

Scientific paper

# Bioacid Hydroconversion over Co, Ni, Cu Mono- and Indium-doped Bimetallic Catalysts

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## Abstract

Caprylic acid (CA) as model reactant was selectively reduced in a flow-through reactor in hydrogen stream at 21 bar total pressure and 240–360 °C over alumina loaded with the adjacent Co, Ni, Cu host and In guest metals. The main target of this research is the recognition of efficient cobalt catalysts for carboxylic group hydroconversion compared to more familiar nickel and copper composites. The catalysts were activated in H<sub>2</sub> flow at 21 bar and 450 °C. By variation of main metal or modification with indium, mono- or bimetallic catalysts can be obtained with low hydrodecarbonylation activity and high alcohol selectivity. These composites have higher hydrodeoxygenation (HDO) activity and alcohol selectivity than the conventional commercial catalysts applied for fatty alcohol production. Great variety of catalytic behavior indicates complexity of the surface reactions determined by several interacting factors.

**Keywords:** Carboxylic acids; hydroconversion; alcohols; indium doping

## 1. Introduction

The necessity for the use of renewable carbon sources has become more evident. Degradation of biomass results in various primary platform molecules of high oxygen content. Upgrading these compounds to valuable products seems to be a challenge, where bi- or trimetallic catalysts can also play important role.<sup>1</sup> Abundant platform intermediates are compounds containing carboxylic groups including aliphatic mono and dicarboxylic acids or various oxo or oxy derivatives.<sup>2</sup> These molecules have to be processed for producing more valuable chemicals or fuel. Heterogeneous catalysts consisting of complex metallic phases seem to gain more and more significance in biomass upgrading technologies.<sup>1–3</sup> Full or partial catalytic hydrodeoxygenation (HDO) is an obvious solution for upgrading oxygen-rich platform materials. The value of the HDO product strongly depends on the catalytic selectivity. For instance, HDO of carboxylic acids can give either hydrocarbons or alcohols, where the latter are of much higher value either as chemicals or even as fuel component.

Development of alternative catalysts is sorely needed instead of conventional catalysts (e.g. Adkins-type

copper chromite, Raney nickel, etc.).<sup>4</sup> The literature describes catalysts comprising of one or more noble metals of Group VIII dispersed on Group III or IV metal oxides. Appearance of bimetallic catalysts seems to be advantageous (e.g. PtSn/SiO<sub>2</sub> for selective reduction of acetic acid and RuSn/Al<sub>2</sub>O<sub>3</sub> for dicarboxylic acids).<sup>5,6</sup> The unexpected properties of bimetallic catalysts inspired extensive investigations. The effect of Sn addition on the catalytic properties of Pt/Al<sub>2</sub>O<sub>3</sub> in numerous important reaction systems has been widely investigated. The promoting effect of the neighbouring indium received much less attention.<sup>7,8</sup> Recent studies concern the HDO of carboxylic acids over alumina supported Ni or Cu catalysts and In-modified forms.<sup>9,10</sup> Indium with Ni main metal was found to suppress the total hydrogenation and hydrodecarbonylation, both resulting in hydrocarbons and to promote alcohol formation.<sup>9</sup>

The properties of hydrotreating catalysts are determined by the type and the state of active metal particles and the supports. Among cheaper, non-precious metal hydrogenating agents (Cu and Ni studied recently profoundly) cobalt is also highly efficient in some important H<sub>2</sub> activating processes. Cressely et al. studied acetic acid hydrogenation at atmospheric pressure over Fe, Co or Cu

