Research Article

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Acetic acid hydroconversion over mono- and bimetallic indium doped catalysts supported on alumina and silicas of various textures

Abstract: Consecutive hydroconversion of acetic acid (AA) to ethanol was compared over monometallic and novel bimetallic (containing In as guest metal) catalysts on alumina and silica supports (*inter alia* highly ordered SBA-15) of different porosity and pore structure. The transformation was studied in a fixed bed, flow-through reactor in the temperature range of 220–380°C using hydrogen flow at 21 bar total pressure. AA hydroconversion activity of Cu and Pt catalysts and the yield of selectively produced alcohol were increased drastically by applying SBA-15 as highly ordered, mesoporous silica support instead of alumina. The most active nickel catalysts do not allow the selective addition of hydrogen to carbon-oxygen bonds independently of supports producing mainly CH_4; however, indium doping can completely eliminate the hydrodecarbonylation activity as found in earlier studies. The textural properties of studied silica supports of various textures such as SBA-15, CAB-O-SIL, and Grace Sylobead have a profound impact on the catalytic performance of Ni and Ni_2In particles.

Keywords: acetic acid hydroconversion, ethanol, bimetallic catalyst, indium co-catalyst, SBA-15

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1 Introduction

Short chain bioacids (mainly acetic acid) are readily obtained either by anaerobic fermentation or by pyrolysis of biomass [1]. Selective reduction of these acids to alcohols (e.g. acetic acid to ethanol) offers a new route for generation of liquid biofuel or valuable chemicals requiring, novel, efficient catalysts. In general, bimetallic catalysts usually have properties that are distinct from those containing one of the metals only and give favorably enhanced activity, selectivity and stability needed, for instance, to upgrade raw materials of biomass origin to fuels and chemicals [2]. From the 1960s extensive investigations resulted in many widely utilized catalytic applications. As long as the effect of tin as a second metal, for example, on the catalytic properties of Pt/Al_2O_3 has been reported in numerous studies [3], the promoting effect of the neighboring indium received much less attention [4-6].

Short chain fatty acids seem to be important biomass platform molecules. The significance of catalytic reduction of bioacids to fuel or intermediate material production is steadily increasing, however, only a few studies have been devoted to the acetic acid (AA) transformation [3,7-9]. The literature describes catalysts for AA hydrodeoxygenation (HDO) comprised 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 (e.g. noble metals or Ni), hydrogenolysis of C-C bonds is a characteristic reaction. In such cases, hydrodecarbonylation may be the main reaction route producing hardly any alcohols. Presence of indium atoms on the active metal surface (Ni [10] or Pt [11] supported on alumina), results in a drastic mechanism change moving to consecutive hydrogenation of carboxylic group resulting, finally in selective formation of alcohols. Recently, we discovered novel bimetallic, Pt-In [11], Cu-In and Ni-In supported catalysts [12], which are highly active and selective in the reduction of octanoic acid to octanol [10,12] or AA to ethanol [11,13,14]. In nickel-

containing bimetallic catalysts, the appearance of a Ni_2In phase seemed to be responsible for the significant enhancement of the desired hydrogenation activity and alcohol selectivity in comparison with the corresponding properties of the monometallic forms. Although, the properties of the metal particles (e.g. Ni or Ni_2In) are decisive, certain features of the support can be also significant. Rachmady et al. studied a series of platinum catalysts on TiO_2, SiO_2, Al_2O_3 and Fe_2O_3 supports and Pt powder catalyst without support [7]. Hydrodecarbonylation and decomposition reactions dominated on Pt powder, Pt/SiO_2 and Pt/Al_2O_3 similarly to what we found for Ni/Al_2O_3 catalyst [10]. A recent study 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 [9]. These catalysts proved to be as poor as the supported Pt catalysts used by Rachmady et al. [7] Pt/TiO_2 catalysts were found to be the most active for AA hydrogenation and provided the highest ethanol selectivity (up to 70%) [7]. Evidence was obtained that the reaction involves both metal (Pt) and oxide support phases. An efficient hydrogenation of long chain fatty acids to alcohols was recently reported using Pt/TiO_2 catalysts compared to other supports (SiO_2, Al_2O_3, CeO_2, ZrO_2) [15].

