

**Ph.D. THESIS**

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**HYDROCONVERSION OF ACETIC ACID OVER  
SUPPORTED METAL AND INDIUM MODIFIED  
SUPPORTED METAL CATALYSTS**

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## INTRODUCTION

Due to the tightening supply of fossil energy resources and their disadvantageous environmental impacts, the research interest is increasing to produce high value products from renewable carbon sources. Biomass is renewable carbon source available in large amounts difficult to be converted to useful products by the well-known chemical methods. Conversion of the non-edible biomass should be the best solution. We can produce several types of platform molecules, including 2-6 carbon chain length aliphatic carboxylic acids by mechanical, thermal, chemical and biological degradation of organic wastes. Catalytic hydrogenation can provide a possible solution to improve the utilization of oxygen-rich platform molecules. Alkanes, alkenes, alcohols, ethers or esters can be produced by the hydroconversion of aliphatic carboxylic acids. Preferred products are short chain alcohols that can be used not only as chemical feedstock, but as biofuel

From the 1930s, the Adkins-type copper-chromite catalysts have been applied to produce fatty alcohols from fatty acid esters. The reaction can be proceeded at 200-300 bar pressure. Because high pressure and chromium containing catalyst raises economic and environmental concerns, researchers are motivated in developing new catalysts.

Literature describes mainly noble metals (Pt, Pd, Ru, Rh) supported on different oxides ( $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ ) as suitable hydrogenation catalysts for producing alcohols from carboxylic

acids. Due to their poor selectivity, beside the alcohols, a large amount of gaseous products, CO<sub>2</sub>, CO, and hydrocarbons are also formed. Therefore, the rational aim of research is to improve the alcohol selectivity by directing the reaction to produce more valuable liquid products, such as short chain alcohols instead of short chain gaseous alkanes. Several papers are dealing with the effect of rhenium, ruthenium and principally addition of tin as second metal on the selectivity of platinum containing catalysts. However, the catalytic behavior of indium, the neighbor element of tin in the periodic table, has received much less attention. Indium is essential and key element for the production of the most advanced electronic equipments. We have recognized that it can also be useful component of novel heterogeneous catalysts. Particularly, it can be utilized as a modifier on oxide supported metal catalysts for the selective reduction of carboxylic acids to alcohols.

## **AIMS**

Our primary objective was to develop chromium-free catalysts for the selective catalytic reduction of acetic acid to ethanol, operating at lower temperature and pressure than Adkins-type catalysts.

Out further aim was to get to know the behavior of copper and nickel basic metals, the two main active components of Adkins- and Raney-type hydrogenation catalysts in the hydrogenation of acetic acid. Based on this knowledge, we also planned to clarify the role of the indium modification and effect of

different supports on the reaction and on the properties of the metal catalysts.

Finally, we intended to find the optimal reaction conditions and the catalysts with high activity and alcohol selectivity.

## **METHODS**

Zeolites,  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$ , two main component oxides of the zeolite framework were used as support for the preparation of Cu- and Ni-catalysts. Basic metals were introduced to zeolites and oxide supports by aqueous ion-exchange and by impregnation method, respectively. Catalyst precursors were created by calcination. Indium modified bimetallic catalysts were prepared by reduction of the solid mixture of Cu- and Ni catalysts and indium-oxide.

The metal content of each samples was determined by atomic absorption spectroscopy (AAS) and inductive coupled plasma emission spectroscopy (ICP-AES).

Specific surface area and pore size distribution of the catalysts was measured by nitrogen physisorption method.

The reduction behavior of the metal-oxide/support system was studied using temperature-programmed hydrogen reduction ( $\text{H}_2$ -TPR) measurements. The process of the metal oxide reduction, formation of the active metal phase, and the structure changes of zeolites were followed by temperature-programmed X-ray powder diffraction (HT-XRD) in hydrogen atmosphere at required temperatures. The average metal particle diameter was determined

by transmission electron microscopy (TEM) and by the X-ray powder diffraction method using the Sherrer equation.

The selective catalytic hydrogenation of acetic acid was carried out in a high-pressure fixed bed flow-through reactor at 21 bar total pressure in the temperature range of 220-380 °C. The space velocity was  $1 \text{ g}_{\text{AA}}/\text{h} \times \text{g}_{\text{cat}}$ .

## **RESULTS, THESES**

1. The possible reaction routes of acetic acid hydroconversion over copper, nickel and indium modified copper, and nickel catalysts on different oxide supports were determined. We separated the reaction steps assigned to the supports and to the active metallic phases, respectively. Based on this knowledge, we could develop more efficient catalysts with higher activity and total ethanol selectivity, compared to chromium-containing Adkins-type ones. The optimal reaction conditions for their selective operation were also determined.
2. Our preparations have comparable or higher activity than Adkins catalysts and can convert acetic acid to ethanol at moderate reaction conditions without any loss of activity. By our results on acetic acid reduction, we suggest that the new bimetallic catalysts can also be beneficially applied for the

hydroconversion of other oxygen-containing platform molecules.

