



## Short Communication

Indium, as an efficient co-catalyst of Cu/Al<sub>2</sub>O<sub>3</sub> in the selective hydrogenation of biomass derived fatty acids to alcohols

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## ARTICLE INFO

## Article history:

Received 29 February 2012

Received in revised form 17 April 2012

Accepted 20 April 2012

Available online 27 April 2012

## Keywords:

Biomass

Fatty acids

Hydroconversion

Alcohols

Cu/alumina

In<sub>2</sub>O<sub>3</sub> doping

## ABSTRACT

Octanoic acid (OA) as model reactant of medium chain length, and its reduced products, octanal and octanol were hydroconverted over different components of a CuIn/Al<sub>2</sub>O<sub>3</sub> composite catalyst. A fixed-bed flow through reactor was used at 21 bar total pressure in the temperature range of 240–360 °C. Fatty acid hydroconversion activity of alumina supported Cu catalyst and mainly the yield of selectively produced octanol can be greatly increased by In<sub>2</sub>O<sub>3</sub> doping, suppressing the dehydration side reactions. Appearance of metallic indium on alumina supported reduced copper catalyst can arrest the consecutive catalytic reaction at the alcohol formation step prior to further dehydration to ether or alkenes. An industrial, conventionally used Adkins catalyst (72 wt.% CuCr<sub>2</sub>O<sub>4</sub> and 28 wt.% CuO) and the novel bimetallic composite (CuIn/Al<sub>2</sub>O<sub>3</sub>) were compared: both produce octanol with high selectivity, but the new chromium-free fatty acid hydrogenation catalyst is more active, nearly as active as earlier investigated NiIn/Al<sub>2</sub>O<sub>3</sub>.

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## 1. Introduction

The actual significance of the catalytic reduction of carboxylic acids to alcohols has been surveyed in the previous paper [1] wherein the applicability of Ni/Al<sub>2</sub>O<sub>3</sub> with co-catalyst In<sub>2</sub>O<sub>3</sub> was discussed. Indium doped Ni/Al<sub>2</sub>O<sub>3</sub> catalyst proved to be highly efficient for directing the hydrogenation of fatty acids to aliphatic alcohols opening a novel route for catalyst development. Copper catalysts enable the selective addition of hydrogen to carbon–oxygen bonds but are relatively inactive in the hydrogenolysis of the carbon–carbon bonds unlike nickel catalysts [2]. From the early 1930s it is recognised that the chromium promoted copper catalysts show much higher activity and selectivity for alcohol formation than unpromoted ones [3]. Due to what happened the promotion effect of indium for copper catalyst can be also similarly efficient as for nickel and may substitute the chromium promoter applied in copper catalysts.

Highly dispersed copper particles were generated on special aluminosilicate supports formed by destructive hydrogen reduction/dehydration of Cu zeolites. These samples have the lowest Si/Al ratios and consequently the highest cation content of quite homogeneous distribution. They show high activity and selectivity in the catalytic hydroconversion of carboxylic acids [4]. The activity and the selectivity to alcohols over these specially supported Cu catalysts can be effectively increased by In<sub>2</sub>O<sub>3</sub> doping [4] similarly to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst [1]. Indium (III) oxide supported on zeolite or alumina has

been found to be a suitable catalyst for the de-NO<sub>x</sub> reactions [5], for dehydrogenation of propane to propylene with carbon dioxide [6,7]. However such supported In<sub>2</sub>O<sub>3</sub> based materials have received limited attention as hydrogenation catalysts, where indium can be present in metal phase.

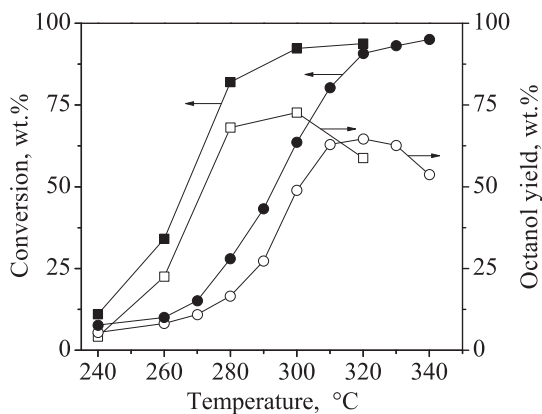
Cu or Cu<sub>2</sub>In catalysts supported on destructed zeolites (zeolite structures collapsed in consequence of unstable H-form formation, during reduction of charge compensating cations) having less than 30 m<sup>2</sup>/g specific surface area, depending on the type of zeolite precursors [4]. Alumina support has more than six times higher surface area and its structure is well defined compared with the collapsed zeolite structures becoming X-ray amorphous and containing small islands of unknown different phases. Indium doping to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst cannot give reliable information on indium doping to copper oxide since these two metals differ, e.g., the nickel oxide is partly reduced in hydrogen at the usual pretreatment temperature 450 °C whereas copper oxide is fully reduced to metal (see later). The aim of present research is to learn more about influences of indium metal for the different active metals in the selective hydrogenation of carboxylic acid to alcohols.

