-001-1262) and $Al_{0.47}Co_{0.53}$ phase (JCPSD 00-044-1264) for ZBRW-10 and ZBRW-11 catalyst precursors. Considering the melting process and metallic iron presence, the peaks should be ascribed to metallic iron phase with higher probability. During the melting process cobalt occurs in the oxide form (Co^{2+}). On the basis of the ternary system Co-Fe–O [18] we can conclude that cobalt oxide forms a solid solution with wustite.

From the enlargement of peaks corresponding to the non stoichiometric phase of $Fe_{1-x}O$ in the 2Θ region approximately of 61° the shift of their maximum was observed. It results from the change of d parameter in the Bragg equation, what corresponds to the distance between atom layers in the crystal lattice of the investigated catalysts. The decrease in the interplanar distance is caused
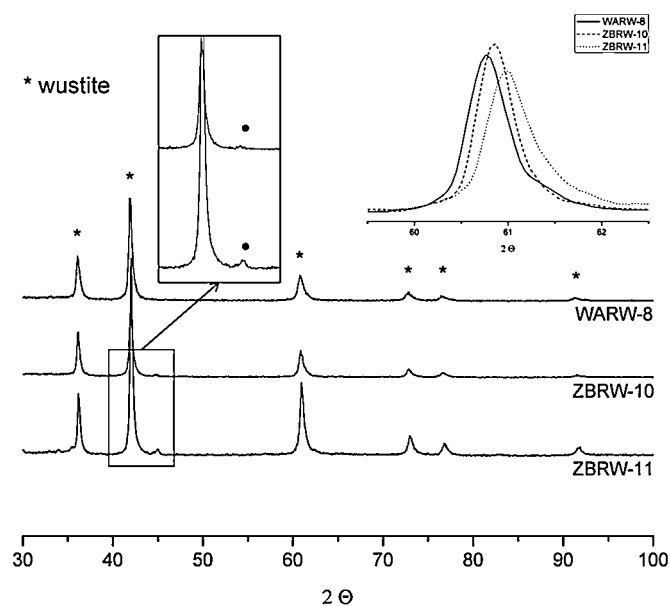

Fig. 1. X-ray ptterns of WARW-8, ZBRW-10 and ZBRW-11 catalyst precursors samples.