

Scientific paper

Carboxylic Acid Reduction over Silica Supported Cu, Ni and Cu₂In, Ni₂In Catalysts

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Abstract

Hydroconversion of caprylic acid as model compound was studied in a flow-through fixed-bed reactor at 21 bar total pressure and 240–360 °C reaction temperature over various hydrogenating active phases: pure metal (Cu, Ni) and intermetallic compound (Cu₂In, Ni₂In) nanoparticles. Different silicas produced by dissimilar methods and a commercial γ -alumina were compared as appropriate supports. Catalyst precursors were activated in reducing H₂ flow at 21 bar and 450 °C as routine pretreatment. Catalysts of high activity and selectivity for alcohol production can be obtained by varying the supports, the main metals and their indium modified bimetallic forms. Diversity of catalytic behavior reflects the complexity of the surface reactions. Caprylic alcohol formation was substantiated to proceed through caprylic aldehyde intermediates, however it can be also dehydrated to dicaprylic ether or octenes over alumina support. Silica supports, especially a less compact variant seem to be more inert for side reactions than alumina. Different morphology of studied silicas can highly influence the catalytic performances taking place over different metal particles.

Keywords: Carboxylic acids; alcohols; hydrogenation; indium co-catalys

1. Introduction

Heterogeneous catalysts applying bimetallic phases seem to gain more and more significance in the biomass upgrading technologies.^{1,2} Hydroprocessing to valuable products seems to be a challenge, where various metallic composites as reducing agents can play important role.¹ There is a sore need for development of alternative catalysts for more facile hydrogenation of organic acids than the conventional copper chromite (Adkins-type) catalysts.³ Such catalysts should be active in the reduction of carbonyl group to methylene group, but shows low activity in alcohol dehydration and hydrogenolysis of C-C bonds resulting in high selectivity for alcohol production.

The patent literature describes catalysts for carboxylic acid reduction to alcohols comprising of one or more noble metals of Group VIII dispersed on Group III or IV metal oxides. Vanice et al. studied a series catalysts carrying platinum on TiO₂, SiO₂, Al₂O₃ and Fe₂O₃ supports and catalyst Pt powder without support.⁴ Hydrodecarbonylation and decomposition reactions of acetic acid do-

minated on Pt powder, Pt/SiO₂ and Pt/Al₂O₃ similarly to that we found and reported about for Ni/Al₂O₃ catalyst.⁵ A recent study concerns the performance of various commercial supported noble metal catalysts (Ru/C, Pd/C, Pt/C, Ru/Al₂O₃, Pd/Al₂O₃ and Pt/Al₂O₃) in aqueous phase hydrogenation of acetic acid.⁶ These catalysts were shown to be just as poor as the supported Pt catalysts used by Vanice et al.⁴ A systematic catalytic study of commercial supported noble metal, and Raney Ni or Cu catalysts combined with density functional theory calculations also showed to be most advantageous Ru/C catalyst, however alkane production was still significant.⁷ Manyar et al.⁸ found most efficient Pt/TiO₂ catalyst for steric acid hydrogenation applying various supports similarly to Vanice et al.⁴ and the selectivity was further improved by Re admission. Mentioned results clearly show the importance of data gathering about support effects in the hydrodeoxygenation catalysis. Appearance of bimetallic catalysts seems to be advantageous for hydrogenation of various carboxylic acids (PtSn/SiO₂ for selective reduction of acetic acid⁹ and RuSn/Al₂O₃ for dicarboxylic and fatty acids¹⁰). As long as the effect of Sn addition on the catalytic properties

of Pt/Al₂O₃ has been investigated in numerous studies (among them for acetic acid hydroconversion⁹), the promoting effect of the neighbouring indium has received much less attention.^{11–13}

Recent studies concern the hydroconversion of carboxylic acids over catalysts obtained by reduction and In-modification of Cu- and Ni-zeolites.^{14–18} Although the zeolite based samples proved to be efficient, the regular microporous systems did not come up to expectations in formation of reactive metal clusters inside the highly ordered aluminosilicate crystals. Applying only one of the zeolite components as support, higher efficiency can be attained over alumina loaded with Cu or Ni and modified with indium guest metal.^{19,5} Indium-additive doping Ni host metal was found to suppress the total hydrogenation and hydrodecarbonylation reaction – both resulting in hydrocarbons – and promote selective alcohol formation.^{19–20}