## 2. Experimental

The catalytic reduction of octanoic acid (OA) (Aldrich) as a model reactant with medium chain length, octanal (C8AL) (Fluka) as intermediate compound, and catalytic conversions of octanol (C8OL) (Fluka) as product are also investigated under similar conditions as in ref. [1] (in general at 20 bar hydrogen, 1 bar octanoic acid partial pressures in the temperature range of 240–360 °C. Catalyst

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**Fig. 1.** Comparison of the conversion (●■) and the target product evolution (○□) over 9Cu/Al<sub>2</sub>O<sub>3</sub> + 10% In<sub>2</sub>O<sub>3</sub> (circles) and 9Ni/Al<sub>2</sub>O<sub>3</sub> + 10% In<sub>2</sub>O<sub>3</sub> (squares) catalysts in the hydroconversion of octanoic acid as a function of reaction temperature at 21 bar total pressure. WHSV of OA was 2.0 h<sup>-1</sup>.

pretreatment was carried out in hydrogen flow in situ in the reactor at 450 °C, 21 bar for 1 h). Product analysis as well as representation of results in stacked area graphs is similar as in ref. [1], i.e. the distance between two neighboring curves represents the concentration of a given product at a given temperature in weight percent.

γ-Al<sub>2</sub>O<sub>3</sub> (Ketjen CK 300, Akzo-Chemie, BET: 199 m<sup>2</sup>/g) activated at 550 °C was impregnated with NH<sub>4</sub>OH solution (Reanal Finechemical Co.) of Cu (acetate)<sub>2</sub> (Merck) applying incipient wetness method, dried, and calcined at 550 °C. After impregnation the specific surface area changed to 180 m<sup>2</sup>/g, corresponding to 207 m<sup>2</sup>/g<sub>alumina</sub>. The samples contained 3, 9 and 20 wt.% copper designated as 3-, 9-, 20Cu/

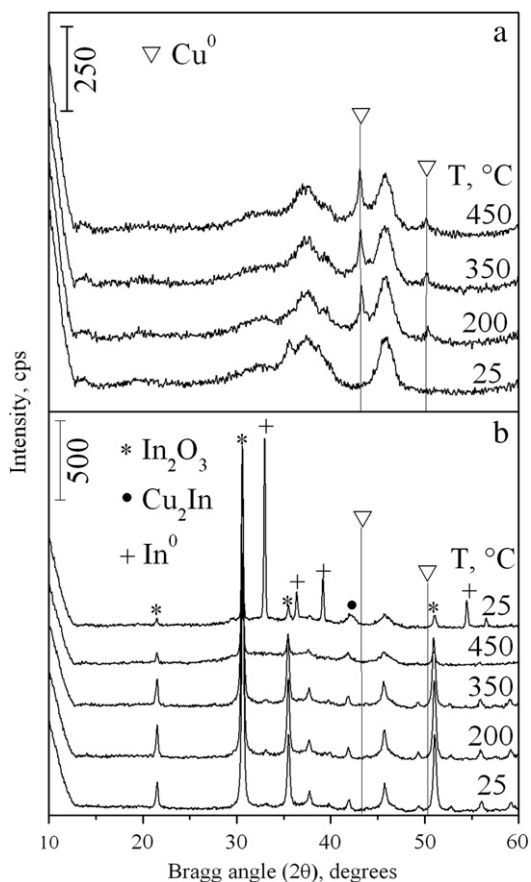
Al<sub>2</sub>O<sub>3</sub>. Composite catalysts were prepared by adding indium (III) oxide powder to the Cu/alumina samples and grinding the mixture in agate mortar. 159 m<sup>2</sup>/g was the specific surface area of the composite which is equal to 203 m<sup>2</sup>/g<sub>alumina</sub>.

X-ray patterns were recorded and evaluated as in ref. [1].

