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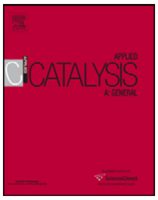

Ammonia synthesis over cobalt catalysts doped with cerium and barium. Effect of the ceria loading

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ABSTRACT

The effect of ceria loading on the activity and thermal stability of a cobalt catalyst for ammonia synthesis has been studied. The concentration of CeO_2 in the $Co_3O_4 + CeO_2$ mixtures ranged from 0 to 29 wt%, whereas the barium content was constant and equaled 13 wt% in relation to Co_3O_4. Kinetic measurements in NH_3 synthesis were carried out in a flow differential reactor operating under standard conditions ($p = 6.3$ MPa, $T = 400\,^{\circ}C$, $H_2{:}N_2 = 3{:}1$). The kinetic measurements of NH_3 synthesis were supplemented with the characterization studies of the obtained materials – N_2 physisorption, XRPD, H_2 chemisorption, TPR-TG/DTG-MS and SEM-EDS. It has been found that ceria plays the role of a structural promoter; it hinders the sintering of Co_3O_4 during calcination and stabilizes the surface area of Co under reaction conditions. Moreover, it seems that ceria stabilizes the hcp phase of metallic cobalt, which results in a higher activity of the cobalt catalysts. The co-promoted cobalt catalyst containing 11.5 wt% of CeO_2 (symbol Co/Ce(11.5)/Ba) was shown to be more active in NH_3 synthesis than the conventional fused iron catalyst (KM I, H. Topsoe). Moreover, the catalyst Co/Ce(11.5)/Ba is very resistant to overheating. Heat treatment at 600 °C for 160 h ($3H_2{:}N_2 = 30.0$ l/h, $p = 0.1$ MPa) results in a decrease of its activity in NH_3 synthesis by only a few percent.

1. Introduction

Ammonia synthesis is one of the most important and the largest, in terms of the production scale, catalytic processes in the chemical industry today. The global production of NH_3 was estimated to be 124 million tons in 2006 and continues to exhibit a steady increase [1]. Ammonia is used in the production of fertilizers, explosive materials, and as a refrigerant. Since the hydrogen used in fuel cells has to be pure, i.e. not contaminated with carbon oxides, ammonia is thought to become the best source of hydrogen suitable for this application in the near future [2–7]. The catalytic reaction of hydrogen and nitrogen, which leads to the formation of ammonia, is of significant importance in the development of catalysis. Two Nobel Prizes have been awarded for research on this topic [8]. Moreover, studies on ammonia synthesis have led to many significant improvements and innovations. The basic terms used in catalysis, such as promoter or poison, were first used with regard to ammonia synthesis. Furthermore, new catalytic concepts, e.g. structure sensitivity of a reaction, have been developed during studies of ammonia synthesis catalysts [9].

For the above reasons, the researchers from industrial centres and academia are still active in the field of NH_3 synthesis and they try to work out a completely new catalyst [10–18] or to improve the formula and properties of the conventional iron one [19–25]. Among several new catalytic systems investigated in the last 40 years, only ruthenium supported on high surface area graphite (HSAG) has been implemented in the industrial practice so far. A combination of both the conventional iron (first catalytic bed) and the modern Ru/C catalyst (last three beds) in the so called Kellog Advanced Ammonia Process (KAAP) has been shown to be very advantageous [26,27], i.e. the pressure in ammonia loops could be significantly reduced (to 9.0 MPa), thus resulting in a lower energy consumption.

However, the high price of ruthenium and its tendency to catalyzes the depletion of the support, i.e. methanation [28–31], are the main reasons why the ruthenium catalyst did not revolutionize the process of NH_3 synthesis. Research on the development of an entirely new catalytic system with other metals which exhibit catalytic activity in this reaction [32] is still ongoing. Cobalt-based catalysts are among the most frequently investigated systems [15,33–35]. The latest research of Raróg-Pilecka et al. has shown

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