Properties of such hydroprocessing catalysts are basically determined by the type and the state of active metal phase. However, the support can significantly influence the formation of active metal particles, hence the quality of catalytically efficient surface. Recent paper showing promotional effects over a series of bimetallic Ni-Fe catalysts for CO₂ hydrogenation reflects great differences applying alumina or silica supports of exactly same specific surface area.²¹ Cu and Ni hydrotreating agents, especially with indium doping are highly efficient in H₂ activating processes for step-by-step reduction of carboxylic acids. Pioneering research on indium doping is continued: the aim of present work was to investigate the change of the support from one component (Al₂O₃) of earlier profoundly investigated crystalline aluminosilicates, zeolites for the second one (SiO₂). Two intrinsically different types of silica were picked up together with a commercial alumina, as well-known catalyst support using caprylic acid (CAC) of medium carbon-chain, as model reactant. It seems to be practical to compare the novel, chromium-free catalyst composites with the highly efficient, but old-fashioned Adkins contact, which was developed for selective reduction of fatty acid esters to aliphatic alcohols nearly one century ago.

2. Experimental

2.1. Catalyst preparation

Commercial silica gel (Grace) /SI1/ (BET: 302 m²/g) is an efficient conventional adsorbent. Commercial CAB-O-SIL M-5 (Cabot Corp.) /SI2/ is a fumed silica (BET: 200 m²/g) with a still much wider mesopore distribution consisting of agglomerated amorphous, colloidal silicon dioxide particles. These different silica samples and activated γ -Al₂O₃ (Ketjen CK 300, Akzo-Chemie, BET 199 m²/g) /AL/ were applied as supports to prepare catalysts by the incipient wetness impregnation method with

aqueous solution of NH₃ (Reanal, Hungary) of Ni(acetate)₂ (Aldrich) or Cu(acetate)₂ (Aldrich), dried at 120 °C, and calcined at 550 °C in air. The sample designation, e.g., 9Ni/SI1 formula represents a catalyst preparation containing 9 wt.% Ni on SI1. Bimetallic catalysts were prepared by adding indium (III) oxide (Aldrich) to the calcined in air, NiO containing, 9Ni/silica or 9Ni/alumina samples in amounts to attain Ni₂In or Cu₂In stoichiometric composition of metallic phase and the mixture was grinded in an agate mortar. Each catalyst precursor (both containing one or two metal oxides) was reduced in hydrogen flow *in situ* in the reactor at 450 °C for 1 h in order to generate active supported metal prior to the catalytic test.

For comparison a commercial Adkins catalyst (consisting of 72 wt.% CuCr₂O₄ and 28 wt.% CuO) was also tested applying the same activation and reaction conditions as for the catalysts of the present study.

2.2. Characterization

Nitrogen adsorption measurements were carried out at –196 °C using Quantochrome Autosorb 1C instrument. Before measurements, the samples were outgassed under vacuum at 350 °C for 24 h. The specific surface area was determined by the Brunauer-Emmet-Teller (BET) method. The pore size distribution was calculated from desorption branch of the isotherms by the Barrett-Joyner-Halenda (BJH) method.

The XRD patterns of the catalysts were recorded by Philips PW 1810 diffractometer applying monochromatized CuK_α ($\lambda = 0.15418$ nm) radiation (40 kV, 35 mA) at elevated temperatures in hydrogen flow using a high temperature XRD cell (HT-XRD). The crystalline phases were identified using the JSPDS ICDD database. The main size of active metallic particles was determined by the Scherrer equation evaluating the full width at half maximum (FWMH) values with profile fitting method.

The reducibility and the extent of reduction of the samples were examined by temperature-programmed H₂-reduction (H₂-TPR) using a flow-through quartz micro-reactor. About 30 mg catalyst was pretreated in a flow of 30 ml min⁻¹ nitrogen at 350 °C for 1 h. The pre-treated sample then cooled to room temperature in the same N₂ flow before was contacted with a 30 cm³ min⁻¹ flow of 9.7 % H₂/N₂ mixture. The reactor temperature was ramped up at a rate of 10 °C min⁻¹ to 800 °C and maintained for 1 h at latter temperature. The effluent gas was passed through a liquid nitrogen trap and a thermal conductivity detector (TCD). Data were recorded and processed by computer. Calculation of the corresponding hydrogen consumptions based on the peak areas was carried out by using the calibration value determined with the H₂-TPR of CuO reference material. All samples could be reduced completely under the condition of investigations, that is, hydrogen consumptions are equal with the amount of loaded reducible metals.