dispersed on an inert silica support, and Co loaded on various supports or using bimetallic combinations of the mentioned metals.<sup>11,12</sup> Their results showed that Cu/SiO<sub>2</sub> was active and quite selective for the production of ethanol, acetaldehyde and ethyl-acetate through consecutive reduction of acetic acid, whereas Fe/SiO<sub>2</sub> resulted in the production of acetone and CO<sub>2</sub> following the ketonization reaction route. However over Co/SiO<sub>2</sub>, dominantly decomposition products (CH<sub>4</sub> and CO<sub>2</sub>) were obtained. The high selectivity of Cu/SiO<sub>2</sub> for ethanol, acetaldehyde and ethyl-acetate production was confirmed one and half decade latter and in our recent studies.<sup>13,14</sup> A contemporary patent claims that under super-atmospheric pressure over cobalt-containing catalysts high ethanol production is dominant.<sup>15</sup> The aim of present work is to clarify product selectivity discrepancies found in the literature as for the behavior of cobalt in carboxylic acid hydroconversion using caprylic acid (CA) as model reactant and for comparing with Cu and Ni supported on a conventional  $\gamma$ -alumina. Furthermore, applying the solid state indium doping method, using oxide-precursors, six different catalysts can be obtained, which can provide wide facilities in carboxylic acid reduction.

## 2. Experimental

### 2.1. Catalyst Preparation

Activated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Ketjen CK 300, Akzo-Chemie, Specific Surface Area (SSA) = 199 m<sup>2</sup>/g) was impregnated with Co(NO<sub>3</sub>)<sub>2</sub> (Reanal, Hungary) solution, or NH<sub>4</sub>OH solution (Reanal, Hungary) of Ni(Ac)<sub>2</sub> (Aldrich) or Cu(Ac)<sub>2</sub> (Aldrich), dried at 120 °C, and calcined at 400 °C in air stream obtaining metal-oxide containing catalyst precursors. The sample designation, e.g., 9Co/Al<sub>2</sub>O<sub>3</sub> formula represents a catalyst sample containing 9 wt.% Co on alumina. Bimetallic catalysts were prepared by adding 10 wt.% indium(III)oxide (Aldrich) to the samples in amounts to attain Me<sub>2</sub>In stoichiometric composition of metallic phase (which is typical in the intermetallic compounds: Ni<sub>2</sub>In or Cu<sub>2</sub>In) and the mixture was grinded in an agate mortar. After *in situ* reduction in hydrogen flow in the catalytic reactor monometallic catalysts contain 9 wt.% host metal and the quantum of bimetallic forms were enlarged to 108.3 wt.% with 8.3 wt.% guest metal indium. So, catalyst beds contain equal amount of main metal comparing mono- or bimetallic catalysts.

For comparison an industrial Adkins catalyst (72 wt.% CuCr<sub>2</sub>O<sub>4</sub> and 28 wt.% CuO) was also used under the same activation and reaction conditions as for catalysts of the this study.

### 2.2. Characterization

Nitrogen adsorption isotherms were measured at -196 °C using Quantochrome Autosorb 1C instrument.

Before measurements, the samples were outgassed under vacuum at 350 °C for 24 h. Specific surface area was determined by the BET method. Pore size distribution of alumina support was calculated from desorption branch of the isotherm using the BJH method.

The XRD patterns of the catalysts were recorded by Philips PW 1810 diffractometer applying monochromatized Cu<sub>K $\alpha$</sub>  radiation (40 kV, 35 mA) at elevated temperatures in hydrogen flow using a high temperature XRD cell (HT-XRD). Crystallite size was determined by the Scherrer equation. Crystalline phases were identified using the JSPDS ICDD database. The corresponding ICDD card numbers were: Co<sub>3</sub>O<sub>4</sub>: 43–1003,  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>: 10–425, In<sub>2</sub>O<sub>3</sub>: 06–0416, Co<sup>0</sup>: 5–0806, In<sup>0</sup>: 01–1042.

