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RESEARCH ARTICLE

Non-precious Metal Catalysts for Acetic Acid Reduction

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Abstract

Acetic acid (AA) hydroconversion was studied over various monometallic (Fe, Co, Ni, Cu, Zn, Pt) and bimetallic (doped with In as second, guest metal) catalysts loaded on a highly mesoporous, fumed silica support. The transformations were investigated in a fixed bed, flow-through reactor in temperature range of 240-380°C using hydrogen flow at 21bar total pressure. The catalyst precursors were activated in H_2 flow at 21bar and 450°C as routine pre-treatment. Catalytic performances of the studied metal catalysts have nothing in common. Activities and the yields of main products contrast strikingly. Diversity of catalytic behaviour reflects the complexity of the surface reaction network. Contrary to the highly ethanol selective Co or Cu forms, over Ni catalyst mainly methane was produced. Indium doping can completely eliminate the hydrodecarbonylation activity and turn to the consecutive reduction route resulting in high ethanol yield. Metallic phases of different peculiarities can offer promising contacts for upgrading various oxygenates obtainable from biomass degradation.

Keywords

acetic acid, ethanol, hydroconversion, non-precious metals, indium co-catalyst

1 Introduction

Both academia and industry are looking forward to utilize renewable, carbon neutral biomass to produce biofuels and value-added chemicals. Among the various biomass derived platform molecules, acetic acid (AA) is focused on the due to its easy production by thermal or biological degradation at localities near biomass sources. Heterogeneous catalysts applying mono- or bimetallic phases seem to gain more and more significance in the biomass upgrading technologies [1, 2]. Hydroprocessing to valuable products is a challenge, where various metallic composites as oxygen content reducing agents can play important role [1]. There is a sore need of development 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 the 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.

Recently, catalysts obtained by reduction and indium-doping of Cu- [4-7] and Ni-zeolites [8] for the hydroconversion of carboxylic acids were surveyed. 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 one of the zeolite building components (only alumina) as more stable and mesoporous support higher efficiency can be attained [9-12]. The indium-additive doping of Ni host metal was found to suppress the total hydrogenation and hydrodecarbonylation reaction - both resulting in hydrocarbons - and promote selective alcohol formation [13, 14].

The properties of such catalysts are determined by the type and the state of active metal phase however the support can significantly influence the formation of active metal particles, the quality of the catalytically efficient surface. Recent paper showing promotional effects over a series of bimetallic Ni-Fe catalysts for CO_2 hydrogenation reflects great differences applying alumina or silica supports of exactly same specific surface area [15]. In acetic acid hydroconversion Vannice et al. [16] studied a series of platinum catalysts supported on

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TiO_2, SiO_2, Al_2O_3 and Fe_2O_3 and Pt powder catalyst without support. Hydrodecarbonylation and decomposition reactions dominated on Pt powder, Pt/SiO_2 and Pt/Al_2O_3 similarly to that we found for Ni/Al_2O_3 catalyst [13]. Vannice et al. [16] obtained the best ethanol selectivity using a titania-supported Pt catalyst. Efficient hydrogenation of long chain fatty acids to alcohols was recently reported [17] also using Pt/TiO_2 catalysts compared to other supports (SiO_2, Al_2O_3, CeO_2, ZrO_2). Pt/TiO_2 catalysts were found the most active for AA hydrogenation and provided the highest ethanol selectivity (up to 70 %) [16]. We confirmed the results with titania (mainly anatase) support [13], as reported in ref. 16. Alcala et al. used fumed silica support (CAB-O-SIL (Cabot Corp.)) for supporting Pt [18] and could not produce ethanol selectively in accordance with results of Vannice et al. [16] who applied a quite different SiO_2 (Davison, Grade 57). A recent study [19] concerns the performance of various commercial supported noble metal catalysts (Ru/C, Pd/C, Pt/C, Ru/Al_2O_3, Pd/Al_2O_3 and Pt/Al_2O_3) in aqueous phase hydrogenation of AA. Technically aqueous-phase hydrogenation of AA over transition metals is more important. Among commercial catalysts Ru/C seemed to be the most efficient [20-21]. Use of computational methods DFT calculations suggest directions for designing new transition metal catalysts [20-21]. However, these catalysts still proved to be as poor as the supported Pt catalysts used by Vannice et al. [16]. However, the addition of Sn to Pt/SiO_2 catalysts inhibits the decomposition of AA to H_2O, CO and CH_4 and ethanol was selectively produced [18] similarly to our findings when In was added to other metals and supports [12, 13]. Using indium co-catalyst side reactions could be completely eliminated regardless of the support TiO_2 or Al_2O_3 [12].