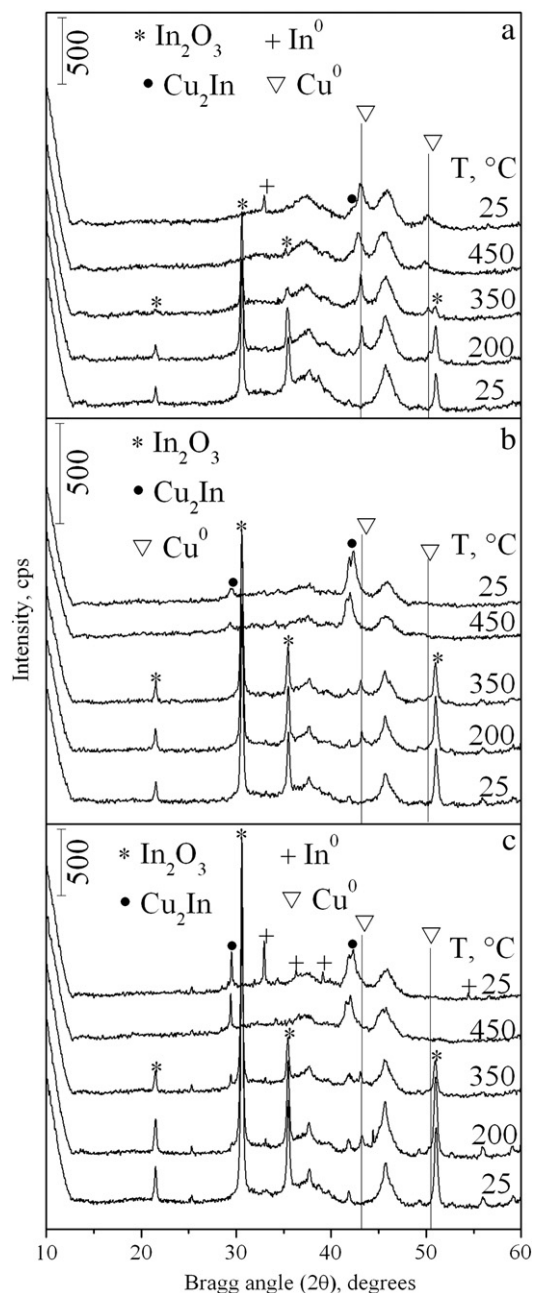
### 3. Results and discussion

NiIn/Al<sub>2</sub>O<sub>3</sub> catalyst is more active in octanoic acid hydroconversion than CuIn/Al<sub>2</sub>O<sub>3</sub> since the conversion and octanol yield curves are shifted by 20–30 °C to higher temperatures for Cu,In/Al<sub>2</sub>O<sub>3</sub> (Fig. 1). However, the product distributions are the same on the two bimetallic catalysts. Hence similarity of catalytically active phases seems probable.

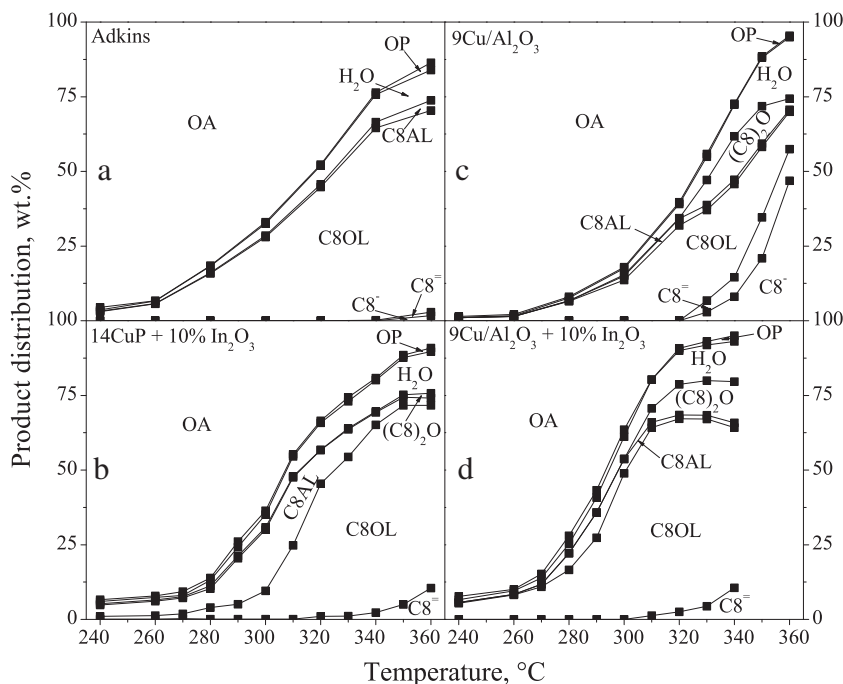
For 9Ni/Al<sub>2</sub>O<sub>3</sub> catalyst at the routine pretreatment temperature, at 450 °C only a small part of NiO is reduced and a complete reduction can be attained only at 650 °C [1]. Contrarily, in 9Cu/Al<sub>2</sub>O<sub>3</sub> catalyst



**Fig. 2.** HT-XRD patterns of 9Cu/Al<sub>2</sub>O<sub>3</sub> (a) and 3Cu/Al<sub>2</sub>O<sub>3</sub> + 10% In<sub>2</sub>O<sub>3</sub> (b) catalysts treated step by step up to 450 °C in H<sub>2</sub> flow for half an hour.



