

**CATALYTIC HYDRODENITROGENATION (HDN) OF ORGANIC  
NITROGEN COMPOUNDS OVER SUPPORTED NICKEL PHOSPHIDE  
CATALYSTS**

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## INTRODUCTION AND OBJECTIVES

Due to the tightening supplies, harder and increasingly uncertain availability of carbon and fossil energy resources, it is needed to develop technologies for the conversion of renewable carbon source (biomass) to value-added chemicals, liquid or gaseous energy carriers. Organic wastes and by-products of food industry and agriculture are carbon sources of second generation bio-fuels. Pyrolysis is considered as an effective and advantageous way of biomass conversion. From animal by-products pyrolysis gives biochar, combustible gas and pyro-oil. The pyrolysis oil is viscous, corrosive and chemically unstable liquid, thus without any refining the direct use of pyro-oil as fuel or fuel additive is very limited. Due to the high nitrogen content the direct combustion of pyro-oil leads to excessive formation of environmentally hazardous nitrogen oxides. The removal of nitrogen heteroatom is necessary in order to get environmentally friendly energy carrier, environmentally acceptable bio-fuel from the oil.

The catalytic technologies of petrochemical industry, available for heteroatom removal from different feedstocks, do not necessarily suit for the hydrodenitrogenation (HDN) of pyrolysis oils. The reason is that mineral oil fractions usually contain nitrogen and also sulfur compounds in aromatic heterocyclic molecules, thus the hydrotreatment aims the sulfur removal by hydrodesulfurization (HDS) and the simultaneous removal of nitrogen by hydrodenitrogenation (HDN). In contrast, pyro-oils have high nitrogen (8-12%), relatively low oxygen content (~5%) and virtually no sulfur. Thus, reactions of HDN and hydrodeoxygenation (HDO) must proceed together. The hydrotreatment breaks C-S, C-N and C-O bonds providing saturated hydrocarbons,  $\text{H}_2\text{S}$ ,  $\text{NH}_3$  and  $\text{H}_2\text{O}$ , respectively. The catalytic hydrodenitrogenation of pyrolysis oils, having high nitrogen content, can be economic, because hydrocarbon and ammonia are formed in the process, which are useful precursors of fuel and fertilizer, respectively.

Generally the industrial catalysts for hydrotreating are transition metal sulfides. The sulfur content of the oil is important in maintaining the activity of these catalysts. Transition metal phosphides, having similarly high or higher activity in the simultaneous HDS/HDN reaction than the transition metal sulfides. These phosphide catalysts preserve their activity in absence of sulfur, therefore, they are more suitable catalysts for catalytic hydrotreating of pyro-oils than the transition metal sulfides.

The economic production of liquid hydrocarbon fuel or any useful chemicals from biomass is a real challenge for the research, development and engineering. The goal of the

present work is to establish scientific bases to a technology that can be used for refining pyro-oil obtained from meat and bone meal (MBM). The most characteristic nitrogen compounds in the pyro-oil are aliphatic amines and nitriles. The HDN process of the oil was modeled by the catalytic hydrodenitrogenation reaction of propylamine (PA) and propionitrile (PN) over oxide supported  $\text{Ni}_2\text{P}$  catalysts. We revealed relationships between the conditions of catalyst synthesis, the properties of the oxid support and the structure and activity of the  $\text{Ni}_2\text{P}$  phase, formed on the support. Our goal was to understand the catalytic mechanism and to establish scientific bases to the development of a more effective catalyst for the pyro-oil HDN reaction.

## EXPERIMENTAL METHODS

In the present work oxide supported nickel-phosphide catalysts were prepared from silica gel, silicalite-1, SBA-15, laponite and silica pillared laponite. Wet impregnation of the support was followed by calcination and controlled reduction of the obtained nickel-phosphide precursor compounds. The lowest reduction temperature, where the  $\text{Ni}_2\text{P}$  phase could form, was determined from the results of temperature-programmed reduction ( $\text{H}_2$ -TPR) and *in situ* high temperature XRD measurements. The Ni and P content of each catalysts was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES). XRD method was applied to identify the  $\text{Ni}_2\text{P}$  active phase on the support and to follow the changes of the catalyst structure. The average metal particle size was determined by transmission electron microscopy (TEM) and X-ray powder diffractometry using the Sherrer-equation. Specific surface area of the catalysts was determined by the BET method from nitrogen adsorption isotherm, obtained at the temperature of liquid nitrogen. Temperature-programmed hydrogen desorption measurement ( $\text{H}_2$ -TPD) was applied to determine the dispersion of particles. Metal centers in different states, formed in the catalyst, were characterized by the infrared spectroscopic examination of carbonyl bands obtained from adsorbed CO. Catalytic experiments were carried out in a flow-through microreactor, in the temperature range of 200-400°C, at total pressure of 30 bar and  $\text{H}_2$ /reactant molar ratio of 10. *Operando* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was applied to learn about the species on the surface of the working catalyst under reaction conditions. For these experiments a high-temperature and high-pressure DRIFT spectroscopic cell was used.