The support can play important role as examples demonstrated above. For example it can simple enhance the specific surface area of the active metal and/or affect the activity and the selectivity on various ways. For example, formation of alloys or intermetallic compounds, change in the reducibility, stabilization of the metal nanoparticles, homogeneous distribution inside the pore structure of the support, control the migration of metal atoms to bigger aggregates can be important. The Cu and Ni hydrotreating agents, especially with indium doping were found highly efficient in H_2 activating processes for step by step reduction of carboxylic acids. Pioneering research applying indium doping is continued in the present study. The support from one component (Al_2O_3) of earlier profoundly investigated crystalline aluminosilicates (zeolites) for the second one (SiO_2) is changed. Picked up different types of silicas and compared with commercial alumina support, extra-special fumed silica (commercial CAB-O-SIL M-5 similarly to ref. 18) can be concluded to be a quite inert and highly mesoporous support for loading various hydrogenating metals.

The literature describes catalysts for AA hydrodeoxygenation (HDO) comprising of one or more noble metals of Group VIII dispersed on oxides of elements of Group III/A or IV/A. However, over monometallic forms hydrogenolysis of C-C bonds is a characteristic reaction. In such cases, hydrodecarbonylation may be the main reaction route hardly producing alcohols. Non precious metals of Group VIII have been more rarely studied. Among cheaper non noble metal hydrogenating agents (Cu and Ni) the adjacent cobalt in the periodic table is also highly efficient in some important H_2 activating processes. Cressely et al. studied acetic acid hydrogenation at atmospheric pressure over Fe, Co or Cu dispersed on an inert silica support [22], and Co loaded on various supports or using bimetallic combinations of the mentioned metals [23]. Their results showed that Cu/SiO_2 was active and quite selective for the production of ethanol, acetaldehyde and ethyl acetate through consecutive reduction of acetic acid, whereas Fe/SiO_2 resulted in the production of acetone and CO_2 following the ketonization reaction route. However, over Co/SiO_2, dominantly decomposition products (CH_4 and CO_2) were obtained. The high selectivity of Cu/SiO_2 for ethanol, acetaldehyde and ethyl acetate production was confirmed one and half decade later [24] and in our recent studies. However, a patent is of an age with ref. 19 and 20 claims that under super-atmospheric pressure over cobalt-containing catalysts high ethanol production is dominant [25]. Present work aimed to clarify discrepancies found in the literature as for the behaviour of cobalt and to compare succeeding metals (Fe, Co, Ni, Cu, Zn) adjacent in the periodic table supported on fumed silica in carboxylic acid hydroconversion using acetic acid as model compound. For comparison with noble metals from VIII group platinum was also applied from the Pt group in the periodic table under nickel. Applying our novel, solid state indium doping method, amalgamation with nascent indium, twelve different catalysts can be obtained, an ensemble of which can provide wide facilities in carboxylic group reduction.

2 Experimental

2.1 Catalyst preparation

Commercial CAB-O-SIL M-5 (Cabot Corp.) is a fumed silica (SiO_2(1), BET: 200m^2/g) with a wide mesopore distribution consisting of agglomerated amorphous, colloidal silicon dioxide particles. Catalysts were prepared by the incipient wetness impregnation method with NH_4OH solution (Reanal, Hungary) of Ni(acetate)$_2$ (Aldrich), Cu(acetate)$_2$ (Aldrich) or Zn(acetate)$_2$ (Aldrich) and Co(nitrate)$_2$ (Aldrich) or Fe(nitrate)$_3$ (Aldrich), dried at 120 °C, and calcined at 550°C in air. The sample designation, e.g., 9Ni/SiO_2 formula represents a catalyst preparation containing 9wt.% Ni on, similarly to Cu, Zn, Co, and Fe. Less precious metal, only 1 wt. % platinum was added to the silica support using H_2PtCl_6 (Aldrich) precursor. Cobalt-catalysts were also prepared with other silica supports: a commercial microporous silicagel (Grace-Sylobead, SiO_2(2), BET: 563m^2/g) and a mesoporous silicagel (Grace, SiO_2(3), BET: 291m^2/g). For comparison 9Cu/Al_2O_3 catalyst was also prepared using a commercial alumina support (Ketjen CK300, Akzo-Chemie, BET: 199m^2/g). Bimetallic catalysts were prepared by adding 10 wt. % indium (III) oxide (Aldrich) of the samples loaded with the host metals and the mixture was grinded in an agate mortar. Each catalyst precursor was reduced in hydrogen flow *in situ* in the reactor at 450°C for 1h in order to generate active supported metal prior to the catalytic test.

