



Effect of preparation conditions and promoters on the structure and activity of the ammonia decomposition reaction catalyst based on nanocrystalline cobalt



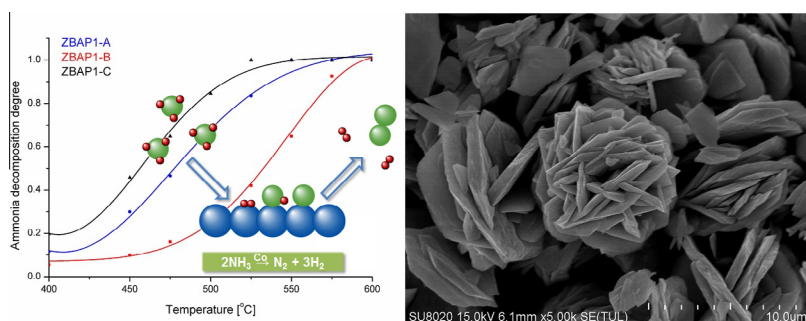
Łukasz Czekajło, Zofia Lendzion-Bieluń*

West Pomeranian University of Technology, Szczecin, Institute of Chemical and Environment Engineering, Pułaskiego 10, 70-322 Szczecin, Poland

HIGHLIGHTS

- Effect of preparation conditions and promoters on the properties of cobalt catalyst.
- Triple promoted catalyst has the highest sintering resistance and NH_3 decomposition.
- Ammonia was decomposed almost completely at a temperature of 525 °C.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:

Received 13 October 2015
Received in revised form 22 December 2015
Accepted 28 December 2015
Available online 2 January 2016

Keywords:

Ammonia decomposition
Cobalt catalyst
Promoters
Structure

ABSTRACT

A cobalt catalyst precursor for the ammonia decomposition, in the form of cobalt oxide (II and III) promoted with oxides of calcium, aluminum, and potassium, was obtained by precipitation method. The increase in the precipitation process temperature reduces the average size of Co_3O_4 crystallites obtained in the calcination process. The addition of alumina has a positive effect on the area of the active surface, surface stability and catalytic activity of the active form of the catalyst, namely metallic cobalt, in the ammonia decomposition reaction. The highest activity was achieved for the catalyst ZBAP1-C promoted with oxides of calcium, aluminum, and potassium, which attained the ammonia decomposition degree of approximately 100% at a temperature of 525 °C. There were no changes observed in the crystalline structure of the ZBAP1-C catalyst during the “in situ” XRD studies of the ammonia decomposition at a temperature of 475 °C when the nitriding potential changed.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

Cobalt oxide (II and III) is widely used in many fields, starting from lithium batteries [1–3], through gas sensors [4–6] up to the catalysts [7–9]. Once reduced to the metallic form it arouses a great interest as a catalyst for the ammonia decomposition to pure hydrogen, which may be a fuel for fuel cells [10,11]. Most studies

connected with the ammonia catalytic decomposition and published in literature were carried out over ruthenium-based catalysts while we have been looking for a cheaper catalyst than the ruthenium based one but equally effective. Investigations on the precipitation method of a cobalt catalyst preparation that would allow to obtain a material with a structure that will help to achieve the best catalytic properties have been conducted [12,13].

Pure metallic cobalt exhibits a low catalytic activity in comparison with other metals commonly used as catalysts. On the volcano-type curve, which describes the dependence of the activity

* Corresponding author.

E-mail address: zosi@zut.edu.pl (Z. Lendzion-Bieluń).

of various catalysts used in the ammonia synthesis on nitrogen adsorption dissociative energy, pure cobalt is on the right side, so that it did not attract a greater interest in this field [14]. Considering this fact, and relying on studies on ammonia synthesis reactions, it may be deduced that only a modified cobalt catalyst is important in practical use.

Sorensen et al. [15] conducted an experiment, in which four non-promoted catalysts, Fe, Ru, Co, Pd were compared with one another. At temperatures of 575 °C and 650 °C, for a gas mixture containing 50% NH₃ in argon the best ammonia decomposition catalyst was cobalt. For both temperatures, result of the experiment expressed as mole H₂/mole metal/s, in the case of cobalt was five times greater than for iron. It is a testament to the fact, that contrary to expectations pure cobalt achieves beneficial results to catalyze the reaction of NH₃ molecules breakdown into hydrogen and nitrogen.

In the study of ammonia decomposition conducted by Dr. Lendzion-Bieluń et al. [14] a catalyst comprising nanocrystalline cobalt promoted with oxides of calcium, aluminum, and potassium was used. Composition (content of promoters) corresponded to the composition of the industrial iron catalyst for the ammonia synthesis, taking into account minor differences in the specific surface area for the benefit of the cobalt catalyst. For the experimental conditions (temperature in the range of 673–823 K, atmospheric pressure, a mixture of hydrogen and ammonia containing approximately 6% NH₃) results showed that the cobalt catalyst was more effective than the iron catalyst in the process of ammonia decomposition. This was indicated by a lower value of activation energy: cobalt – 111 kJ/mole, iron – 138 kJ/mole.