**Fig. 3.** HT-XRD patterns of 9Cu/Al<sub>2</sub>O<sub>3</sub> catalysts with 3% (a), 10% (b) and 20% (c) In<sub>2</sub>O<sub>3</sub> loading treated step by step up to 450 °C in H<sub>2</sub> flow for half an hour.

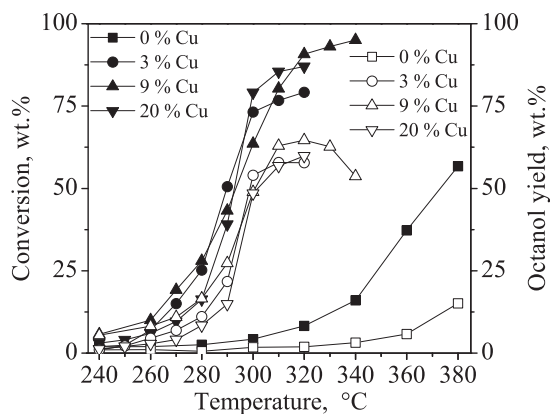


**Fig. 4.** Octanoic acid hydroconversion over commercial Adkins (a), 14CuP + 10% In<sub>2</sub>O<sub>3</sub> (b), 9Cu/Al<sub>2</sub>O<sub>3</sub> (c) and 9Cu/Al<sub>2</sub>O<sub>3</sub> + 10% In<sub>2</sub>O<sub>3</sub> (d) catalysts characterised by distributions of main products between 240 and 360 °C at 21 bar total pressure using stacked area graphs. WHSV of OA was 2.0 h<sup>-1</sup>. (symbols: C8<sup>-</sup>: octane, C8<sup>=</sup>: octenes, C8OL: octanol, C8AL: octanal, (C8)<sub>2</sub>O: dioctyl ether, H<sub>2</sub>O: water, OA: octanoic acid, OP: other products).

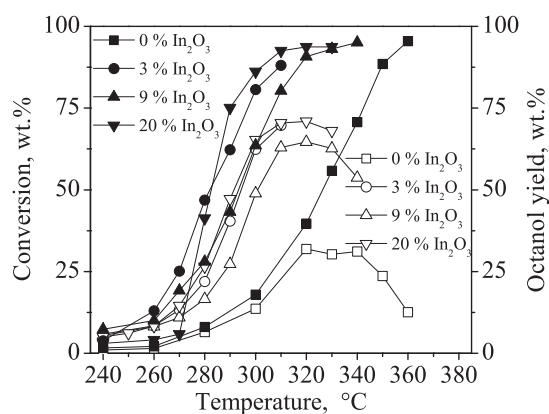
copper oxide is already fully reduced at 200 °C forming small copper particles of ~20 nm average diameter (▽ in Fig. 2a). These particles do not change up to 650 °C (and not only up to 450 °C as shown in Fig. 2a). Reduction of admixed In<sub>2</sub>O<sub>3</sub> can be observed at much higher temperature, i.e., between 350 and 450 °C (see Figs. 2b and 3a, b, c) detected by disappearance of In<sub>2</sub>O<sub>3</sub> diffraction lines (\*). This process is completed up to 450 °C on all 9Cu/Al<sub>2</sub>O<sub>3</sub> samples (see Fig. 3) but not on 3Cu/Al<sub>2</sub>O<sub>3</sub> sample mixed with 10 wt.% In<sub>2</sub>O<sub>3</sub> (see Fig. 2b), where trace indium (III) oxide can be alone detected. This sample of the lowest copper content can already form copper–indium alloy directly with the generated indium metal atoms (\*) above 350 °C. In the case of this composition copper particles cannot be detected below the reduction temperature of In<sub>2</sub>O<sub>3</sub> indicating either the formation of too small Cu<sup>0</sup> nanoparticles not detectable by XRD method. More probably, the alloying of the low concentration Cu<sup>0</sup> with small amount of reduced In<sub>2</sub>O<sub>3</sub> as shown by the appearance of a new phase (marked with • in Figs. 2 and 3) which can be assigned

to some kind of CuIn alloy. Mainly Cu<sub>2</sub>In phase, but Cu<sub>4</sub>In and Cu<sub>9</sub>In<sub>4</sub> phases may also be present in lower concentration. These phases were determined based on ICDD database [8], the corresponding ICDD numbers are Cu<sub>2</sub>In: 42–1475, Cu<sub>4</sub>In: 42–1477 and Cu<sub>9</sub>In<sub>4</sub>: 42–1476.