## NEW SCIENTIFIC RESULTS

### 1. Physical-chemical properties of oxide supported Ni<sub>2</sub>P catalysts

1.1. In contrast to the earlier suggestions it was shown that the Brønsted-acid sites, generated by residual phosphate-like species on supported Ni<sub>2</sub>P catalysts, were formed predominantly on the support and not on the surface of the active Ni<sub>2</sub>P phase.

(Described in publication No.1.)

1.2. According to the infrared spectra of carbon-monoxide, adsorbed on the catalyst, Ni atoms of the active Ni<sub>2</sub>P phase were identified in different oxidation and/or coordination states. It was demonstrated that:

- the carbonyl band at 2195 cm<sup>-1</sup> belongs to the Ni<sup>2+</sup>(CO), not to P=C=O species, which formed from the interaction of P atom of surface phosphate and CO;
- the carbonyl band at 2055 cm<sup>-1</sup> is assigned not to the residual nickel-tetracarbonyl (Ni(CO)<sub>4</sub>), adsorbed on the surface of the support, as suggested by earlier studies, but to nickel-subcarbonyl species (Ni(CO)<sub>x</sub>, x≤3), that are transformed to monocarbonyl when the CO gas was flushed out;
- the carbonyl bands at 2096 cm<sup>-1</sup> and 2035 cm<sup>-1</sup> are assigned to CO adsorbed on terrace atoms of crystal faces and on high-energy defect sites (edges, corners, atomic steps), respectively.

(Described in publication No.1.)

1.3. It was shown that the concentration of the defect sites does not depend on the particle size of the Ni<sub>2</sub>P phase only, but also on the surface characters of the support. Surface hydroxyl groups of the support were substantiated to stabilize defected Ni<sub>2</sub>P crystallites.

(Described in publication No.1.)

1.4. It was shown that on silica-supported Ni<sub>2</sub>P catalysts the catalytically active surface species are generated in the adsorption interaction of the propylamine reactant and the catalyst. During the catalytic reaction the initially defected Ni<sub>2</sub>P particles of the activated catalysts were converted to much ordered Ni<sub>2</sub>P crystals.

(Described in publication No.1.)

## 2. Catalytic properties of oxide supported nickel-phosphides

2.1. It was confirmed that the HDN reaction of propylamine and propionitrile proceeds mainly through secondary amine intermediate. At lower temperatures the  $\text{Ni}_2\text{P}$  catalysts were highly active in the propylamine disproportionation reaction, whereas at higher temperatures the hydrogenolysis of the C-N bond in different order amines became the main reaction.

(Described in publication No.1-3.)

2.2. Two reaction pathways of propane formation were shown to be available for the hydroconversion of propylamine. At lower temperatures ( $<300^\circ\text{C}$ ) propane is the primary product of the hydrogenolysis of propylamine C-N bond, whereas at higher temperatures ( $>300^\circ\text{C}$ ) it is mainly formed as secondary product from the HDN reaction of dipropylamine intermediate.

(Described in publication No.1.)

2.3. It was substantiated that in the HDN reaction of propylamine the yield of dipropylamine intermediate is in relationship mainly with the particle size of  $\text{Ni}_2\text{P}$  phase and not with the Brønsted-acidity of the support. Small particle size favors the formation of dipropylamine.

2.4. It was confirmed that the dipropylamine formation proceeds through imine intermediate. It was substantiated that first propylamine is dehydrogenated to 1-propanimine, which in the reaction with amine, gives propylidene propylamine intermediate that finally becomes hydrogenated to dipropylamine. Thus, dipropylamine formation needs both catalyst of hydrogenation/dehydrogenation activity and the presence of hydrogen.