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 BET method. The pore size distribution was calculated from desorption branch of the isotherms by the BJH method.

The XRD patterns of the catalysts were recorded by Philips PW 1810 diffractometer applying monochromatized Cu_α radiation (40kV, 35mA) at elevated temperatures in hydrogen flow using a high temperature XRD cell (HT-XRD).

The reducibility and the extent of reduction of the samples were examined by temperature-programmed H_2-reduction (H_2-TPR) using a flow-through quartz microreactor. About 30mg catalyst was pretreated in a flow of 30 ml min^{-1} nitrogen at 350°C for 1h. The pretreated sample then cooled to room temperature in the same N_2 flow before was contacted with a 30 cm^3 min^{-1} flow of 9.7%H_2/N_2 mixture. The reactor temperature was ramped up at a rate of 10 °C min^{-1} to 800°C and maintained for 1h 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 H_2-TPR of CuO reference material.

2.3 Investigation of catalytic properties

The catalytic hydrogenation of AA (96% Molar Chemicals Kft, Hungary) was carried out in a high-pressure fixed bed flow-through reactor (16 mm inner diameter and 120 mm length) at 21bar total pressure in the temperature ranges of 240-380°C. Space time was $1g_{AA}/g_{cat.}$h WHSV, applying 2 g of catalysts and 2 g/h mass flow of AA. 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 Restek Rt-U-BOND 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 mole percent.

3 Results and Discussion

This study reveals that for the hydroconversion of carboxylic acids the role of novel bimetallic phases in the catalysts can be decisive, but non-precious monometallic forms can be rivals. Furthermore, the properties of the supports seem to be also quite significant under formation of metallic particles and under the reaction conditions. The variety of the most suitable catalysts for hydroconversion of bioacids is expanded in this study. Further improvement can be attained by optimization of the support and the catalyst preparation technique. First hand experiences showed, that highly mesoporous fumed silica is advantageous of overriding. Nature of silica surface excludes side reactions (e.g. mono- or bimolecular dehydration) which are characteristic for alumina and other supports having significant acidity. Esterification of the reactant acetic acid and primary product ethanol results in ethyl acetate as secondary product. The rate of this reaction can be also increased by the increasing number of acidic sites on the surface of the support (compare alumina and silica supports in Fig. 1).

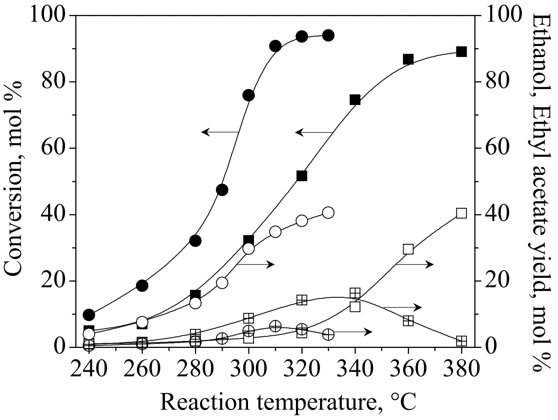

Fig. 1 AA hydroconversion curves (solid symbols, ●, ■) and the main product yields (ethanol: empty symbols, ○, □ and ethyl acetate: empty symbols (○, □) with +) as a function of reaction temperature over monometallic copper catalysts supported by alumina (squares) and fumed silica (circles) at 21bar total pressure and $1g_{AA}/g_{cat.}$·h WHSV.

Beside the surface properties of the silica supports their pore structure, morphological feature was turned out a success. Loading fumed silica support with copper much higher activity can be attained than over the alumina supported catalyst (compare in Fig. 1), although the specific surface areas are practically equal (~200m^2/g). This study applies the quite inert fumed silica support to compare the properties of various metal particles so clearly as possible besides limited support influences. This fumed silica support is a loose mesoporous material as reflected by the nitrogen ad- and desorption isotherm and the pore size distribution shown in Fig. 2.