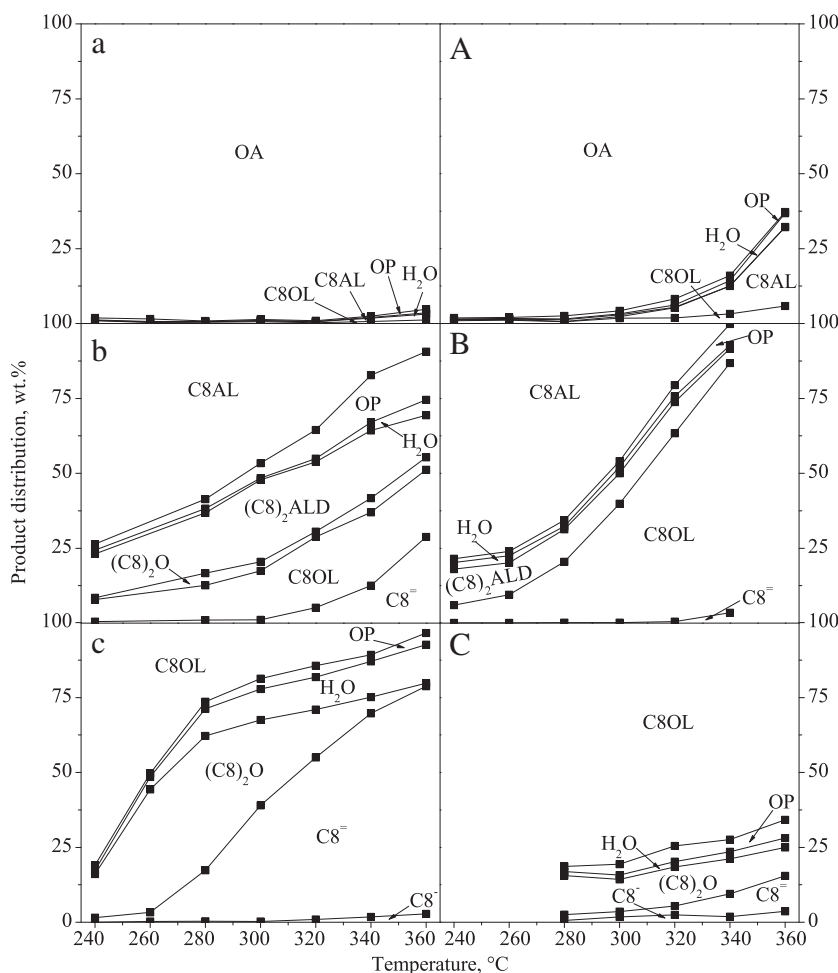
After treatment at 450 °C for half an hour the 3Cu/Al<sub>2</sub>O<sub>3</sub> sample mixed with 10 wt.% In<sub>2</sub>O<sub>3</sub> and cooling down the composite sample to R.T. the presence of excess solid metallic indium phase (+) can be also detected (see Fig. 2b) similarly to diffractograms of 9Cu/Al<sub>2</sub>O<sub>3</sub> sample admixed with 20 wt.% In<sub>2</sub>O<sub>3</sub> containing also excess indium beyond the amount needed to alloy formation (Fig. 3c). Frozen indium particles with average sizes of ~130 nm are larger than copper particles indicating higher mobility of indium atoms above the melting point (156.4 °C) than that of copper atoms. The 9Cu/Al<sub>2</sub>O<sub>3</sub> + 10 wt.% In<sub>2</sub>O<sub>3</sub> composite contains Cu and In nearly in 2:1 atomic ratio, so all amounts of two metals are consumed in formation of the alloy phase (Cu<sub>2</sub>In) having average sizes of ~10 nm



**Fig. 5.** Comparison of the conversion (●■▲▼) and the target product evolution (○□△▽) over 10% In<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with different Cu loadings in the hydroconversion of octanoic acid as a function of reaction temperature at 21 bar total pressure. WHSV of OA was 2.0 h<sup>-1</sup>.



**Fig. 6.** Comparison of the conversion (●■▲▼) and the target product evolution (○□△▽) as a function of reaction temperature over 9Cu/Al<sub>2</sub>O<sub>3</sub> catalysts with various amounts of In<sub>2</sub>O<sub>3</sub> admision in the hydroconversion of octanoic acid at 21 bar total pressure. WHSV of OA was 2.0 h<sup>-1</sup>.



**Fig. 7.** Hydroconversion of octanoic acid (a-A), octanal (b-B) and octanol (c-C) over  $\text{Al}_2\text{O}_3$  (a, b, c) and over  $\text{Al}_2\text{O}_3$  with 10% of  $\text{In}_2\text{O}_3$  (A, B, C) as a function of reaction temperature at 21 bar total pressure, using stacked area graphs ((C8)<sub>2</sub>ALD: 2-hexyldec-2-enal, other symbols as in Fig. 4).