Catalytic hydrogenation of caprylic acid (Aldrich, CA) was carried out in a high-pressure fixed bed flow-through reactor at 21 bar total pressure in the temperature and space time ranges of 240–360 °C and 0.3–2 h, respectively. Each catalyst precursor was reduced in pure hydrogen flow at 21 bar *in situ* in the reactor at 450 °C for 1 h in order to generate active supported metal prior to the catalytic test. The reactor effluent was cooled to room temperature, liquid and gas phase products were separated. The liquid was analyzed using a gas chromatograph (GC, Shimadzu 2010) equipped with flame ionization detector and a CP-FFAP CB capillary column. The gas was analyzed using an on-line GC (HP 5890) equipped with thermal conductivity detector and Carboxen 1006 PLOT capillary column. The activity and the selectivity of the catalysts were characterized by product distributions represented as stacked area graphs. In this representation, the distance between two neighboring curves gives the yield of the specified product in weight percent.

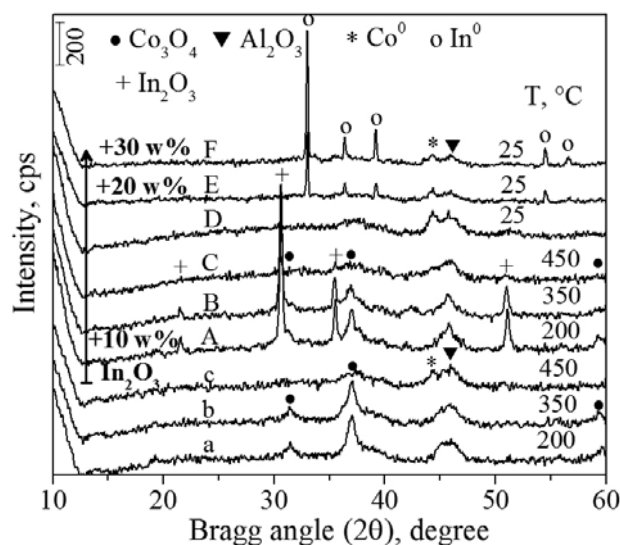
## 3. Results and Discussion

The applied conventional parent alumina support is mesoporous material as reflected by the nitrogen ad- and desorption isotherms and the pore size distribution (not show). It has a not too wide pore size distribution around 8 nm. The isotherms of all derivatives (mono- or bimetal loaded forms) are practically overlapping corresponding to nearly equal specific surface areas around 200 m<sup>2</sup>/g which means that the presence of the mono- or bimetallic particles does not influence the porosity due to the three-dimensional, quite wide pore structure excluding pore blocking.

The HT-XRD patterns (Fig. 1) show the reduction of first added (cobalt) and thereafter admixed second metal (indium) oxides similarly as for nickel in ref. 9 (Fig. 6) and copper in ref. 10 (Figs. 2–3). The reductive treatment of the 9Co/Al<sub>2</sub>O<sub>3</sub> catalyst precursor generates small Co metal particles (Fig. 1a,b,c). The average size of Co or Ni particles is smaller (7 and 12 nm) while in 9Cu/Al<sub>2</sub>O<sub>3</sub> catalyst Cu is completely reduced already at lower tempera-

ture and after heating to the routine pretreatment temperature much larger aggregates (20 nm) are formed.  $\text{Co}_3\text{O}_4$  diffraction lines completely disappear heating in  $\text{H}_2$  above  $350\text{ }^\circ\text{C}$ , whereas the intensity of Co line still started to increase at  $450\text{ }^\circ\text{C}$ . For this temperature gap the limited sensitivity of XRD technique is responsible. Particles above a minimum crystallite size ( $\sim 5\text{ nm}$ ) can be only detected. Some increase of Co diffraction line can be still observed above  $450\text{ }^\circ\text{C}$  however most of the cobalt atoms are already in fully reduced state at the routine pretreatment process in contrast with nickel supported on alumina.<sup>9</sup> Concluding from the HT-XRD results the reduction temperature of the host metal oxides seems to increase in the order  $\text{Cu} < \text{Co} < \text{Ni}$  as reflected in Table 1. Nickel strongly interacts with alumina forming nickel aluminate-like spinel species which is the reason of its strikingly difficult reduction.