2. 3. Investigation of Catalytic Properties

The catalytic hydrogenation of CAC 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. The reactor effluent was cooled to room temperature and the liquid and gas phase products were separated. The liquid was analyzed by a gas chromatograph (GC, Shimadzu 2010) equipped with flame ionization detector and a CP-FFAP CB capillary column. The gas was analyzed by 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 by 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 parent silicas and alumina used as supports in this study are mesoporous materials as reflected by the nitrogen ad- and desorption isotherms and the pore size distributions shown in Fig. 1. These substrates are significantly different following different manufacturing. The specific surface areas are nearly related, however these samples have diverse pore size distributions around 8 nm /AL/, 13 nm /SI1/ and 27 nm /SI2/ with strikingly different width. This feature can determine fundamentally the formation, consequently the quality of active metallic particles and the mass transport properties in the prepared catalyst highly influencing the catalytic properties under reaction conditions. Isotherms of all derivatives (precursors, mono- or bimetal loaded forms too) are practically overlapping (so only the

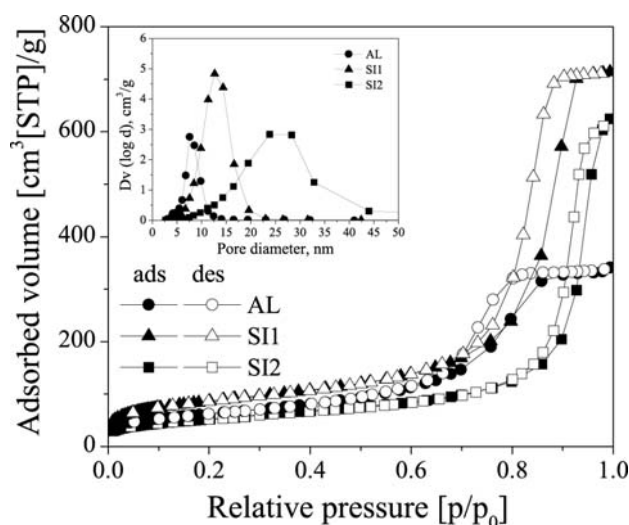


Figure 1. Ad- and desorption isotherms of nitrogen at -196 °C and pore size distribution of parent alumina (AL) and silica (SI1 /gel/ and SI2 /fumed/) supports.

parent samples are shown in Fig. 1) resulting in nearly the same specific surface area. This means that there is no significant influence of mono- or bimetal particle formation for accessibility of full volume inside the catalyst particles. The reason is that these three-dimensional, quite capacious pore structures exclude the pore blocking effect. The fumed silica /SI2/ has the most opened pore structure which can be highly advantageous from catalytic point of view.

The HT-XRD patterns given in Fig. 2 represent the formation of silica supported active metal particles. The step-by-step reduction of added host (copper or nickel)

