

## ***In-situ* XRPD analysis of active carbon supported Co-Mo ammonia synthesis catalysts activation**

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Up today researchers work to obtain new catalytic systems for a next-generation ammonia synthesis process, which could reduce the energy costs and CO<sub>2</sub> emission. Cobalt molybdenum nitrides are potential candidates in this field, since they have higher activity in the synthesis of ammonia than the commercially used promoted iron catalyst [1]. The activity of the cobalt molybdenum catalyst can be further increased by addition of alkaline promoters such as caesium or potassium [2]. However, the addition of these promoters has a negative effect on the specific surface area of the cobalt molybdenum catalyst. The development of an effective method to counteract these limitations is crucial to the potential application of cobalt molybdenum nitrides on a larger scale.

Only a few studies addressing the development of the cobalt molybdenum nitrides with a higher specific surface area were conducted. The change in the conditions of the activation process by additional temperature treatment is suggested [3]. The typical precursor consisting CoMoO<sub>4</sub> was changed to the Co(en)<sub>3</sub>MoO<sub>4</sub>, in which (en) denotes ethylenediamine molecule [4]. The addition of citric acid, which acts as a chelating agent, results in increased surface area and higher activity [5]. Double promotion with the use of potassium and chromium leads to simultaneously more active and more stable material, in which chromium acts as a structural promoter [6].

In this study, the problem of low thermal stability and tendency to sinter of cobalt molybdenum nitrides during ammonia synthesis was addressed by using catalyst support in form of active carbon. The supported catalysts were formed by the wet impregnation of the support with an aqueous solution of cobalt and molybdenum salts, followed by vacuum evaporation. The precursor was filtered, dried and subjected to a reduction under an ammonia atmosphere to obtain nitrides. Despite very high surface area, activated carbon in applications as catalyst carrier has a major disadvantage. It undergoes methanation under the conditions of ammonia synthesis, i.e. reacts with hydrogen to form methane [7].

To make insight into the activation process, in this study the ammonolysis of the precursors was examined via *in-situ* X-ray powder diffraction with the use of PANalytical X'pert Pro MPD diffractometer equipped with Anton Paar XRK 900 reaction chamber. Under the ammonolysis conditions, several structural transformations of the precursor were observed. Apart from broad hump peaks originated from activated carbon, several sharp peaks corresponding to intermediate phases were identified during ammonolysis process. Following phases were identified: MoC, metallic Co and Co<sub>3</sub>Mo<sub>3</sub>C. Cobalt molybdenum nitrides which are active in the ammonia synthesis were not present in the product.

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