

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

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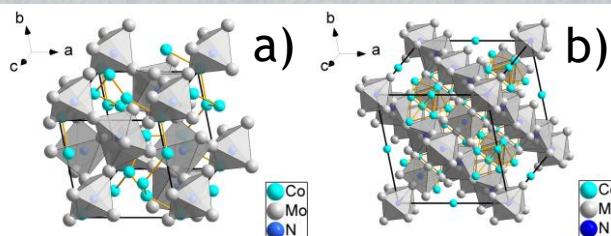
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27 Co cobalt 58,93 u	42 Mo molybdenum 95,95 u	7 N nitrogen 14,01 u
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Introduction: The catalytic activity of cobalt molybdenum nitrides in ammonia synthesis depends on $\text{Co}_2\text{Mo}_3\text{N}$ (a) to $\text{Co}_3\text{Mo}_3\text{N}$ (b) ratio. However, the synthesis of catalyst with controlled stoichiometry is hard to accomplish. In our research group we are working at developing new, controlled synthesis routes, such as mechanochemical. The main goal of this study is to make insight into the ammonolysis process of the mixture of cobalt and molybdenum salts with the defined Co:Mo molar ratio via *in-situ* X-ray powder diffraction.

Experimental: 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. Phase transformations occurring during ammonolysis of samples were thoroughly studied via *in-situ* XRPD with the use of the Anton Paar XRK 900 (c) reaction chamber mounted on Philips X'pert Pro MPD (d) powder diffractometer (Cu radiation source).



Catalyst	Activity [$\mu\text{mol}\cdot\text{h}^{-1}\cdot\text{g}^{-1}$]	Conditions
$\text{Co}_2\text{Mo}_3\text{N}$ rich	918 (our goal)	500 °C; 0.1 MPa
$\text{Co}_3\text{Mo}_3\text{N}$ rich	771	500 °C; 0.1 MPa

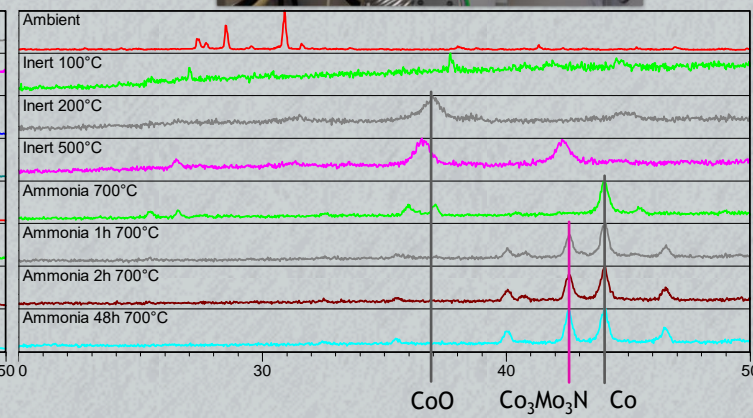
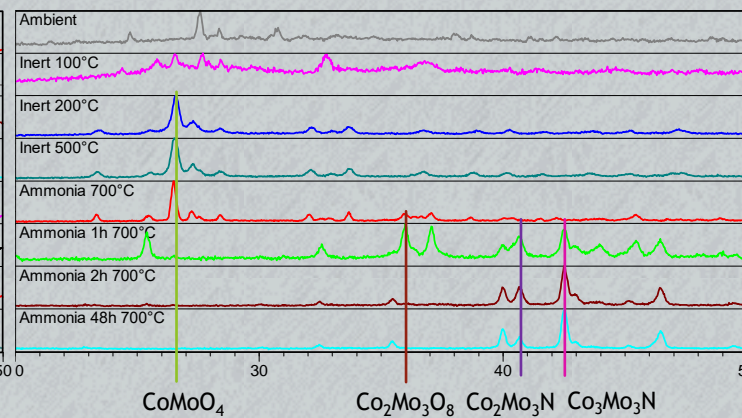
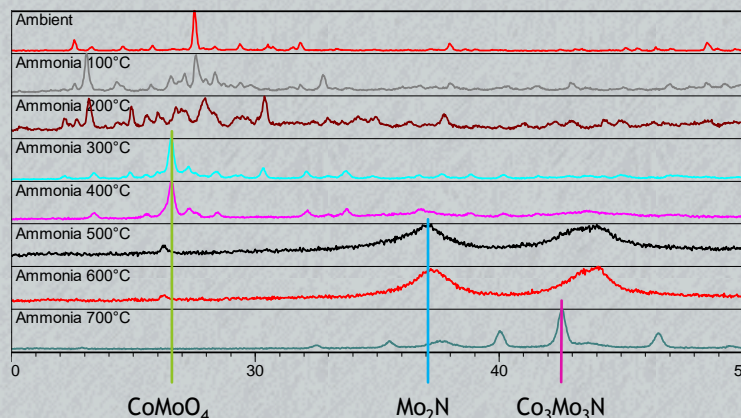


Fig. 1. Diffraction patterns of the Co:Mo (1:2) sample during the *in-situ* experiment course. Sample was heated in diluted ammonia atmosphere.

Fig. 2. Diffraction patterns of the Co:Mo (1:1) sample during the *in-situ* experiment course. Sample was heated in inert atmosphere. Ammonia was introduced to the system at 700 °C.

Fig. 3. Diffraction patterns of the Co:Mo (2:1) sample during the *in-situ* experiment course. Sample was heated in inert atmosphere. Ammonia was introduced to the system at 700 °C.

Results: The precursor phases resulting from substrates mixing could not be identified with the use of PDF database. Under the ammonolysis conditions, the precursors underwent several structural transformations. Intermediate phases were identified as CoMoO_4 (PDF 04-017-6377), $\text{Co}_2\text{Mo}_3\text{O}_8$ (PDF 04-001-9062), Mo_2N (PDF 04-013-4024), CoO (PDF 04-005-4395), Co (PDF 04-014-0167), $\text{Co}_2\text{Mo}_3\text{N}$ (PDF 04-010-6426) and $\text{Co}_3\text{Mo}_3\text{N}$ (PDF 04-008-1301). Phase fractions obtained from the Rietveld refinement of the final products are presented in **Table 1**. Higher Mo content favors obtaining of Mo_2N and $\text{Co}_3\text{Mo}_3\text{N}$. Higher Co content favors obtaining of metallic Co and $\text{Co}_3\text{Mo}_3\text{N}$. Mixture of two bimetallic nitrides $\text{Co}_2\text{Mo}_3\text{N}$ and $\text{Co}_3\text{Mo}_3\text{N}$ was only obtained as a product of ammonolysis of material with equal Co to Mo molar ratio.

Table 1. Concentration of crystalline phase in the samples after ammonolysis, obtained from the Rietveld refinement. Molar ratio of cobalt to molybdenum atoms.

Co:Mo	Co [wt. %]	$\text{Co}_2\text{Mo}_3\text{N}$ [wt. %]	$\text{Co}_3\text{Mo}_3\text{N}$ [wt. %]	Mo_2N [wt. %]	nCo/nMo (Rietveld)
2:1	52	0	48	0	3.93
1:1	0	22	78	0	0.92
1:2	0	0	76	24	0.67