Rachmady et al. obtained the best ethanol selectivity using a titania-supported Pt catalyst [7]. We confirmed the results with titania (mainly anatase) support [11], as reported in [7] Alcala et al. used fumed silica support (CAB-O-SIL / Cabot Corp.) for supporting Pt and could produce ethanol [3], contrary to Rachmady et al. who applied a quite different SiO_2 (Davison, Grade 57) [7]. Using indium co-catalyst, side reactions could be completely eliminated regardless of the support TiO_2 or Al_2O_3. The addition of Sn to Pt/SiO_2 catalysts inhibits the decomposition of AA to CO_2 and CH_4, and ethanol was selectively produced comparably to our findings when In was added to other metals and supports.

In our former studies, the indium doping has been found to efficiently enhance the AA hydroconversion activity and ethanol selectivity of the Cu, Ni or Pt loaded catalysts using various supports (amorphous or crystalline alumino-silicates /zeolites/, alumina, titania, laponite, etc.). However, these supports are not completely inactive under a range of reaction conditions resulting in side reactions (ketonization, esterification, mono- or bimolecular dehydration, etc.). Our former investigations showed that the chemical quality, the structure and the morphology of applied supports significantly influences the selectivity and the hydrogenation activity of the metals in acetic acid hydroconversion. This work is an extension of our former findings and calls attention to the effect of support beside the effect of indium admission. The properties of SBA-15 (highly ordered mesopores, hydrothermally stable, thick wall, large surface area and pore volume) are remarkably relevant towards the application of biorefinery production [16]. The purely siliceous SBA-15 not having any characteristic acidity seems to be an ideal catalyst support of active metal nanoparticles. The aim of the present work is to investigate the applicability of SBA-15 among silicas as support for Cu, Pt and Ni active metals in AA hydroconversion emphasizing the outstanding importance of texture in different silica supports.

2 Experimental

Highly ordered, amorphous, mesoporous SBA-15 silica (having uniform pores of 6 nm diameter) (BET surface area: 893 m^2 g^{-1}) was synthesized by a sol-gel method using an amphiphilic triblock copolymer, Pluronic P123, as an organic structure-directing agent [17]. Commercial CAB-O-SIL M-5 (Cabot Corp.) is a fumed silica (BET: 200 m^2 g^{-1}) with a wide mesopore distribution consisting of agglomerated, amorphous, colloidal silicon dioxide particles. Commercial micro-porous Grace Sylobead SG B 127 (BET: 563 m^2 g^{-1}) spherical silica gel is an efficient drying agent since it selectively adsorbs very small molecules, e.g. water. These silica samples and activated γ-Al_2O_3 (Ketjen CK 300, Akzo-Chemie, Specific Surface Area (SSA) = 199 m^2 g^{-1}) were impregnated with NH_4OH solution (Reanal, Hungary) of $Ni(acetate)_2$ (Aldrich) or $Cu(acetate)_2$ (Aldrich), dried at 120°C, and calcined at 400°C in an air stream. The sample designation, e.g., 9Ni/SBA-15 formula, represents a catalyst preparation containing 9% wt. of Ni on SBA-15. SBA-15 was also impregnated with $H_2[PtCl_6]$ solution (Reanal, Hungary) in a ratio of 1 cm^3 g^{-1} to ensure incipient wetness. Prior to impregnation, the supports were dried overnight at 450°C, then the aqueous Pt-salt solution containing Pt in the required amount was added to the support. Bimetallic catalysts were prepared by adding indium (III) oxide (Aldrich) to the samples in amounts to attain Ni_2In or Cu_2In stoichiometric composition of metallic phase, and the mixture was ground in an agate mortar. Impregnation with water soluble $In(NO_3)_3$ results in samples of the same properties as those obtained by grinding with In_2O_3 as evidenced with alumina and different silica supports. This method was only applied in the case of the rigid Sylobead.