Whole amount of admixed  $\text{In}_2\text{O}_3$  can be converted to  $\text{In}^0$  up to  $450\text{ }^\circ\text{C}$  in hydrogen flow indicated by disappearance of its diffraction lines (Fig. 1A,B,C) and for Ni and Cu containing samples simultaneously new  $\text{Ni}_2\text{In}$  or  $\text{Cu}_2\text{In}$  bimetallic phases appear (shown in refs. 9 (Fig. 6



**Fig. 1.** HT-XRD patterns of the indium free  $9\text{Co}/\text{Al}_2\text{O}_3$  catalysts (a, b, c) and  $9\text{Co}/\text{Al}_2\text{O}_3/10\%$  (A, B, C, D),  $20\%$  (E) and  $30\%$  (F)  $\text{In}_2\text{O}_3$  mixtures, treated in  $\text{H}_2$  flow for 30 min at various reducing temperatures. D, E and F curves were recorded at room temperature following the reduction treatment up to  $450\text{ }^\circ\text{C}$  and cooling down in  $\text{H}_2$  flow.

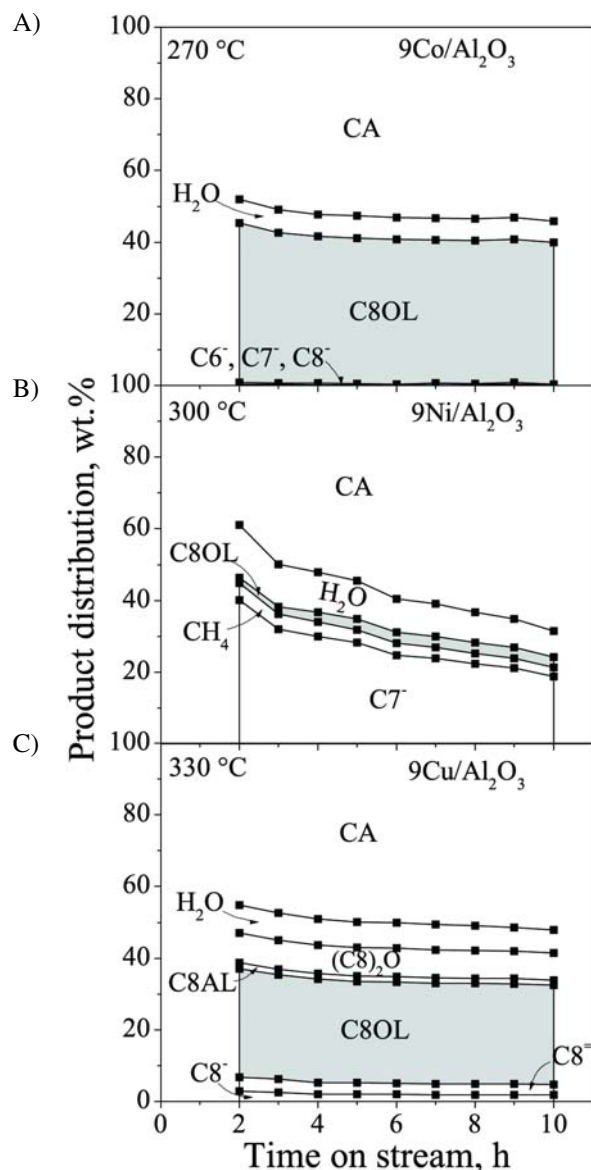
and 10 (Figs. 2–3), while for Co similar bimetallic phase does not appear. The intensity of the  $\text{Ni}_2\text{In}$  diffraction lines increases with the degree of nickel reduction that is higher after higher temperature  $\text{H}_2$  treatment.<sup>9</sup> Studies of the selective catalytic hydroconversion of carboxylic acids to alcohols suggest that the  $\text{Ni}_2\text{In}$  phase is responsible for the favorable catalytic effects.<sup>9</sup> Formation temperature of these compounds is determined by the reduction temperature of less reducible metal in these pairs (Ni or In, as shown in Table 1). In the case of Cu or Ni host metals formation of  $\text{Cu}_2\text{In}$  and  $\text{Ni}_2\text{In}$  phases were unequivocally detected in numerous studies, while intermetallic compound of cobalt with this stoichiometry does not exist. Possible substances should be  $\text{CoIn}_2$  or  $\text{CoIn}_3$  none of them could be detected by HT-XRD (Fig. 1 C,D,E,F), however, their formation as a skin in the external layer of the cobalt particles can not be excluded. After 10 wt.%  $\text{In}_2\text{O}_3$  admission resulting in usual  $\text{Co}/\text{In}=2$  atomic ratio, pure Co phase cannot be detected (Fig. 1 C), and metallic indium cannot be detected either after cooling to room temperature (Fig. 1 D), i.e., below its melting point ( $156.4\text{ }^\circ\text{C}$ ). This observation means that indium may alloy the main metal, cobalt. At  $\text{Co}/\text{In} = 1$  atomic ratio, when more indium is present, metallic indium phase can be detected after cooling to room temperature (Fig. 1 E) and cobalt phase is essentially less, as well, (probably mass transport limitation plays a significant role hindering further penetration of indium atoms resulting in superficial alloy formation). At  $\text{Co}/\text{In} = 2/3$  indium diffraction lines are more intense after cooling to R.T. and remaining cobalt phase is nevertheless observable (Fig. 1 F) reflecting a barrier of full alloying of Co particles.