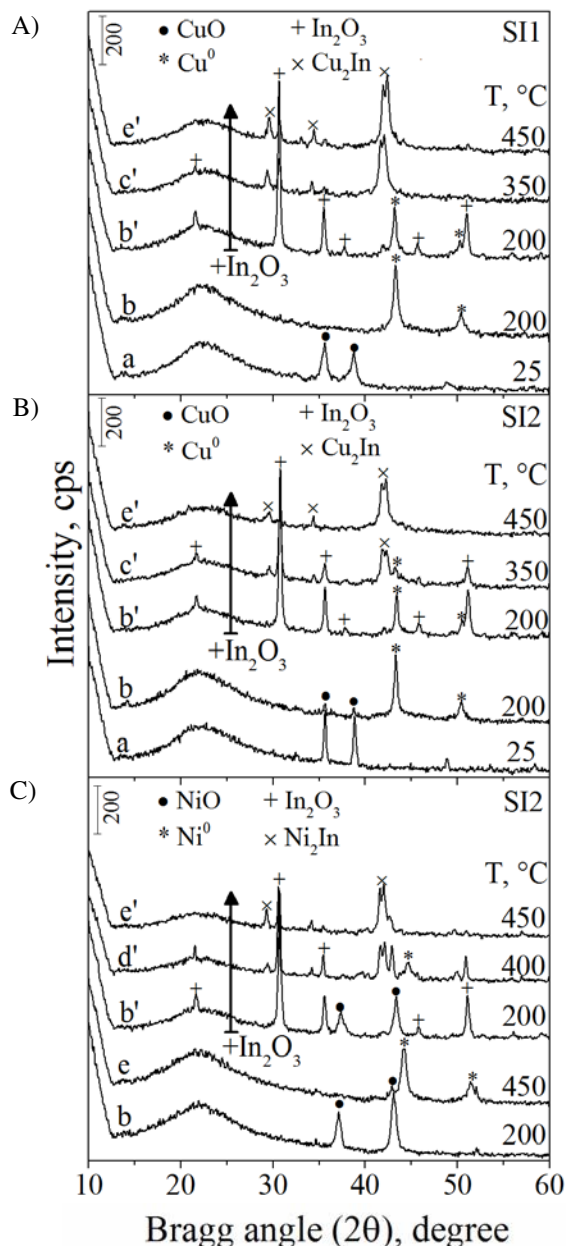


Figure 2. HT-XRD patterns of the indium free (a, b, e) and In loaded catalysts (b', c', d', e') recorded on 9Cu/SI1 (A), 9Cu/SI2 (B) and 9Ni/SI2 (C) precursors with and without 10 wt% In_2O_3 admixed, treated in H_2 flow for 30 min at various reducing temperatures.

and guest (indium) metal oxides to the active hydrogenating mono- or bimetallic phases is shown similarly than for nickel in ref. 5 and copper in ref. 19 on alumina support. Reductive treatment is completely reducing the CuO or NiO phases of the 9Cu/ or 9Ni/SI1 and /SI2 catalyst precursors up to 450 °C, which is the routine pretreatment temperature and generates small Cu or Ni metal particles (Fig. 2 A-a,b, B-a,b, C-b,e). CuO is completely reduced up to 200 °C on each support (Fig. 2 A-b, B-b) and in this case, there is no any difference using alumina or silica supports. The average size of Cu particles (calculated by the Scherrer equation) is 20 nm formed on alumina.¹⁹ Significantly higher values were obtained on silicas /26 nm on SI1 and 35 nm on SI2/. Higher porosity of silicas means smaller diffusional resistance that can result in aggregation of copper atoms into somewhat bigger particles especially in the more porous fumed silica.

The intensity of nickel diffraction lines are still increasing up to 450 °C formed the metal phase at much higher temperature than copper. The reduction temperature of host metal oxides is increasing in the next order: Cu < Ni and on silica < alumina. The lower reduction temperature of NiO on silicas compared to alumina can come from the weaker oxide-oxide interaction and/or lower diffusional resistance in the less compact silicas. The average size of Ni particles is 8 nm formed on alumina and two times bigger (21 nm) particles were obtained on the more porous SI2.

All admixed In₂O₃ seem to be converted to indium atoms up to 450 °C in hydrogen flow indicated by disappearance of its diffraction lines from the HT-XRD patterns (Fig. 2 A, B, C) and that can form immediately new Ni₂In or Cu₂In bimetallic phases (see similarly for alumina support in ref. 5 and ref. 19). The support and the presence of host metal can significantly influence the reduction of the admixed In₂O₃ phase as demonstrated later in Fig. 3. Copper particles are already ready for alloying at 200 °C and can catalyze the reduction of the guest metal indium which can immediately form the bimetallic particles around 350 °C alike in both silica (see Fig.2 A-c' and B-c'). In silica support NiO can be reduced at a shade lower temperature (350–400 °C) than In₂O₃ being also ready for alloying with nascent indium atoms. In this system the guest metal indium can be reduced between 350 and 450 °C needed higher temperature or longer time for the complete formation of bimetallic phase from pure nickel particles (see Fig. 2 C-d' and C-e'). The formed indium (as metal phase can be detectable by XRD only below 156.6 °C, the melting temperature of indium metal /not shown/) can be consumed in the reaction attaining the Ni₂In stoichiometry with the host metal for longer contact time than half hour (compare Fig. 2 C-d' and C-e'). Excess indium cannot be detected excluding the formation of intermetallic compounds with higher Ni-content /Ni₄In, Ni₃In/. Furthermore applying more amount of In₂O₃ NiIn or Ni₂In₃ were also not formed. In the case of Cu or Ni

host metals, formation of Cu₂In and Ni₂In phases were clearly detected in numerous studies.

One reason of the significantly lower activity of alumina supported catalysts compared with silica based samples can be the much slower reduction of NiO bound solidly on the alumina surface compared to the more inert silica. The H₂-TPR curves recorded on alumina /AL/ and the highly mesoporous silica /SI2/ (compare in Fig. 3) in accord with HT-XRD findings reflect important differences induced by diverse supports. Complete reduction of all precursors was found in the measured temperature range on the base of mass balances of added metal oxides and hydrogen. Applying identical linear heating up program for varied oxide precursors in hydrogen flow, the obtained H₂-TPR curves demonstrate that presence of alumina can affect intensely the reduction of supported oxides (NiO or In₂O₃).

