

ABSTRACT OF THE DISSERTATION

“Design and synthesis of new cobalt supported catalyst for ammonia synthesis”

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Catalytic ammonia synthesis from nitrogen and hydrogen is a crucial process in the fertilizers industry. In addition to the production of fertilizers, ammonia is used as feedstock for the manufacturing of many products of everyday use, i.e. soap, paper, and glass. An important new application of ammonia is its use as a hydrogen carrier. Therefore, the ammonia decomposition reaction exhibits great potential as a source of hydrogen for fuel cells. The ammonia synthesis technology was developed by Haber and Bosch almost a century ago. Since the launch of the first ammonia synthesis plant in 1913, this technology has been progressing intensely. The strategic direction of the process development is research on a new catalyst working effectively under reduced pressure and temperature conditions.

The doctoral thesis aimed to develop an efficient ammonia synthesis catalyst based on cobalt supported on $\text{MgO-Ln}_2\text{O}_3$ ($\text{Ln} = \text{La, Nd, Eu}$), which would be an alternative to the commercial iron catalyst. Several tasks were required to accomplish this goal. The support and catalyst composition and preparation methods were selected among them. The obtained materials were subjected to detailed characterisation studies using the following techniques: N_2 physisorption, thermogravimetry coupled with mass spectrometry, X-ray diffraction, electron microscopy, X-ray photoelectron spectroscopy, and temperature-programmed desorption of hydrogen. The catalyst activity in ammonia synthesis was measured in the high-pressure reactor under conditions close to the industrial ones. For the most active catalyst, the kinetic characteristic showing the dependence of the ammonia synthesis rate on the product concentration in the synthesis mixture was determined.

The results indicated a close correlation between the chemical composition of the support and physicochemical properties and activity of the cobalt catalysts in ammonia synthesis. The optimal molar ratio of magnesium oxide to rare earth metal oxide was established, ensuring the presence of many Lewis-type basic centres on the support surface. As a result of the increased basicity of the support surface, increased activity of catalysts in the ammonia synthesis reaction was observed. The studies on the various methods of introducing the cobalt precursor onto the support revealed that the textural and chemisorption parameters characterizing the obtained catalysts differed depending on the preparation method. The cobalt catalyst obtained by wet impregnation was characterized by the highest activity. It was shown that this catalyst had metallic cobalt particles of a size favourable for the occurrence of adsorption sites of different hydrogen bonding strengths. As a result, increased availability of active sites and increased catalyst activity under the ammonia synthesis conditions were observed. In the studies on the influence of the promoter addition on the properties of the cobalt catalyst, it was proved that among the promoters from the group of alkaline earth metals (Ca, Ba), only barium ions had a strong activating effect on cobalt. The observed

increase in activity in relation to the unpromoted catalyst resulted primarily from the change in the nature of active sites for nitrogen and hydrogen chemisorption. The obtained barium-promoted cobalt catalyst showed a 2–5-fold higher reaction rate than the industrial iron catalyst. The assessment of the main properties of the developed cobalt catalyst, i.e. activity and thermal stability, indicated its great potential and the possibility of its application in industrial ammonia synthesis.

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