(Described in publication No.1.)

2.5. It was shown that due to rapid hydrogenation of nitrile to amine the HDN reaction of propionitrile and propylamine has a similar reaction network. The reaction is introduced by partial dehydrogenation or hydrogenation of propylamine and propionitrile, respectively, to 1-propanimine, which is the intermediate of the reactions giving higher order amines. The dehydrogenation is thermodynamically favored at higher, whereas the hydrogenation at lower reaction temperatures. As a consequence higher order amines appear at lower temperatures when propionitrile is the reactant and at higher temperatures when propylamine is the reactant.

(Described in publication No.1-3.)

2.6. It was demonstrated that in contrast to the mechanism, suggested in the literature, the addition reaction of 1-propanimine and propylamine, which is the first step towards dipropylamine formation, does not require any Brønsted-acid site. It was shown that protonated and strongly bonded dipropylamine and propylamine species on Brønsted-acid sites are spectator species not taking part in the reaction.

(Described in publication No.3.)

2.7. It was shown that the Ni/silica catalyst initiates hydrocracking reactions of propylamine and propionitrile giving alkanes, that have lower carbon number than the reactant. In contrast, supported Ni<sub>2</sub>P catalysts are active and selective in the partial or full removal of heteroatoms in a hydroconversion process without breaking C-C bonds.

(Described in publication No.1-3.)

## PUBLICATIONS RELATED TO THE THESIS

### *Articles in journals:*

1. Applied Catalysis B: Environmental 164 (2015) 48–60.

**A study of the hydrodenitrogenation of propylamine over supported nickel-phosphide catalysts using amorphous and nanostructured silica supports**

*Cecília A. Badari, Ferenc Lónyi, Eszter Drotár, Alexander Kaszonyi, József Valyon*

IF<sub>2013</sub>: 6.007

2. Catalysis Communications 58 (2015) 1–5.

**A study of the selective catalytic hydroconversion of biomass-derived pyrolysis or fermentation liquids using propylamine and acetic acid as model reactants**

*A.C. Badari, Sz. Harnos, F. Lónyi, Gy. Onyestyák, M. Štolcová, A. Kaszonyi, J. Valyon*

IF<sub>2013</sub>: 3.320

3. Reaction Kinetics, Mechanisms and Catalysis xxx(2015)xxxx,

DOI: 10.1007/s11144-015-0842-3.

**Catalytic hydrodenitrogenation of propionitrile over supported nickel phosphide catalysts as model reaction for transformation of pyrolysis oil obtained from animal by-products**

*Cecília A. Badari, Ferenc Lónyi, Sándor Dóbé, Jenő Hancsók, József Valyon*

IF<sub>2013</sub>: 0.983

### *Abstracts of posters and oral presentations:*

1. Környezettudományi Doktori Iskolák I. Konferenciája (1<sup>st</sup> Symposium of Doctoral Schools of Environmental Sciences), Eötvös Loránd University, 30-31 August 2012, Budapest

**Nagy nitrogéntartalmú bio-olajokra jellemző modellvegyületek katalitikus hidrogenitrogénezése (Catalytic hydrodenitrogenation of compounds as model molecules for high nitrogen containing bio-oils)**

*Badari Andrea Cecília, Ferenc Lónyi, József Valyon*

2. Kálmán Erika Doctoral Conference, 18-20 September 2012, Mátraháza, ISBN: 978-963-508-624-5, p. 122.

**Hordozós  $\text{Ni}_2\text{P}$  katalizátorok előállítása, jellemzése és vizsgálata n-propil-amin hidrokonzverziós reakciójában (Synthesis, characterization and study of supported  $\text{Ni}_2\text{P}$  catalysts in the hydroconversion of n-propylamine)**

*Badari Andrea Cecília, Lónyi Ferenc, Valyon József*

3. 2<sup>nd</sup> International Conference on Materials for Energy EnMat II, 12-16 May 2013, Karlsruhe, Germany

**Catalytic hydrodenitrogenation of propylamine as model reaction of hydrorefining pyrolysis oil obtained from animal by-products**

*Cecília A. Badari, Ferenc Lónyi, József Valyon*

4. Anyag- és Környezetkémiai Intézet szemináriuma (Seminar of Institute of Materials and Environmental Chemistry), HAS Research Centre for Natural Sciences, 10 June 2014, Budapest