Contrary, NiO loading on SI2 can be completely reduced into pure nickel phase at low temperature below 300 °C and in a very narrow range without appearance of two possible oxidation steps. Just the opposite is the behavior of In₂O₃ (containing larger particles than 100 nm), which simply admixed to SI2 powder by grinding can be

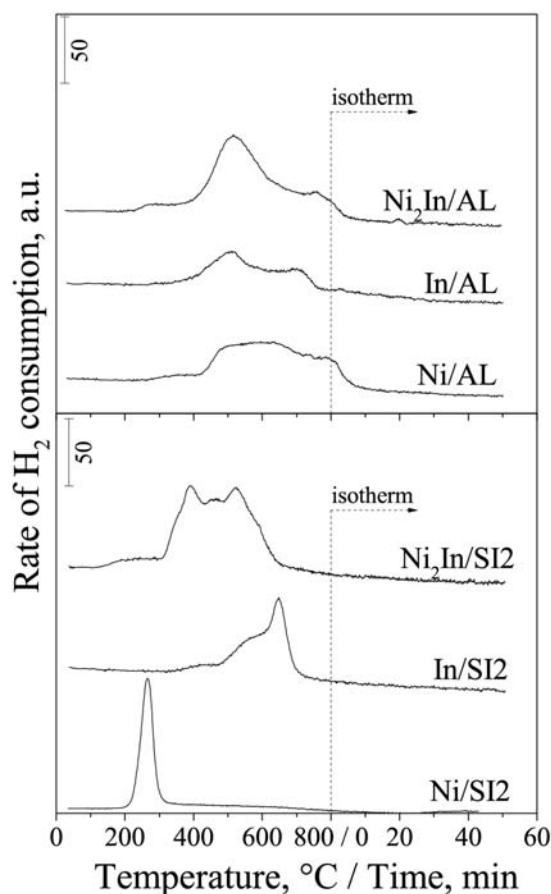
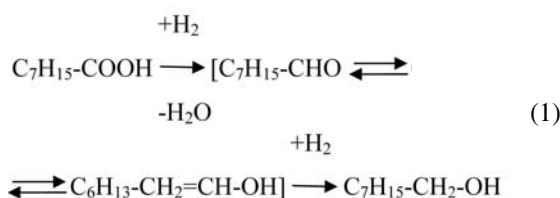


Figure 3. H₂-TPR curves demonstrating the reduction of NiO and In₂O₃ by itself, and jointly supported on alumina (A) and fumed silica (B).

fully reduced only up to 700 °C. Three possible oxidation steps can be clearly detected appearing long-drawn-out in a wide temperature range. Two metal oxide phases being present together in the highly mesoporous fumed silica give an overlapped, merged reduction profile. This is not a simple summation, but the result of a bilateral action, where reduction of NiO is noticeably slowed down, while reduction of In_2O_3 is picked up speed, seems to be significantly catalyzed by nickel formed prior to that.

The same precursors reduced in contact with $\gamma\text{-Al}_2\text{O}_3$ support give quite different pictures. Reduction profiles of both added metal oxides alone can be detected in a very wide temperature range suggesting strong interactions with the aluminium oxide support. Differences during reduction of monometallic components seem to be much less characteristic than on silica and what is more on alumina NiO is slightly less reducible than In_2O_3 . Formation of bimetallic catalyst on alumina shows much less difference from monometallic ones than it was observed on silica. These strikingly different reduction processes on silica and alumina supports should produce active metallic species in some degree different from catalytic point of view.

The product distributions characteristic for copper – loaded on two different silicas applied for the first time in the series of our pioneering studies – are compared in Fig. 4. Diverse catalytic features of the samples need different reaction temperature ranges to attain high level of CAC hydroconversion otherwise under identical experimental conditions. Strikingly different selectivities are attached with the different activities. The dominant reaction route is the step-by-step reduction of CAC through caprylic aldehyde (CAD) to caprylic alcohol (CAL) producing water as byproduct (1). The intermediate compound CAD can be detected over all catalyst samples, consequently this reaction route is confirmed:



On monometallic Cu/SI catalysts balanced activity to hydrogenate C-O and C=C bonds can be observed resulting in selective CAL formation from CAC through CAD (Fig. 4a and 4A). Each of the earlier studied host metals (Cu, Ni, Pt, etc.) can catalyze the hydrogen attack to C-O bonds reducing carboxylic acids. However, copper on alumina or aluminosilicate was not found to be able for the hydrogenolysis of C-C bonds, which hydrodecarbonylation reaction route is characteristic, dominant on more active hydrogenating metals (e.g. Ni, Pt). Copper species formed on fumed silica in Cu/SI2 catalyst are found to be

so active, that at higher reaction temperature, above 80 % conversion hydrodecarbonylation can become dominant resulting in chain shortening of the reactant molecules producing heptane (HEP), carbon monoxide and water (see in Fig. 4A). The strikingly different behavior of Cu/SI1 and Cu/SI2 convincingly demonstrate the outstanding importance of supports. It is an important peculiarity that mainly the morphology of these support is different derived from the different manufacturing.