(Fig. 3b). At lower  $\text{In}_2\text{O}_3$  admission Cu and  $\text{Cu}_2\text{In}$  phases are present altogether (Fig. 3a) and in composites containing indium in excess to the composition of  $\text{Cu}_2\text{In}$  alloy phase, indium can also appear as distinct pure metal phase (see Figs. 3c or 2b), but it can only be detected below its melting point 156.4 °C. The admitted  $\text{In}_2\text{O}_3$  contains crystals with particles of ~70 nm average diameter (\*) however it can form much bigger aggregates and the poor method applied for admission cannot result in homogeneous distribution, which can be true for  $\text{CuO}$ , too. A not uniform distribution can explain the presence of  $\text{In}_2\text{O}_3$  near  $3\text{Cu}/\text{Al}_2\text{O}_3$  at 450 °C in Fig. 2b and In detected at 25 °C after admission only 3%  $\text{In}_2\text{O}_3$  to  $9\text{Cu}/\text{Al}_2\text{O}_3$  (Fig. 3a).

Formation of Cu and/or  $\text{Cu}_2\text{In}$  alloy nanoparticles, and appearance of metallic indium on the support is evident on the basis of HT-XRD results. In view of catalytic properties complete understanding of the multiple behaviors over such a complex ensemble of active sites requires comprehensive catalytic investigations. On adding a large amount of  $\text{In}_2\text{O}_3$  (10 wt.%  $\text{In}_2\text{O}_3$  of the mass of monometallic  $9\text{Cu}/\text{Al}_2\text{O}_3$  catalyst) as a co-catalyst, the activity significantly increases and the selectivity changes strikingly by suppressing of the consecutive octanol dehydration side-reactions (cf. Fig. 4c and d).

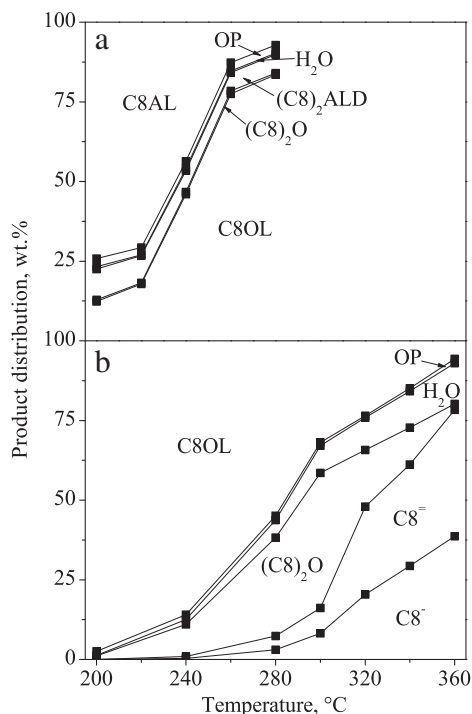
In Fig. 4 the catalytic properties of a commercial, conventionally used Adkins catalyst (consisting of 72 wt.%  $\text{CuCr}_2\text{O}_4$  and 28 wt.%  $\text{CuO}$ , Fig. 4a) and our composites (mono- ( $\text{Cu}/\text{Al}_2\text{O}_3$ , Fig. 4c) or bimetallic alumina supported catalysts ( $\text{CuIn}/\text{Al}_2\text{O}_3$ , Fig. 4d)), and an In doped destroyed  $\text{CuP}$  zeolite (Fig. 4b) are compared along with the increasing reaction temperature under identical conditions. All the samples are able to produce alcohol from fatty acid with high selectivity, but the chromium free samples are able to give good

selectivity in narrower temperature range than the Adkins catalyst. The novel  $\text{CuIn}/\text{Al}_2\text{O}_3$  catalyst seems, however, to be more active: 80% overall conversion of OA on  $9\text{Cu}/\text{Al}_2\text{O}_3$  catalyst doped with 10 wt.%  $\text{In}_2\text{O}_3$  is attained at 310 °C while on copper chromite at 350 °C.

Diocetyl ether ((C8)<sub>2</sub>O) formation in bimolecular octanol dehydration on  $\text{CuIn}/\text{Al}_2\text{O}_3$  sample becomes significant only at high octanol yield above 310 °C (Fig. 4). Monomolecular dehydration of octanol to octene ( $\text{C}_8^=$ ) appears only above nearly full conversion of OA to octanol. Both acid catalysed side reactions may be attributed to alumina. However, these undesirable reactions can be highly mitigated on highly active and stable  $9\text{Cu}/\text{Al}_2\text{O}_3 + 10$  wt.%  $\text{In}_2\text{O}_3$  catalyst composite, using lower reaction temperature and higher space velocity.

