Doctoral dissertation

„Cobalt-Molybdenum Catalysts for Ammonia Synthesis"

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Abstract in English

Ammonia synthesis catalysts, which are composed of cobalt molybdenum nitrides, were subject to the research work carried out as part of the doctoral dissertation. Oxidic precursors were obtained by the precipitation from water solutions of cobalt and Subsequently precursors were activated by reaction with gaseous ammonia.

The crystallographic structure of the precursors precipitated from solutions with a pH ranging from 5.5 to 7.5 was determined. The precursors precipitated from slightly acidic solutions consist of $CoMoO_4 \cdot 0{,}9H_2O$ phase, whereas those precipitated from slightly basic solutions consist $NH_4Co_2OH(MoO_4)_2 \cdot H_2O$ phase. The lattice constants and the space group of both crystallographic phases were determined. The positions of atoms in the unit cell of the precursor obtained in a basic environment were determined.

The activation process of the oxidic precursors leading to the formation of cobalt molybdenum nitrides was studied. The mechanism by which the transformation of the oxide precursor to the active phase proceeds has been determined. At the initial stage of calcination, the process of water removal from the $CoMoO_4 \cdot 0{,}9H_2O$ phase or water and ammonia removal from the $NH_4Co_2OH(MoO_4)_2 \cdot H_2O$ phase takes place. In both cases, cobalt(ll) molybdate $CoMoO_4$ phase is formed. The decomposition of the $CoMoO_4$ phase proceeds with the formation of the bimetallic oxide $CO_2Mo_3O_8$ and the cobalt(ll) oxide CoO. Under an ammonia atmosphere, the two oxides mentioned above are reduced to the intermetallic compound Co_3Mo and metallic cobalt as intermediates. Then these phases undergo nitriding to form cobalt molybdenum nitrides Co_3Mo_3N and Co_2Mo_3N.

The catalyst obtained from the precursor precipitated from acidic solution was composed of Co_3Mo_3N and Co_2Mo_3N nitrides, and the catalyst obtained from the precursor precipitated from basic solution additionally contained the Co_3Mo intermetallic compound. The activity of these catalysts in the ammonia synthesis process was tested. The catalyst obtained by activating the precursor precipitated from the alkaline solution was the most active. Both catalysts are more active in the ammonia synthesis reaction than the industrial iron catalyst. It was shown that the presence of the Co_3Mo intermetallic phase in the catalyst has a positive effect on the activity of these materials in the ammonia synthesis process.

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