The indium doping changed the monometallic active surface to a bimetallic one results in higher CAL yields because of CAC hydroconversion increases more rapidly with the reaction temperature (Fig. 4b and 4B). This is indicating that the indium promotion directed the conversion to a reaction route of higher activation energy (a part of surface Cu atoms are substituted with In atoms: diluting effect). The balance of hydrogenation activity of C-O and C=C bonds can tip up resulting in higher yield of CAD (Fig. 4B and 5B). Naturally, at higher reaction temperature or space time this accumulation can be eliminated attaining again high CAL selectivity. Indium admission can completely eliminate the hydrodecarbonylation reaction similarly to all former findings. The activity is still improved given so efficient catalyst, which can be exceeded only by use of nickel as main, host metal (compare Fig. 4B and 5B) that was proved most active also in our former studies. From former studies, stacked area graphs versus reaction temperature figures are attached to Fig. 4 to show the behavior of Cu/alumina (Fig. 4c) and Adkins (Fig. 4C) catalysts for direct comparison.¹⁹

It is well known that the acidity of alumina support can catalyze the bi- or monomolecular dehydration of the main product alcohol, resulting in appearance of dicaprylic-ether (DCE) and octenes (OE) as well as octane (O) (shown in Fig. 4c).¹⁹ Using the more inert silica gel support, dehydration products can be detected only in trace amounts given CAL with high selectivity (see Cu/SI1 in Fig. 4a). The improvement by indium admission is manifested only in an increase of the activity on the completely selective Cu/SI1 catalyst (compare Fig. 4a and 4b). This catalyst using the conventional silica gel support can already significantly exceed the old-fashioned Adkins catalyst (compare Fig. 4b and 4C).¹⁹ However, this development can be further intensified using a fumed silica support (see Fig. 4B and 4C).

Nickel on alumina ($\text{Ni}/\text{Al}_2\text{O}_3$) was earlier found to be active hydrogenating catalyst, that following the dominant hydrodecarbonylation of carboxylic acids. CO as primer product cannot be detected because of efficient methanation activity resulting in complete methane formation.⁵ Although applying fumed silica as nickel support, the hydrogenolysis of adjacent C-C bond nearby the carboxylic group of CAC is also the main reaction route. The methanation of the product CO is excluded (CH_4 cannot be detected) contrary to the alumina supported nickel ca-