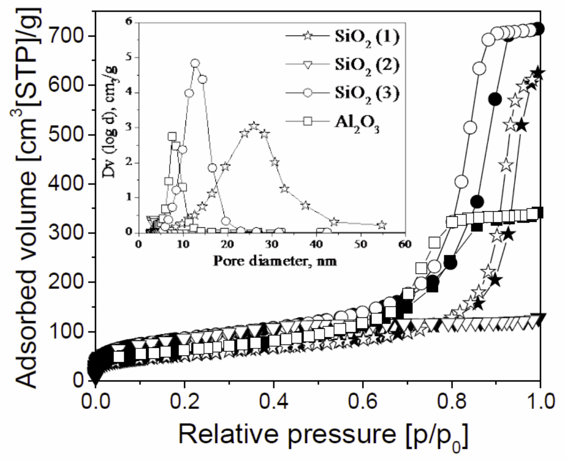

Fig. 2 Adsorption and desorption isotherms of nitrogen with the calculated pore size distributions of cobalt loaded alumina, fumed silica (SiO_2(1) and different silica gels (SiO_2(2) and SiO_2(3)) determined at -196°C.

The sample has 200 m^2/g specific surface area and extremely wide pore size distribution around 27 nm. This feature can determine fundamentally the formation, consequently the quality of active metallic particles and the mass transport properties in the catalysts highly influencing the catalytic performances under reaction conditions. The isotherms of all derivatives (precursors, mono- or bimetal loaded forms, too) are practically overlapping resulting in nearly the same specific surface area. This means that, there is no significant influence of the various mono- or bimetal particle formation for the accessibility of full volume inside the catalyst particles because of these three-dimensional, quite capacious pore structures exclude the pore blocking effect. However this is true only for the mesoporous supports. Fig. 2 represents the porosity of the cobalt catalysts. Decreased nitrogen adsorption, consequently lower specific surface area (instead of 563 m^2/g 298 m^2/g) can be obtained alone on the microporous silica gel following the cobalt loading because of pore blocking. Among mesoporous supports the fumed silica is a most opened pore structure (see pore size distributions in Fig. 2) which seems to be highly advantageous from catalytic point of view (Fig. 1).

One reason of the lower activity of alumina supported catalysts compared with silica based samples can be the difficult reduction of precursor oxides bound solidly on the alumina surface compared to the more inert silica. The H_2-TPR curves recorded on alumina and the highly mesoporous silica 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 H_2-TPR curves demonstrate that presence of alumina can affect intensely the reduction of supported oxides (e.g. NiO). Contrary, NiO loading on SiO_2(1) 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. Cobalt shows highly similar behaviour as nickel (only formation of Co/SiO_2(1) is shown in Fig. 3). Just the opposite is the behaviour of In_2O_3, the precursor of modifying guest metal (containing larger particles than 100 nm) which simply admixed to SiO_2(1) powder by grinding can be fully reduced only up to 700 °C. The three possible oxidation steps can be detected clearly appearing long-drawn-out in a wide temperature range. The two metal oxide phases (precursors of the host and guest metals, Ni and In) 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 catalysed by nickel formed prior to that. The same precursors reduced in contact with γ-Al_2O_3 support give similar pictures, but shifted to higher temperatures. These different reduction processes on silica and alumina supports should produce active metallic species in some degree different from catalytic point of view.

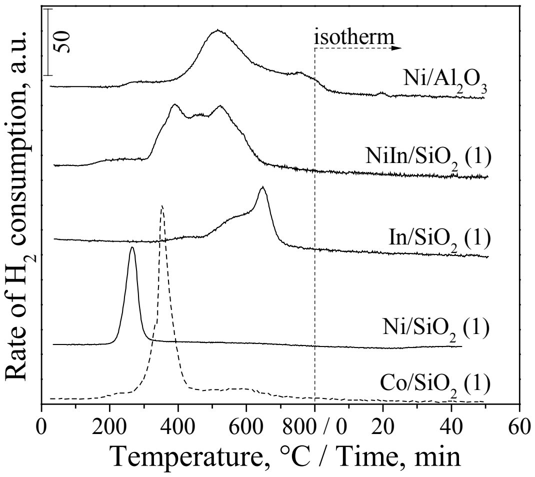

Fig. 3 Selected H_2-TPR curves of Ni, In and Co oxides supported on alumina and fumed silica.

