Influence of the Co to Mo molar ratio on active phase formation of ammonia synthesis catalysts: *in-situ* XRPD analysis

Paweł Adamski[1], Aleksander Albrecht[1], Dariusz Moszyński[1]

[1]West Pomeranian University of Technology in Szczecin, Department of Inorganic Chemical Technology and Environment Engineering, Pułaskiego 10, 70-322 Szczecin, Poland, adamski_pawel@zut.edu.pl

Transition-metal nitrides tend to form structures with variable compositions. The Co-Mo-N system, with known phases of Co_2Mo_3N, Co_3Mo_3N, and Co_6Mo_6N, shows many promising catalytic properties [1]. Cobalt molybdenum nitrides are active in processes such as ammonia synthesis and decomposition, hydrodesulfurization, and NO reduction [2]. They are especially active in ammonia synthesis and therefore are a plausible candidate for replacing industrial iron catalysts [3].

The most commonly used method for the formation of cobalt molybdenum nitrides is a two-stage process consisting of the preparation of the oxidic precursor and the subsequent ammonolysis of the mixed oxide [4]. The synthesis process is influenced by the parameters of the precipitation process and thus by the composition of the precursor. Therefore, it often results in the formation of mixed crystallographic phases with inconsistent properties. The change in stoichiometry can be beneficial or harmful to the applicability, and the lack of reproducibility is an important disadvantage and impedes the upscaling of the technology.

The catalytic activity of cobalt molybdenum nitrides in ammonia synthesis is highly influenced by the composition of the catalyst and depends on the ratio of Co_2Mo_3N to Co_3Mo_3N, which is difficult to control [4]. To address this issue in the present study, a procedure based on the mechanochemical formation of the precursor was applied.

Three mixtures of cobalt(II) nitrate and ammonium heptamolybdate with controlled molar ratio of Co:Mo (2:1, 1:1, 1:2) were prepared by simple mixing with mortar and pestle. The obtained mixtures were reduced under an ammonia atmosphere with simultaneous collection of powder X-ray diffraction patterns. The X'pert Pro MPD diffractometer equipped with the Anton Paar XRK 900 reaction chamber was used to observe the transformation of cobalt molybdate present in precursors into mixed cobalt molybdenum nitrides. The influence of the Co:Mo molar ratio on the final composition was examined.

[1] Hargreaves JSJ. Heterogeneous catalysis with metal nitrides. Coord. Chem. Rev., 257, 2015-2031 (2013),
[2] Gurram VRB, Enumula SS, Chada RR, Koppadi KS, Burri DR, Kamaraju SRR. Synthesis and Industrial Catalytic Applications of Binary and Ternary Molybdenum Nitrides: A Review. Catalysis Surveys from Asia, 22, 166-180 (2018),
[3] Kojima R, Aika K. Cobalt molybdenum bimetallic nitride catalysts for ammonia synthesis. Part 1. Preparation and characterization. Appl. Catal. A, 215, 149-160 (2001),
[4] Alconchel S, Sapina F, Beltran D, Beltran A. Chemistry of interstitial molybdenum ternary nitrides MnMo3N (M=Fe, Co, n=3; M=Ni, n=2). J. Mater. Chem., 8, 1901-1909 (1998),
[5] Moszyński D, Adamski P, Nadziejko M, Komorowska A, Sarnecki A. Cobalt molybdenum nitrides co-promoted by chromium and potassium as catalysts for ammonia synthesis. Chem. Papers, 72, 425-430 (2018).

The scientific work was financed by The Polish National Centre for Research and Development, grant „Lider", project No. LIDER/10/0039/L-10/18/NCBR/2019.