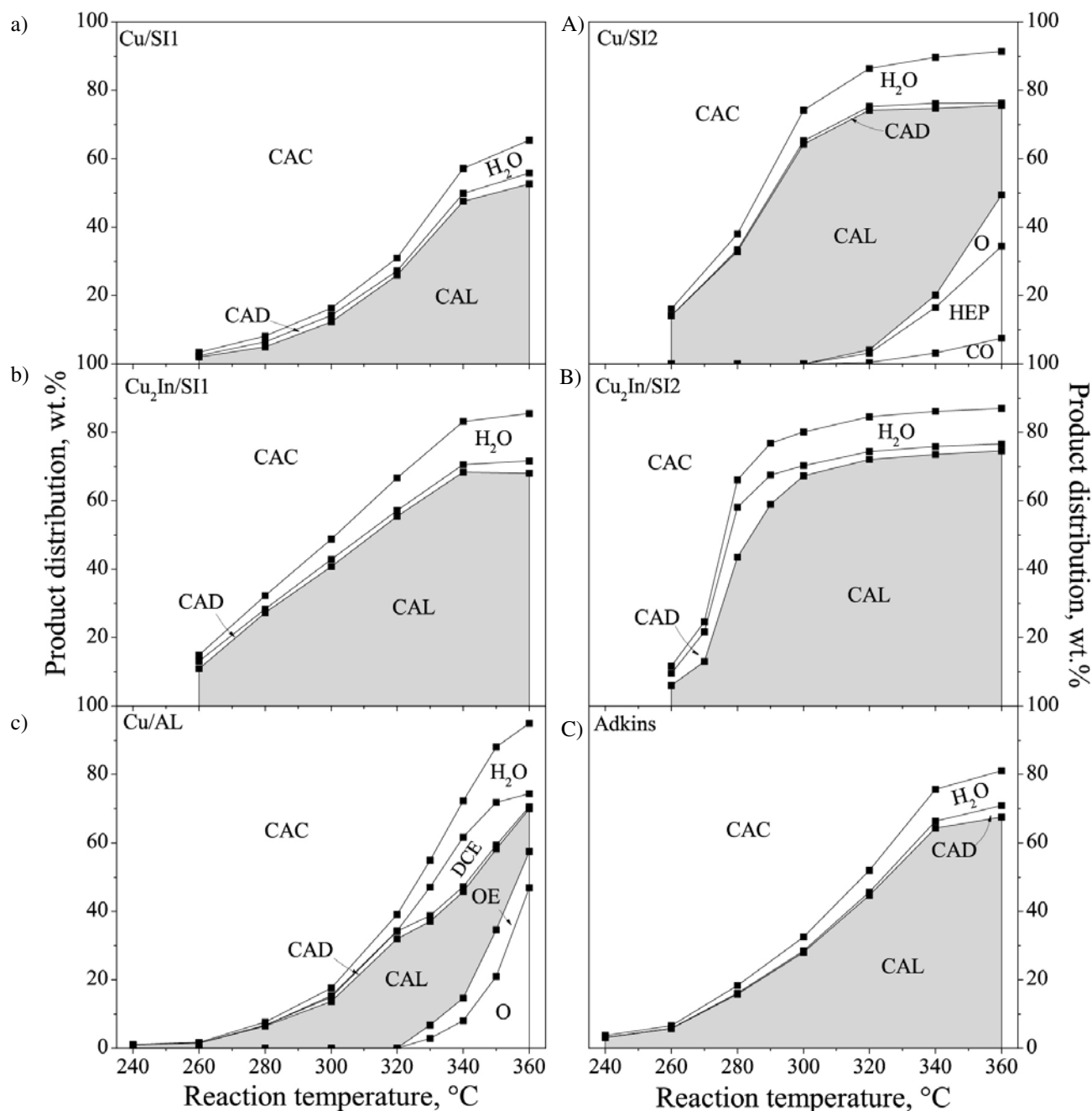


Figure 4. Stacked area graphs of product distributions obtained from the hydroconversion of CAC over catalysts (a) Cu/Si1, (b) Cu₂In/Si1, (c) Cu/AL, (A) Cu/Si2, (B) Cu₂In/Si2 and (C) commercial Adkins catalyst as a function of reaction temperature. The total pressure was 21 bar and the WHSV of CAC was 2 h⁻¹. Legend: CAC: caprylic acid, H₂O: water, CAD: caprylic aldehyde, CAL: caprylic alcohol, O: octane, OE: octenes, HEP: heptane, CO: carbon monoxide, DCE: dicaprylic ether.

talyst (compare ref. 10 and Fig. 5A). Indium doping shows the already well-known, never-failing efficiency to improve of Ni/Si2 to a fully alcohol selective catalyst (see Fig. 5B), which is significantly more active than the Cu-form. Catalytic performance of Ni₂In/Si2 and formerly studied Ni₂In/AL catalysts can be compared in Fig. 5B and 5C.⁵ In these most active catalysts, the efficiency of the metallic component in the consecutive CAC reduction

to CAL seems to be commensurable independently on the support. The difference of supports loaded with the alcohol selective Ni₂In phase clearly manifests itself in ability of dehydration of product CAL. It is evidenced that dehydration activity of acidic sites of alumina cannot be influenced (acidic centres are not poisoned) by indium admission, therefore the inert silica surface is really more advantageous as support.