The HT-XRD patterns given in Fig. 4-6 represent also the formation of silica supported active metal particles. The upper temperatures in Fig. 4 are those at which a complete reduction was observed and there may be a correlation with the standard reduction potentials of the investigated metals. The step by step reduction of added oxides of host (Cu, Ni, Co, Fe) and guest (In) metals to the active hydrogenating mono- or bimetallic phases is demonstrated in pure forms (Fig. 4-5) and in those mixtures (Fig. 6). The reductive treatment of the 9Cu/ or 9Ni/ and 9Co/SiO_2(1) catalyst precursors generates small Cu, Ni or Co metal particles (Fig. 4) completely reducing the CuO, NiO or Co_3O_4 phases up to 450°C which is the routine pre-treatment temperature before catalytic measurements. CuO is already completely reduced up to 200°C 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. Significantly higher value (35 nm) was obtained on SiO_2(1). The higher porosity of silica means smaller diffusional resistance, which can result in aggregation of copper atoms into somewhat bigger particles in the more porous fumed silica. The average size of metal particles formed at higher temperature than copper was found around 20 nm. Iron-oxide seemed to be less reducible. This course is completed only up to 550°C.

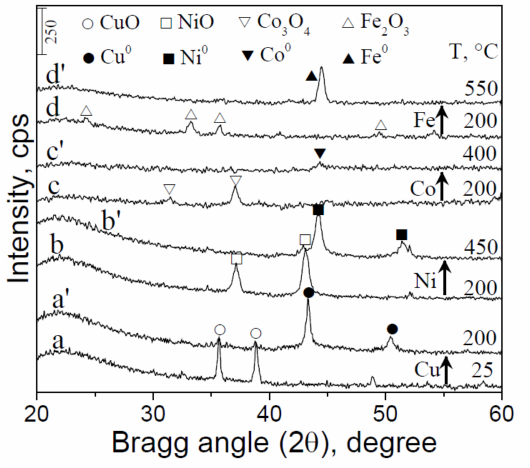

Fig. 4 Evolution of active monometallic phases reflected by the selected HT-XRD patterns on SiO_2(1) loaded with host metal oxides after reducing in H_2 flow step by step for 30min at 200, 400 or 450 or 550°C.

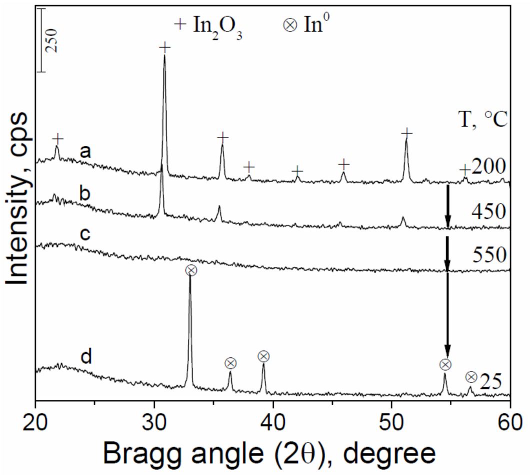

Fig. 5 Evolution of guest metallic phase reflected by the selected HT-XRD patterns of SiO_2(1) admixed with 10%In_2O_3 reduced in H_2 flow step by step for 30min at 200 (a), 450 (b), 550°C (c) and finally cooled down to R.T. (d).

Contrary to dynamical H_2-TPR measurement, in the HT-XRD cell In_2O_3 heated up step by step in H_2 flow the reduction is almost completed already at 450°C (see Fig. 5). At 550°C In_2O_3 is fully reduced to liquid In^0 (melting point is 156.6°C) and cooling down to room temperature the presence solid indium metal particles can be detected. So complete formation of bimetallic phases (e.g. Ni_2In or Cu_2In) can be controlled by disappearance of indium diffraction lines from the HT-XRD patterns at R.T.

Formation of bimetallic catalyst can be demonstrated in Fig. 6. All admixed In_2O_3 seem to be converted to indium atoms around 450°C in hydrogen flow indicated by disappearance of its diffraction lines from the HT-XRD patterns and that can form immediately new Ni_2In (or Cu_2In [9-10]) bimetallic phases. Copper particles are ready for alloying already at 200°C and can catalyse the reduction of the guest metal indium which can immediately form the bimetallic particles around 350°C. In silica support NiO can be reduced at a shade lower temperature (350-400°C) than In_2O_3 being also ready for alloying with nascent indium atoms.