Boisen et al. [11] investigated the cobalt catalyst modified with molybdenum. On the basis of obtained results it was proved, that it had significant potential for the ammonia decomposition reaction under conditions, where a conventional promoted iron catalyst could not have been used due to a large amount of nitrides generated by it.

The aim of this study was to determine the effect of the preparation conditions, precipitation process temperature, and the type of promoters on the structural and catalytic properties of obtained cobalt oxide (II and III) – catalyst precursor.

2. Experimental

2.1. Preparation of catalysts

Cobalt catalyst precursor, cobalt oxide (II and III), was obtained by precipitation and calcination. Precipitation of the cobalt hydroxide precipitate from an aqueous solution of cobalt nitrate (V) by 25% aqueous ammonia solution, was carried out at three temperatures of 80 °C, 60 °C and 40 °C. During the precipitation pH of the solution was controlled. The process was terminated when the solution achieved pH = 8.5.

The resulting precipitates were filtered off under reduced pressure and then rinsed with distilled water and dried at 100 °C for 12 h. Calcination process was carried out at 300 °C for 2 h in air. As a result, three samples of Co₃O₄ (ZBAP1, ZBAP2, and ZBAP3) were obtained.

Oxides promoters namely calcium, aluminum, and potassium were introduced by impregnation of cobalt oxide (II and III) with corresponding nitrate salt solutions. The type and content of each salt were adjusted to get the assumed composition and weighting of the promoters in the catalyst. This process was carried out using a rotary evaporator (Rotavapor R-210, BÜCHI). Then, after drying at 100 °C for three hours samples were calcined at 500 °C for 2 h in air. In this way, ZBAP1-A, ZBAP1-B, and ZBAP1-C catalyst precursors were obtained.

2.2. Characterization of catalysts

The phase composition and an average size of crystallite grains of obtained cobalt oxide (II and III) were determined with XRD method on Philips X'Pert Pro apparatus. The average Co₃O₄ crystallite size was calculated on the basis of the width of reflections using Scherrer equation.

The topography of the obtained materials was examined using a scanning electron microscope (Hitachi SU-8800). With the use of the EDX analyzer mapping of triplicate promoted catalyst surface was performed.

The analysis of the quantitative composition of the samples after impregnation process was performed with ICP-OES method using a Perkin Elmer spectrometer Optima 5300DV type.

Temperature programmed reduction (TPR) for each catalyst was also carried out. The samples were reduced with the mixture of 10% H₂ in argon using temperature ramp rate 10 °C/min to 1000 °C.

Measurements of specific surface area and a temperature-programmed desorption of hydrogen (H₂-TPD) were performed on the reduced forms of the catalysts, which are the active forms of the catalysts, using an Autochem II 2920 apparatus from Micromeritics. The reductions of the catalysts were carried out in an atmosphere of pure hydrogen at three different temperatures: 500 °C, 550 °C, and 600 °C for 16 h.

Measurement of the specific surface area of the catalysts was done with the aid of the one-point low-temperature nitrogen adsorption method at liquid nitrogen temperature.

TPD-H₂ measurement was preceded by adsorption of hydrogen at 20 °C on the surface of the catalysts reduced at above-mentioned temperatures. The final desorption temperature was equal of the temperature used in the reduction process.

The activity of the cobalt catalyst samples in the ammonia decomposition reaction was examined in a differential reactor equipped with a conductometric hydrogen analyzer and thermogravimeter that allowed a tracking of changes in mass. The fraction of the catalyst with dimensions of 1.0–1.2 mm was placed as a single layer in a platinum basket hung inside the reactor in the installation shown in [14] has been studied. Before the activity measurement, the catalysts were subjected to polythermal hydrogen reduction with a load of 0.2 dm³ g⁻¹ min⁻¹ at a temperature increasing from 20 °C to 600 °C at the rate of 15 °C/min under atmospheric pressure conditions. When masses of samples were stabilized they were additionally soaked for three hours at a final reduction temperature at hydrogen atmosphere.

For the activity studies approximately 0.5 g weighed amounts of previously pre-reduced catalysts were used. After calibration of the hydrogen analyzer signal for a flow of pure NH₃ and H₂ at a room temperature, catalysts were heated up to working temperature under hydrogen stream until the weight was stabilized. In the first place, the effect of temperature changes on the decomposition rate at a constant load of pure NH₃ under atmospheric pressure was studied. The space velocity of ammonia was set at 19,544 h⁻¹. The activity of the catalysts was tested in the temperature range of 400–600 °C. The ammonia decomposition degree was controlled basing on the change in concentration of H₂ detected by hydrogen analyzer. The gas samples for analysis were taken directly from the space above the catalyst bed. Temperature changes were made after settling stationary states. In these conditions, both the composition of the gas and solid phase did not change. Hydrogen molar fraction was calculated from the calibration formula.

The ammonia decomposition reaction at 475 °C under the atmospheric pressure by introducing an ammonia-hydrogen mixtures of variable composition into the reactor was examined. Changes in the composition of the mixture at the reactor inlet were made after 15 min when the steady states were established. Using

Download English Version:

<https://daneshyari.com/en/article/145817>

Download Persian Version:

<https://daneshyari.com/article/145817>

[Daneshyari.com](https://daneshyari.com)