Changes of product distribution at approx. equal conversion are plotted as function of time-on-stream over the monometallic catalysts in Fig. 2. Because of different activities of the samples measurements were carried out at different temperatures to ensure similar level of the hydroconversion under otherwise identical experimental conditions. The order of the increasing activity can be expressed with the decreasing reaction temperature needed to attain similar conversions:  $9\text{Cu}/\text{Al}_2\text{O}_3$  ( $330\text{ }^\circ\text{C}$ )  $<$   $9\text{Ni}/\text{Al}_2\text{O}_3$  ( $300\text{ }^\circ\text{C}$ )  $<$   $9\text{Co}/\text{Al}_2\text{O}_3$  ( $270\text{ }^\circ\text{C}$ ). Selectivities are strikingly different. The dominant reaction route is the reduction of CA to octanol over  $9\text{Cu}/\text{Al}_2\text{O}_3$  and  $9\text{Co}/\text{Al}_2\text{O}_3$  catalysts however, the reaction temperature is essentially higher for the less active Cu-form where octanal as intermediate product is detectable. The bimolecular dehydra-

**Table 1.** Formation of active metal components in  $\text{H}_2$  flow reflected by HT-XRD patterns

	$\text{In}^{3+}/\text{In}$	$\text{Co}^{2+}/\text{Co}$	$\text{Ni}^{2+}/\text{Ni}$	$\text{Cu}^{2+}/\text{Cu}$
Standard reduction potential, $E^\circ(\text{V})$	-0.34	-0.28	-0.23	+0.34
Reduction temperature, ( $^\circ\text{C}$ ) /XRD/	350–450	350–450	450–650	150–250
Average particle size (nm) /XRD/	liquid	8	12	20
Alloy formation temperature, ( $^\circ\text{C}$ )		n.d.	450–650	350–450

tion of main product alcohol, forming dioctyl-ether in higher extent, and octenes and some octane as products of monomolecular dehydration (see in Fig. 3C) proceeding at high temperature can be attributed to alumina support. Formation of octanol is negligible on Ni/Al<sub>2</sub>O<sub>3</sub> where hydrogenolysis of C-C bonds is preferred resulting in hydrodecarbonylation as main reaction route and thus shortening the chain of the reactant molecules. The main product is heptane (see in Fig. 2B). Nickel is a so strong hydrogenating catalyst that CO as primary product cannot