Use of indium as efficient promoter with  $\text{Cu}/\text{Al}_2\text{O}_3$  catalyst turned out also to be a success (Fig. 4) similarly to  $\text{In}_2\text{O}_3$  doped  $\text{Ni}/\text{Al}_2\text{O}_3$  samples [1]. However, for  $\text{In}_2\text{O}_3$  doped  $\text{Cu}/\text{Al}_2\text{O}_3$  samples at constant indium content (10 wt.% in Fig. 5) the conversion and the octanol yield (the product distribution) is hardly influenced by the Cu-content between 3 and 20 wt.%. Similar behavior can be observed at a fixed Cu-loading (9 wt.%) changing the amount of added indium oxide in 3–20 wt.% range (see in Fig. 6). Hence it seems likely to apply in low concentration the expensive, but strongly efficient  $\text{In}_2\text{O}_3$  co-catalyst. It can be estimated that both active metal components can be used in about 10 wt.% to attain high carboxylic acid conversion with high and stable octanol yield (failing of these catalysts was not observed).

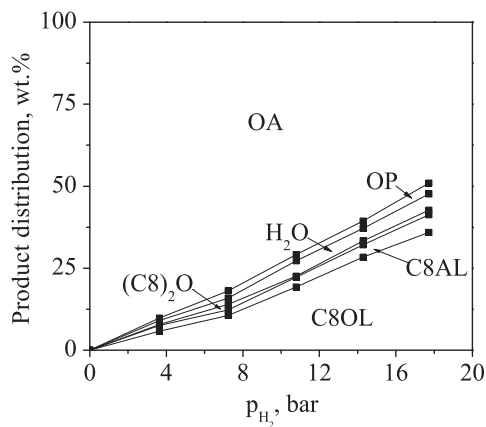
The weak influence of the concentration changes of both active metals in a wide range can be explained by supposing the most



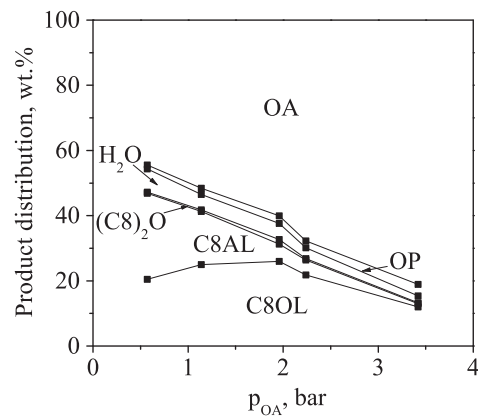
**Fig. 8.** Octanal (a) and octanol (b) hydroconversion over  $9\text{Cu}/\text{Al}_2\text{O}_3 + 10\% \text{In}_2\text{O}_3$  catalyst characterised by distributions of main products between 200 and 360 °C at 21 bar total pressure using stacked area graphs. WHSV of octanal and octanol was  $2.0 \text{ h}^{-1}$  similarly to octanoic acid reactant (symbols as in Fig. 4).

efficient active sites on the surface of the  $\text{Cu}_2\text{In}$  alloy. This phase surpasses the activity of copper or mainly indium metal surfaces while the composition and the mass of bulk phase inside the metal particles does not affect significantly the surface reactions (Figs. 5 and 6).

Beyond the metal phase which is active in hydrogenation, the support applied and its interactions with the  $\text{In}_2\text{O}_3$  co-catalyst may be of importance to ensure the advantageous catalytic properties. Fig. 7 demonstrates the catalytic effects observed for alumina support and the copper free composite interacting with the reactant OA (Fig. 7a, A), with the intermediate product aldehyde (Fig. 7b, B) and with the desired final product alcohol (Fig. 7c, C). The support has no activity contrary to the presumably well dispersed indium metal (working highly above its melting point), which shows some hydrogenating activity



**Fig. 9.** Yields and selectivities of OA conversion on  $9\text{Cu}/\text{Al}_2\text{O}_3 + 10\% \text{In}_2\text{O}_3$  catalyst as function of hydrogen partial pressure at 21 bar total pressure and 300 °C. The WHSV of OA was  $2.0 \text{ h}^{-1}$ . The partial pressure of OA was 1.7 bar.  $\text{H}_2$  partial pressure was changed by changing the  $\text{H}_2/\text{He}$  ratio (symbols as in Fig. 4).