**Szerves nitrogénvegyületek katalitikus hidrogenitrogénezése (HDN) hordozós nikkel-foszfid katalizátorokon (Catalytic hydrodenitrogenation (HDN) of organic N-compounds over supported nickel phosphide catalysts)**

*Badari Andrea Cecília, Lónyi Ferenc, Valyon József*

5. Closing Meeting on Chemical Processes of Biomass Utilization in the Slovak-Hungarian Frontier Region, HAS, Research Centre for Natural Sciences, 3 July 2014, Budapest

**A study of the hydrodenitrogenation of propylamine and propionitrile over silica-supported nickel phosphide catalysts**

*Badari Andrea Cecília, Ferenc Lónyi, József Valyon*

6. 12<sup>th</sup> Pannonian Symposium on Catalysis, 16-20 September 2014, Trest, Czech Republic

**Catalytic hydrodenitrogenation of propylamine and propionitrile as model reaction of hydrorefining pyrolysis oil obtained from animal by-products**

*Cecília A. Badari, Ferenc Lónyi, József Valyon*



7. Kálmán Erika Doctoral Conference, HAS Research Centre for Natural Sciences, 10-12 December 2014, Budapest, ISBN: 978-963-7067-29-7, p. 48.

**Szerves nitrogénvegyületek katalitikus hidrogenitrogénezése (HDN) hordozós nikkel-foszfid katalizátorokon (Catalytic hydrodenitrogenation (HDN) of organic N-compounds over supported nickel phosphide catalysts)**

*Badari Andrea Cecília, Lónyi Ferenc, Valyon József*

**Sum impact factor related to the thesis ( $\Sigma_{IF}$ ):10.310**

## OTHER PUBLICATIONS

### *Articles in journals:*

1. Catalysis Communications 28 (2012) 100–104.

**Operando DRIFT spectroscopy on unprecedented influence of  $\text{Cu}^{2+}$  over NiAl LDHs for isomerization of eugenol**

*C.M. Jinesh, C.A. Badari, F. Lónyi, S. Kannan*

IF<sub>2013</sub>: 3.320

2. Open Chemistry 13 (2015) 517-527.

**Acetic acid hydroconversion over mono- and bimetallic indium doped catalysts supported on alumina or silicas of various textures**

*György Onyestyák, Szabolcs Harnos, Andrea Cecília Badari, Eszter Drotár, Szilvia Klébert, Magdalena Štolcová, Alexander Kaszonyi and Dénes Kalló*

IF<sub>2013</sub>: 1.329

2. Reaction Kinetics, Mechanisms and Catalysis xxx(2015)xxxx,

DOI: 10.1007/s11144-014-0825-9.

**Hydroconversion of acetic acid over indium- and phosphorus-modified nickel/laponite catalysts**

*Gy. Onyestyák, Sz. Harnos, C.A. Badari, Sz. Klébert, A. Kaszonyi, J. Valyon*

IF<sub>2013</sub>: 0.983

### *Articles in conference proceedings:*

1. 46<sup>th</sup> International Conference of Petroleum Processsing, 7 June 2013, Bratislava, Slovak Republic, ISBN: 978-80-969792-4-0.

**Novel Cu-Fe-P-O catalysts for selective oxidation of methane to formaldehyde**

*Veronika Hergelová, György Onyestyák, Szabolcs Harnos, Ferenc Lónyi, Andrea Cecília Badari, József Valyon, Alexander Kaszonyi and Magdaléna Štolcová*

2. 5<sup>th</sup> International Symposium on Advanced Micro- and Mesoporous Materials, 6-9 September 2011, Golden Sands, Bulgaria, ISSN: 1314–0795

**Conversion of Acetic Acid to Ethanol over Novel InNi/faujasite and InNi/SBA-15 Catalysts: Comparison of Micro- and Mesoporous Supports**

*Gy. Onyestyák, Sz. Harnos, C.A. Badari, Sz. Klébert, E. Drotár, J. Valyon*

*Abstracts of posters:*

1. 11<sup>th</sup> Pannonian International Symposium on Catalysis, 3-7 September 2012, Obergurgl, Austria

**Steam reforming of bio-oil from pyrolysis of MBM over particulate and monolith supported Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts**

*Andrea C. Badari, Ferenc Lónyi, József Valyon*

**Sum impact factor ( $\Sigma_{IF}$ ): 15.942**