**Fig. 2.** Stacked area graphs of product distributions obtained from the hydroconversion of CA over catalysts (A) 9Co/Al<sub>2</sub>O<sub>3</sub> at 270 °C, (B) 9Ni/Al<sub>2</sub>O<sub>3</sub> at 300 °C [9], and (C) 9Cu/Al<sub>2</sub>O<sub>3</sub> at 330 °C as a function of time on stream. The total pressure was 21 bar and the WHSV of CA was 2 h<sup>-1</sup>. (symbols: CA: caprylic acid; C8OL: capryl alcohol; C8AL: capryl aldehyde; (C8)<sub>2</sub>O: dioctyl ether; C6: hexane; C7: heptane; C8: octane; C8<sup>o</sup>: octene; H<sub>2</sub>O: water; CH<sub>4</sub>: methane).

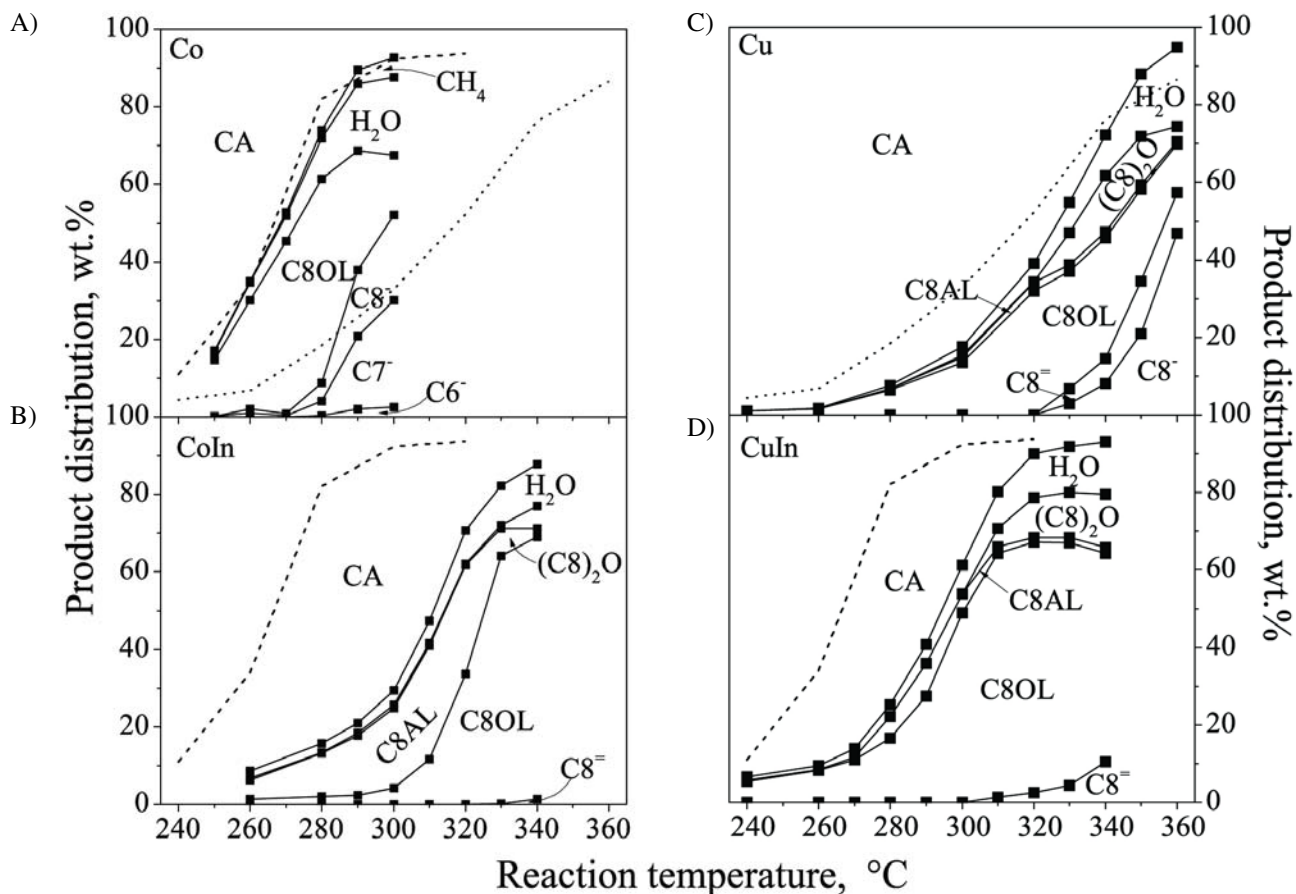
be detected at all because of efficient methane formation being also a secondary product. 9Ni/Al<sub>2</sub>O<sub>3</sub> shows significant activity decay with time-on-stream contrary to the other two catalysts.