**Fig. 10.** Yields and selectivities of OA conversion on  $9\text{Cu}/\text{Al}_2\text{O}_3 + 10\% \text{In}_2\text{O}_3$  catalyst as function of OA partial pressure at 21 bar total pressure and 300 °C. The WHSV of OA was  $2.0 \text{ h}^{-1}$ . The partial pressure of  $\text{H}_2$  was 17.6 bar. The OA partial pressure was changed by changing the OA/He ratio. (symbols as in Fig. 4).

producing mainly octanal and less octanol. The intermediate octanal is extremely reactive in aldol type condensation leading to formation of 2-hexyldec-2-enal /  $(\text{C}_8)_2\text{ALD}$  / in high concentration mainly on alumina (Fig. 7b). Furthermore aliphatic octyl aldehyde can easily be reduced to octyl alcohol in presence of indium, as reflected in Fig. 7b. Octanol then can be dehydrated to octenes over the naked alumina support, as confirmed in Fig. 7c using octanol as reactant. At lower reaction temperature, the dominant reaction route of octanol transformation is the bimolecular dehydration which forms dioctyl ether. Increasing the temperature, monomolecular dehydration becomes the main reaction pathway resulting in olefin formation. Probably this change of dehydration pathway is essentially affected by the decreasing alcohol coverage on the surface controlled by the increasing temperature. Using octanal as reactant, dioctyl ether yield is very low because the alcohol formation is suppressed by competing aldol condensation on the alumina surface (Fig. 7b). Comparison of the two sides of Fig. 7 gives some insight to the role of indium: i., OA can be reduced although with much lower rate on indium (Fig. 7A) than on copper particles (squares in Fig. 6); ii., aldol condensation of octanal and octanol dehydration are greatly suppressed by indium (Fig. 7b–B) and iii., the secondary reactions of octanol are suppressed as well by indium suggesting that indium can cover at least partly the surface of the alumina support (Fig. 7c–C). However the low, but significant production of ether and alkenes from octanol indicates that the missing components: copper or octanoic acid should have some influence on suppressing the dehydration of alcohol. Fig. 8b proves that the presence of fatty acid plays an important role to poison the active centers of dehydration together with indium, because octanol can be highly dehydrated over  $\text{CuIn}/\text{Al}_2\text{O}_3$  catalyst, i.e., in presence of copper and indium on alumina, but in absence of the organic acid reactant. Fig. 8a shows that copper and indium can promote the reduction of the aldehyde with hydrogen at a much lower temperature than indium alone (Fig. 7b).

The octanoic acid conversion to octanol over the  $9\text{Cu}/\text{Al}_2\text{O}_3$  catalyst doped with 10 wt.%  $\text{In}_2\text{O}_3$  similarly increases roughly linearly with increasing hydrogen partial pressure between 4 and 18 bar (Fig. 9) and inversely with octanoic acid partial pressure (Fig. 10), i.e., to the coverage of active sites by adsorbed fatty acid seems to suppress hydrogen as in the case of  $\text{Ni}/\text{In}/\text{Al}_2\text{O}_3$  [1]. Both observations are in accordance with the Langmuir–Hinshelwood kinetics. Unlike indium doped  $\text{Ni}/\text{Al}_2\text{O}_3$  catalyst [1] the lower activity of  $\text{CuIn}/\text{alumina}$  composite is reflected in the dependence on octanoic acid partial pressure, too. At lower coverage of the carboxylic acid, where hydrogen coverage may be higher resulting in higher OA conversion, the yield of octanol is lower, but the less reduced intermediate, the octanal is higher. This finding opens a way of aldehyde production instead of alcohol broadened the list of available products.

#### 4. Conclusions

Indium doping has been discovered to be highly efficient in reduction of fatty acids with hydrogen, opening a novel route for catalyst development. Hydrogenation of carboxylic acid of medium chain length resulting selectively in alcohol production can be increased by  $\text{In}_2\text{O}_3$  doping similarly over both Cu or Ni/ $\text{Al}_2\text{O}_3$  catalysts. Presence of metallic indium or rather alloying copper particles supported on alumina can effectively stop the step by step catalytic hydrogenation of fatty acids after alcohol formation inhibiting the following mono- or bimolecular dehydrations. High conversion with high level of octanol selectivity can be attained in a wide loading range of Cu and In on alumina support. Copper oxide can be more easily reduced to metallic nanoparticles at lower temperature than indium (III) oxide, but equally below the pretreatment temperature (450 °C). This difference is not reflected by any change of catalytic behaviour in a wide range of Cu and In content.

Appearance of  $\text{Cu}_2\text{In}$  alloy phase on the surface of metal particles results in significant increase of hydrogenation activity, beyond this, the presence of well-dispersed indium atoms or clusters in liquid state on the surface of alumina support seems to be decisive in selective poisoning the alcohol dehydration capability of the support.

The activity dependence on the reactant partial pressures reveals Langmuir–Hinshelwood kinetics with rate controlling surface reaction over a  $\text{CuIn}/\text{Al}_2\text{O}_3$  composite catalyst.

#### Acknowledgements

The authors wish to express their appreciation to Mrs. Ágnes Farkas Wellisch for her technical assistance.

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