

## **New nanomaterials for chemoselective hydrogenation of nitrocyclohexane to cyclohexanone oxim under a flow condition**

Sustainable development requires constant research for safe and economic methods of preparation of synthetic construction materials. To fulfill this expectations, modern chemical industry is based on heterogeneous catalysis. First of all, application of catalysts makes chemical reaction possible, but also significantly affect its efficiency. Polyamides are one of the most important synthetic materials with annual demand 1 mln tons (only in the Europe). This materials, which are produced by the main chemical manufacturers, found application in many industries (textile, aviation, automotive). Synthesis of one of the most popular polyamides – Polycaprolactam (also known as: Nylon-6, PA6, Perlon) is mainly based on direct polymerization of  $\epsilon$ -Caprolactam. This compound is the result of multi-step process, that involves oxidation of cyclohexane to cyclohexanone followed by reaction with hydroxylammonium sulphate which gives cyclohexanone oxime. As a result of Beckmann rearrangement of cyclohexanone oxime,  $\epsilon$ -Caprolactam is formed. There are some disadvantages of this process like poor efficiency of cyclohexane oxidation (maximally 8-10% with cobalt catalyst usage), but also it is resulted in formation of huge amount of ammonium sulphate waste. Taking into consideration enormous annual production of the final product, even minor changes in the synthesis of one of the substrates can make a difference for the whole process.

The goal of this research is to create completely new nanomaterials, based on readily available transition metals (Ni, Cu, Co) active in direct chemoselective hydrogenation of nitrocyclohexane (NC) to cyclohexanone oxime (CHO) in flow conditions. Catalytic hydrogenation is structural sensitive. Hence, process of catalyst development will give unique opportunity to understand reaction constraints and to investigate factors crucial to selectivity. This reaction pathway was under investigation of big chemical consortia for reaction conducted in batch at elevated pressure and temperature, which resulted in DuPont patent from 1961. So far, there is not active and selective catalysts in flow hydrogenation. Our preliminary studies proved that this reaction can be conducted in flow conditions under atmospheric pressure. This give a chance to develop cheap and effective solutions in perspective.

Direct hydrogenation of nitrocyclohexane to cyclohexanone oxime is very challenging because of the consecutive hydrogenation of products. We assume that the research goal can be achieve by chemoselectivity of metal supported catalysts in combination with optimization of reaction conditions (space velocity and temperature). There are two possible approaches to this task. First of them involves application of low-cost transition metals (Ni, Cu, Co) supported on materials with balanced amount of acidic centres (or lack of them). Another method is based on modification of monometallic catalysts with very low amount of very active metals (Pt, Pd).

Synthesis of novel catalysts with various parameters (e.g. metal loading, particles size and their distribution, acidic properties of the support), that will be tested in catalytic reactions will allows to determine important structural factors that have impact on their activity and selectivity. An application of various characterization methods (XRD, HRTEM, chemisorption, FTIR, XPS, etc.) will allow to determine the relationship between structure and reactivity in the catalytic systems.