The catalytic behavior of 9Ni/Al<sub>2</sub>O<sub>3</sub> can be changed drastically by indium admission forming a highly stable and active, selectively alcohol producing catalyst (conversion curve is inserted into Fig. 3A, B, D with dashed lines).<sup>9</sup> 9Co/Al<sub>2</sub>O<sub>3</sub> catalyst showing the highest activity at moderate reaction conditions among monometallic forms (and same activity as indium doped 9Ni/Al<sub>2</sub>O<sub>3</sub>) can produce octanol with perfect selectivity below 280° (see in Fig. 2A). On increasing the reaction temperature over 9Co/Al<sub>2</sub>O<sub>3</sub> catalyst the dominant reaction paths change. At higher temperatures octanol can be dehydrated presumably on alumina support to octenes which are fast hydrogenated to octane and following hydrogenolysis results in formation of heptane and hexane. However this side reaction route can be successfully blocked by indium doping similarly to nickel (Fig. 3B).

Figs. 3C and D show that indium admission to copper results in more active catalyst of higher selectivity to alcohol formation.<sup>10</sup> In the contrary indium doping essentially decreases the activity of cobalt (compare Fig. 3A and B). One of the possible explanations (simple geometric effect) is that cobalt atoms are much more diluted with indium on the surface because cobalt is not able to form Co<sub>2</sub>In phase, only such intermetallic compounds are existing where the indium content is four or six times higher than in Cu or Ni composites. Although such a high amount of indium is not added, however on the catalytically active surface, in the upper layers of metal particles CoIn<sub>2</sub> or CoIn<sub>3</sub> compositions may exist. This supposal is confirmed by admixing only 2 wt % In<sub>2</sub>O<sub>3</sub> to 9Co/Al<sub>2</sub>O<sub>3</sub> catalyst (1/5 of the 10 wt.% routine amount) and the same, practically totally overlapping conversion curves (not shown) are obtained. The approx. same 50 °C difference in reaction temperature to attain full hydroconversion over mono- (Co) and bimetallic (CoIn) alumina supported catalysts can be also observed with acetic acid, a much shorter carboxylic acid reactant /not shown/. This observation reflects that only the direct interaction of the carboxylic group and metallic surface is decisive.

To Fig. 3A, B and D the conversion curve obtained over the most efficient Ni<sub>2</sub>In/alumina catalyst is displayed as dashed line for comparison. It is clearly demonstrated that the simple monometallic 9Co/Al<sub>2</sub>O<sub>3</sub> catalyst can be equally efficient under limited conditions (below 280 °C) as the more complicated bimetallic composite. Comparable product distribution at approx. equal conversion are summarized as function of reaction temperature over the all investigated catalysts in Table 2.