The formed indium (as metal phase can be detectable by XRD only below 156.6 °C, the melting temperature of indium metal) can be consumed in the reaction attaining the Ni_2In stoichiometry with the host metal. Excess indium cannot be detected (not shown) excluding the formation of intermetallic compounds with higher Ni-content /Ni_4In, Ni_3In/, furthermore applying more amount of In_2O_3 NiIn or Ni_2In_3 were also not formed. In the case of Cu or Ni host metals, formation of Cu_2In and Ni_2In phases were clearly detected in numerous studies and the selective catalytic hydroconversion of carboxylic acids to alcohols suggest that these phases are unequivocally responsible for the favourable catalytic effects. Summarized, Cu and Ni amalgamation with indium only to Cu_2In and Ni_2In intermetallic compounds can be attained among various opportunities.

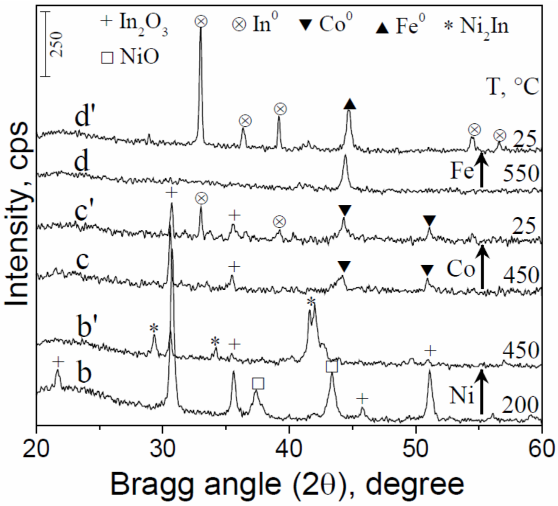

Fig. 6 Evolution of selected bimetallic catalysts reflected by the HT-XRD patterns.

Contrary to Cu and Ni, Co and Fe host metals in presence of indium liquid phase are not able for simple solid state amalgamation, for formation of intermetallic compounds in full extension of the metal particles under the investigated conditions. CoIn and FeIn intermetallic compounds cannot be detected by XRD technique and the unused indium phase can be observed cooling down to room temperature. Naturally, alloying of the upper layer can be possible, which can be proven catalytically.

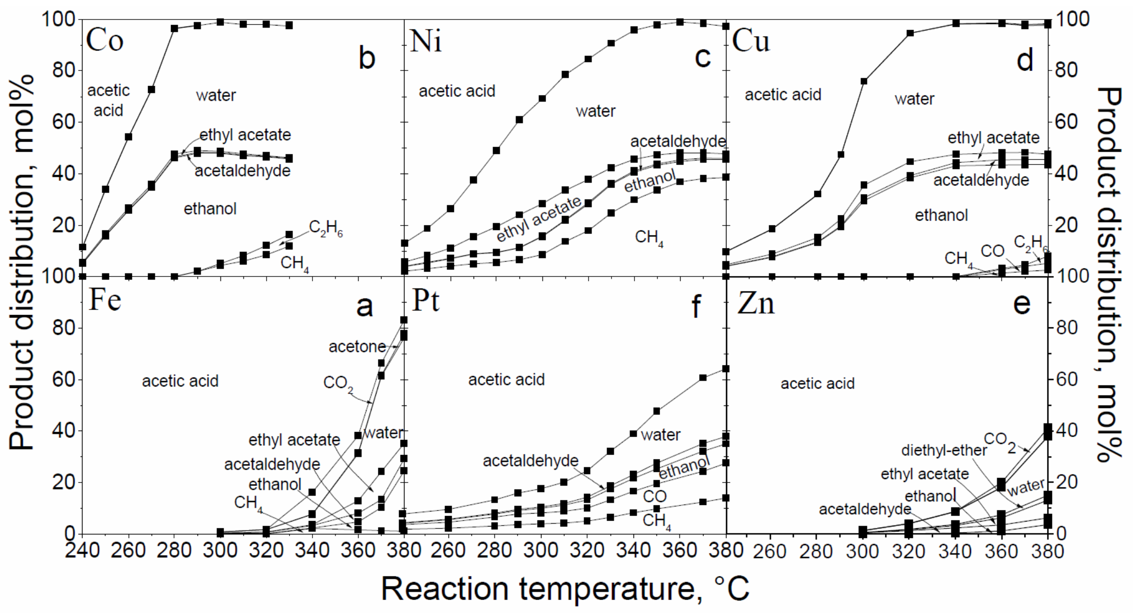

Fig. 7 Stacked area graphs of product distribution of AA hydroconversion as a function of the reaction temperature at 21bar and $1g_{AA}\cdot/g_{cat.}\cdot h$ WHSV over fumed silica (SiO2(1)) supported In-free monometallic catalysts.