3. On low silica and high alumina containing P-, A- and X-zeolites, total amount of copper, but only a small part of nickel can be reduced to metallic state by activation in hydrogen at 450 °C. It was shown that the rate of reduction and the extent of framework collapse depend on the parent zeolite structure and the redox potential of the metals. By reduction of metal ions, the structure of zeolite-X deteriorated the least, whereas zeolite-P suffered the highest damage, regardless of the quality of metal ions.
4. It was found that among the possible intermetallic phases,  $\text{Cu}_2\text{In}$  or  $\text{Ni}_2\text{In}$  intermetallic phases dispersed on various supports are formed by co-reduction of mechanical mixtures of Cu or Ni ion or oxide containing supports and indium(III)oxide in hydrogen atmosphere.
5. It was shown that indium modification can enhance the activity and the selectivity of Cu- and Ni-catalysts in acetic acid hydroconversion to ethanol. We demonstrated that the advantageous catalytic properties can be attributed to the  $\text{Cu}_2\text{In}$  and  $\text{Ni}_2\text{In}$  intermetallic phases formed on the support.

6. It was shown that  $\text{SiO}_2$  support having weak support-metal interaction is more favorable than  $\gamma\text{-Al}_2\text{O}_3$  with stronger interaction. Considering the structure and morphology, supports with highly permeable mesoporous structure proved to be favorable.
7. It was found that the effect of indium modification on the nickel with higher hydrogenation activity is more significant than on the copper with lower hydrogenation activity. Modification by indium can eliminate the undesirable C-C bond hydrogenolysis activity of nickel during acetic acid hydroconversion.
8. Apparent activation energy of the acetic acid reduction over indium-free and indium containing metal catalysts was determined. It was found that the reaction activation energy is increasing by addition of the modifier. This change was explained by the geometric effect of indium, e.g. diluting the other metal, and by its electronic effect decreasing the electron density of the metal surface.
9. We have found that chemical quality, the structure, and the morphology of the applied supports have significant effect on selectivity and hydrogenation activity of the metals in acetic

acid hydroconversion. However, the apparent activation energy and the pre-exponential factor were found to be independent of the support quality by introducing  $\text{Ni}_2\text{In}$  active metal particles to a well-defined support. This suggests that, in contrast to literature, the support does not play a direct role in the reaction mechanism of acetic acid hydrogenation. However, it certainly influences the formation and the accessibility of the active metallic surface.

10. We have studied the acetic acid hydroconversion as a function of partial pressure of reactants. It can be concluded that according to Langmuir-Hinshelwood mechanism the reaction takes place between the adsorbed hydrogen and acetic acid molecules.



## PUBLICATIONS RELATED TO THE THESIS

1. **Szabolcs Harnos**, György Onyestyák, Róbert Barthos, József Valyon  
Novel Cu and Cu<sub>2</sub>In/aluminosilicate type catalysts for the hydroconversion of biomass-derived volatile fatty acids to alcohols  
*Central European Journal of Chemistry* 10(6) (2012) 1954-1962.  
I.F.: 1.073
2. György Onyestyák, **Szabolcs Harnos**, Szilvia Klébert, Magdalena Štolcová, Alexander Kaszonyi, Dénes Kalló  
Selective Reduction of Acetic Acid to Ethanol over Novel Cu<sub>2</sub>In/Al<sub>2</sub>O<sub>3</sub> Catalyst  
*Applied Catalysis A: General* 464-465 (2013) 313-321.  
I.F.: 3.383
3. György Onyestyák, **Szabolcs Harnos**, Alexander Kaszonyi, Magdalena Štolcová, Dénes Kalló  
Acetic acid hydroconversion to ethanol over novel InNi/Al<sub>2</sub>O<sub>3</sub> catalysts  
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I.F.: 2.827
4. György Onyestyák, **Szabolcs Harnos**, Dénes Kalló  
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*Catalysis Communications* 16 (2011) 184–188.  
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5. **Szabolcs Harnos**, György Onyestyák, Dénes Kalló  
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6. György Onyestyák, **Szabolcs Harnos**, Dénes Kalló  
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8. **Szabolcs Harnos**, György Onyestyák, Szilvia Klébert, Magdalena Štolcová, Alexander Kaszonyi, József Valyon  
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I.F.:1.104
  
9. György Onyestyák, **Szabolcs Harnos**, Dénes Kalló  
Unique efficiency of copper-indium catalyst in octanoic acid reduction  
*Catalysis. Communications* 40 (2013) 32-36.  
I.F.: 2.827
  
10. György Onyestyák, **Szabolcs Harnos**, Ágnes Szegedi, Dénes Kalló  
Sunflower oil to green diesel over Raney-type Ni-catalysts  
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I.F.: 3.357

## BOOK CHAPTER RELATED TO THE THESIS

1. Görgy Onyestyák, **Szabolcs Harnos**, Dénes Kalló  
Indium: Properties, Technological Applications and Health Issues  
Chapter title: Indium an Efficient Co-Catalyst in Novel Cu or Ni  
Catalysts for Selective Reduction of Biomass Derived Fatty Acids  
to Alcohols  
Editors: Hsiao G. Woo, Huang Tsai Choi  
Nova Publishers, New York, 2013, P 53-81.  
ISBN: 978-1-62257-696-8

## OTHER PUBLICATIONS

11. **Szabolcs Harnos**, György Onyestyák, Dénes Kalló  
Hydrocarbons from sunflower oil over partly reduced catalysts  
*Reaction Kinetics, Mechanisms and Catalysis 106 (2012) 99-111.*  
I.F.:1.104

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