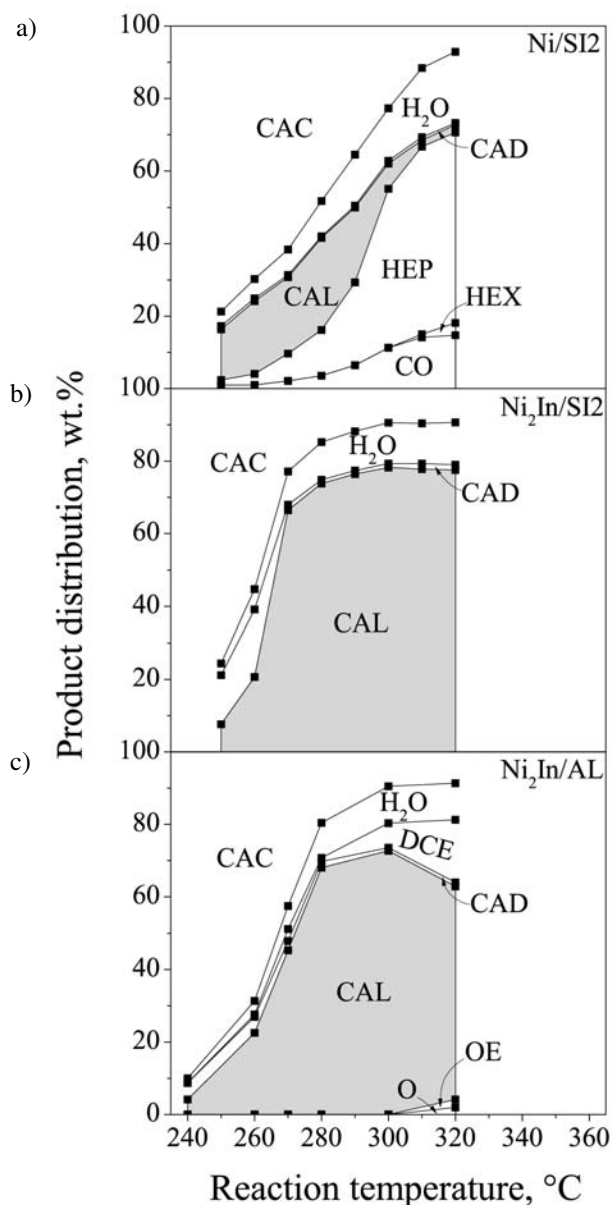


Figure 5. Stacked area graphs of product distributions obtained from the hydroconversion of CAC over catalysts (a) Ni/SiO₂, (b) Ni₂In/SiO₂ and (c) Ni₂In/Al as a function of reaction temperature. The total pressure was 21 bar and the WHSV of CAC was 2 h⁻¹. Legend as in Fig. 4. In addition: HEX: hexane.

4. Conclusions

Novel indium doped Ni catalysts were found to be outstandingly efficient for selective reduction of carboxylic acids to alcohols. Over Ni₂In intermetallic compound, – where the host metal is diluted with the guest metal indium in this favorable composition, – hydrogen cannot cut the C–C bond, and can attack the C–O bonds, and can saturate the C=C bond of vinyl alcohol, the tautomer of aldehyde, to generate alcohol. This study reveals that the role of novel highly efficient bimetallic phases is decisive.

However, the properties of the supports seem to be also quite significant. Highly mesoporous fumed silica was proven to be advantageous of overriding. Nature of silica surface excludes side reactions (e.g. mono- or bimolecular dehydration), which are characteristic for alumina. Beside the surface properties of the silica supports, their pore structure and morphological feature was turned out a success. Loading fumed silica support with the less active hydrogenating copper metal, the properties of the more active nickel catalysts can be explicitly approached. Variety of the most suitable catalysts for hydroconversion of bioacids is expanded and a further improvement can be attained by optimization of the support and the catalyst preparation technique. These findings reflect that by future preparation of well-defined ordered silica structures the efficiency of the *in situ* formed active metallic phase can be effectively controlled.

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Povzetek

Konverzijo kaprilne kisline, kot modelne spojine, smo študirali v pretočnem reaktorju pri tlaku 21 barov in temperaturi reakcij med 240 in 360 °C z uporabo različnih aktivnih faz: čiste kovine (Cu, Ni) in nanodelci intermetalnih spojin (Cu_2In , Ni_2In). Primerjali smo tudi ustreznost različnih nosilcev katalizatorja: silicijeve spojine pripravljene z različnimi metodami in γ -aluminijev oksid. Katalitske prekurzurje smo predhodno aktivirali v reduktivni atmosferi H_2 pri 21 barih in 450 °C. Katalizatorje za proizvodnjo alkohola, ki imajo tudi visoko aktivnost in selektivnost, lahko pripravimo s spreminjanjem nosilca, kovine in modifikacijo indijevih intermetalnih spojin. Raznolikost katalitskega obnašanja je posledica kompleksnosti reakcij na površini. Predvidevamo, da nastanek kaprilnega alkohola poteka preko aldehidnega intermediata, vendar lahko pride tudi do dehidracije in nastanka dikapril etra ali oktena pri uporabi Al_2O_3 nosilca. Nosilci na osnovi silicija, zlasti manj kompaktni, so bolj inertni, z manj stranskih reakcij. Različna morfologija nosilcev močno vpliva na katalitske sposobnosti kovinskih delcev.