The product distributions characteristic for silica supported monometallic catalysts are compared in Fig. 7. The diverse catalytic features of the samples need different reaction temperature ranges to attain high level of the acetic acid hydroconversion under otherwise identical experimental conditions. Strikingly different selectivities are attached with the different activities. One of the dominant reaction routes is the step-by-step reduction of acetic acid through acetaldehyde to ethyl alcohol producing water as by-product.

The intermediate compound acetaldehyde can be detected over all catalyst samples confirmed this reaction route. On monometallic $Cu/SiO_2(1)$ and $Co/SiO_2(1)$ catalysts formed almost selectively ethanol. Each of the studied metals (Co, Ni, Cu, Pt, Fe and Zn) can catalyse the hydrogen attack to C-O bonds reducing carboxylic acids however on Ni, Pt, Fe and Zn AA hydrodecarbonylation to CH_4, CO and H_2O seems to be significant. Activity of $Fe/SiO_2(1)$ and $Zn/SiO_2(1)$ is very low compared to other studied samples. Furthermore platinum is one of the most expensive metals. Among the tested six metals only Co, Cu and Ni seems to be promising. The ethanol selective cobalt and copper species formed on fumed silica are found also active in hydrodecarbonylation resulting in the formation undesired by-products: methane, carbon monoxide and water, but only at higher reaction temperature than a complete AA reduction to ethanol has been attained. Over the monometallic Co and Cu catalysts the extension of rival competing, parallel reaction routes can simply be controlled by the reaction condition. The highly active nickel catalyst prefers the AA hydrodecarbonylation in the investigated wide reaction temperature range. However, this unwanted reaction can be completely eliminated with modification of the active metallic surface (see Fig 8B) [12, 26].

The indium doping of nickel changed the monometallic particles to bimetallic ones, the active surface results in higher yield of acetaldehyde as intermediate compound and ethanol as main product. Indium admission can eliminate completely the hydrodecarbonylation reaction similarly to all former findings and the activity is still improved given so efficient catalyst which can be exceeded only by use of nickel as main, host metal which was proved most active also in our former studies. New findings, that this high activity and selectivity can be attained with a more simpler monometallic catalysts, $Co/SiO_2(1)$ (compare Fig. 7b and Fig. 8B). What is more the monometallic $Co/SiO_2(1)$ exceeds the properties of bimetallic $Ni_2In/SiO_2(1)$ sample at lower reaction temperature. Interestingly, indium admission to cobalt catalysts results in lower activity (see $CoIn/SiO_2(1)$ in Fig. 8A). Important observation is that in the case of Co-catalysts after indium doping the complete improvement of selectivity is attached with a significant decrease of the activity, i.e. full conversion can be attained only at higher temperature. One of the possible explanations (simple geometric effect) is that cobalt atoms on the surface are much more diluted with indium because cobalt can form only $CoIn_2$ or $CoIn_3$ phases as intermetallic compounds contrary to existence of Cu_2In or Ni_2In.

On fumed silica supported Ni and Co catalysts indium doping shows inverse effect regarding the change of catalytic activity (compare Fig. 8A and B). Adding indium guest metal to $Cu/SiO_2(1)$ the activity was hardly influenced and the effect for the selectivity was also slight. It can be concluded that selective hydroconversion of acetic acid to ethanol can be achieved over different catalysts.