Fig. 3A and C show also the conversion curve (dotted line) obtained over a commercial, conventionally used Adkins catalyst, having the composition of 72 wt.% Cu-



**Fig. 3.** Stacked area graphs of product distributions obtained from the hydroconversion of CA over catalysts (A) 9Co/Al<sub>2</sub>O<sub>3</sub>, (B) 9Co/Al<sub>2</sub>O<sub>3</sub>/10% In<sub>2</sub>O<sub>3</sub> (C) 9Cu/Al<sub>2</sub>O<sub>3</sub> [10] and (D) 9Cu/Al<sub>2</sub>O<sub>3</sub>/10% In<sub>2</sub>O<sub>3</sub> [10] as a function of reaction temperature. The total pressure was 21 bar and the WHSV of OA was 2 h<sup>-1</sup>. Dashed lines are the conversion curves of 9Ni/Al<sub>2</sub>O<sub>3</sub>/10% In<sub>2</sub>O<sub>3</sub> and dotted lines of a commercial Adkins catalyst. (symbols as in Fig. 2.).

**Table 2.** Comparison of the product distributions at approx. 50 wt. % isoconversion (48–59 wt.%)

	Co	CoIn	Ni	NiIn	Cu	CuIn	Adkins
T <sub>reac.</sub> °C	270	310	300	270	330	300	320
Heptane			33.3				
Methane			3.7				
Water	7.1	7.0	12.8	7.0	6.8	7.2	6.4
CA	50.8	51.7	50.0	42.9	46.4	41.2	47.8
C8AL		28.2		1.6	2.0	2.4	1.6
C8OL	41.9	11.8	0.9	44.4	28.4	44.4	44.7
(C8) <sub>2</sub> O			3.9		8.1	3.9	
Octene	0.6				4.7		
Octane	0.3				2.0		

Cr<sub>2</sub>O<sub>4</sub> and 28 wt.% CuO, as a function of reaction temperature. All the catalysts were able to produce alcohol from the investigated fatty acid with sufficient selectivity depending on the conditions, but the chromium-free 9Co/ and the Ni<sub>2</sub>In/alumina catalysts showed total hydroconversion at much lower temperatures and in narrower temperature range than the Adkins catalyst.

## 4. Conclusions

Indium-modified, alumina supported Ni catalyst has been earlier discovered to be highly efficient for partial reduction of carboxylic group by hydrogen. Alloying of Ni particles with indium effectively directs the hydrodeoxygenation of carboxylic acid to alcohol in consecutive steps instead of its hydrodecarbonylation. The presence of in-

dium hinders the chain shortening of bioacids and mono- or bimolecular alcohol dehydration side reactions. This study reveals that a monometallic catalyst (e.g. Co/Al<sub>2</sub>O<sub>3</sub>) can be competitive with the most efficient bimetallic composites although under limited reaction conditions. It seems that the choice of the most suitable catalyst for hydroconversion of bioacids is expanded and a further improvement can be attained optimizing the support and refining the catalyst preparation technique.

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## Povzetek

Kaprilno kislino, ki smo jo izbrali kot modelno spojino, smo reducirali v pretočnem reaktorju v toku vodika pri 21 barih in temperaturi med 240 °C in 360 °C. Kot katalizator smo uporabili nosilec  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> z dodanimi Co, Ni, Cu ter tudi In. Glavni cilj teh raziskav je bil prepoznati uspešnost katalizatorja s Co v primerjavi s kompoziti Ni in Cu. Katalizatorje smo uporabljali pri reakcijah hidriranja karboksilnih skupin. Aktivirali smo jih v toku vodika pri 21 barih in temperaturi 450 °C. S spremembami množine kovin (Co, Ni, Cu) oziroma dodatki lahko pripravimo mono ali bimetalne katalizatorje, ki imajo nizko aktivnost za hidredekarboksilacija in visoko selektivnost za nastanek alkohola. Ti kompoziti imajo višjo aktivnost za hidredeoksigenacijo in selektivnost za nastanek alkohola kot konvencionalni komercialni katalizatorji, ki se uporabljajo za pripravo alkoholov. Raznolikost katalitske aktivnosti nakazuje na kompleksnost reakcij na površini.