Fig. 9 reflects that the texture of the supports can be very important. It is still easy to accept that microporous silicagel cannot be suited for catalyst support because of its extremely

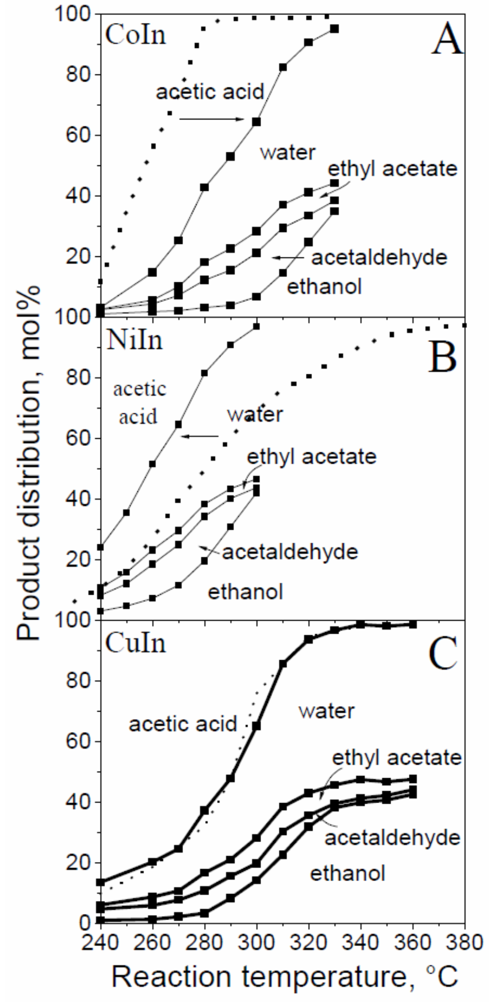

Fig. 8 Product distributions over the indium modified forms of the satisfactorily active monometallic catalysts in stacked area graphs of AA hydroconversion compared with the conversion curves of monometallic catalysts (see dotted lines).

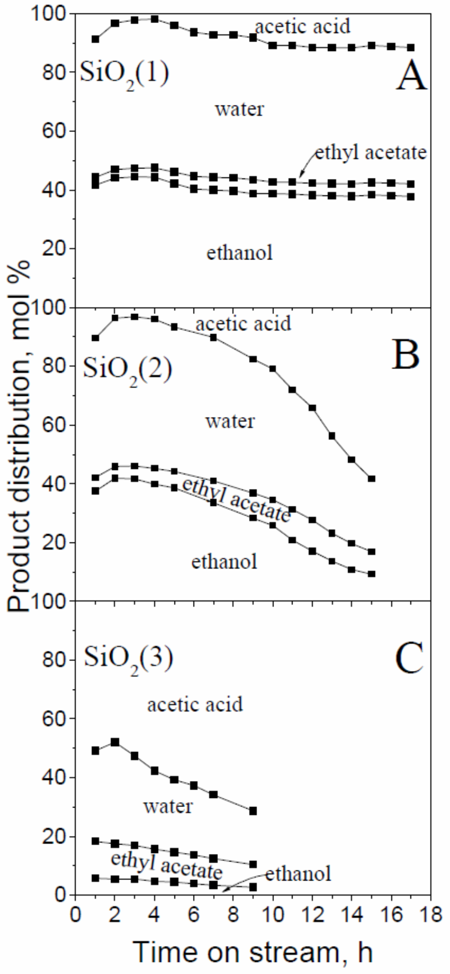

Fig. 9 Stability of cobalt loaded catalysts depending on different silica supports (A - fumed silica, B - mesoporous silica gel, C - microporous silica gel) shown in stacked area graphs of AA hydroconversion at 280 °C and 21bar applying 1g_{AA}·/$g_{cat.}$·h WHSV.

high diffusional resistance. However, the great differences observed using different mesoporous silicas manufactured with different methods seem to be quite strange.

SiO_2(3) having narrower pores can be characterized with significantly higher specific surface area than SiO_2(1). At an early stage both show similar high activity however over Co/SiO_2(3) a fast activity decrease can be observed. Here also a mass transport problem can be supposed to explain the fast activity loss at increasing time-on-stream (see Fig. 9B). Important finding that different metal catalysts prepared with fumed silica, SiO_2(1) were proven stable under reaction conditions resulting in high AA conversion.

4 Conclusions

In former studies highly efficient Ni_2In bimetallic catalysts were found to be outstandingly efficient for selective reduction of aliphatic carboxylic acids to alcohols. This study reveals that although the role of the 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, morphological feature was turned out an important factor. Loading fumed silica support with the less active hydrogenating metal, copper the properties of the more active nickel catalysts can be explicitly approached. Using cobalt on this special silica support a highly active and selective catalyst can be obtained which can replace expensive precious metals. The variety of the most suitable catalysts for hydroconversion of bioacids is further expanded and additional improvement can be attained by optimization of the support and the catalyst preparation technique.

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