The catalyst sample was inserted into the a high-pressure, fixed bed, flow-through reactor and reduced in a flow of 100 cm^3 min^{-1} pure hydrogen *in situ* in the reactor

at 450°C and 21 bar for 1 h to obtain active metal particles. The hydrogenation of AA (96%, Reanal, Hungary) was studied at 21 bar total pressure and 240-380°C. The reactor effluent was cooled to room temperature, and liquid and gaseous products were separated. Steady state was attained generally in 1-2 hours after setting parameters then samples were collected in half hour periods. The liquid was analyzed using gas chromatograph (Shimadzu 2010) equipped with a Restek Rt-U-BOND capillary column and a flame ionization detector. The gas was analyzed by in-line gas chromatograph (HP5890) equipped with thermal conductivity cell and Carboxen 1006 PLOT capillary column. Conversion of acetic acid was determined from a carbon mass balance based on the analysis of compounds detected in both separated liquid and gaseous effluent streams. Components appearing in gas chromatograms for both product lines were calibrated with the exception of water, and by measuring the total mass flows in both lines, discrete mass flows were determined for each of the components. Although the complete mass balance was checked several times allowing longer periods for sampling, in the course of routine measurements, the amount of water formed could simply be calculated while the product composition was given in mol%. The product distributions are represented as stacked area graphs where the distance between two neighboring curves represents the yield of a given product in mole percents.

XRD patterns of the catalysts were recorded at elevated temperatures in hydrogen flow using Philips PW1810 diffractometer provided with a high temperature XRD cell. The mean crystallite size of the metal particles was estimated by the Scherrer equation. The morphological analysis of the samples was carried out with a FEI Morgagni 268D type TEM. Nitrogen physisorption measurements were carried out at -196°C using Quantochrome Autosorb 1C sorptometer.

The reduction of the samples was studied using temperature-programmed H_2-reduction (H_2-TPR) using a flow-through quartz microreactor. 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 was cooled to room temperature in the same N_2 flow, then, 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 1 h at this 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.

3 Results and Discussion

The hydrogenolysis of C-C bond resulting in the hydrodecarbonylation of carboxylic acids is not characteristic of copper catalysts showing lower activity in hydrodeoxygenation reactions than nickel or noble metals. Using alumina support ethanol can be produced selectively from acetic acid (Fig. 1a). Ethyl acetate is formed only as a by-product. Esterification of ethanol proceeds both on basic and acidic sites (of alumina) or in a non-catalytic route. However, this ester can be easily hydrogenated to two ethanol molecules over metal (e.g. copper) catalyst resulting in ethanol production with high selectivity at higher reaction temperature, and a total conversion is realized in this way. Replacing the alumina support for silica, the activity and the ethanol yield is strikingly increased, attaining similar conversion and selectivity as over alumina supported copper by 50°C lower temperature (Fig. 1b). The conversions and product distributions were the same for 9 wt% copper loaded CAB-O-SIL, although the specific surface area of SBA-15 is essentially higher than that of CAB-O-SIL (893 and 200 m^2 g^{-1}, resp.) The latter has strictly the same BET surface area as applied alumina. The chemical composition of the support deeply influences the catalytic behavior. When the very effective SBA-15 support is applied for copper, the introduction of indium slightly improves the catalytic behavior (Fig. 1c). By indium doping the alumina supported copper, catalysis can be highly improved and similar behavior is observed as for the exchange of support shown above [18].

The hydrodecarbonylation of carboxylic acids through the hydrogenolysis of C-C bond is the main reaction over 1Pt/alumina catalyst (Fig. 2a) and traces of the valuable products are only detected. Change of the support results in a drastic change of catalytic properties (Fig. 2b), while indium admission results only in some increase of activity (Fig. 2c). Parallel with activity increase, the reaction route completely turns from hydrodecarbonylation into consecutive reduction of acetic acid to ethanol (compare Fig. 2a and 2b). Improvement of the catalytic properties seems to be attained in a comparable extent either by indium admission or by support exchange from alumina to silica (Fig. 2) [11]. This support substitution seems to be much more efficient, as observed by use of TiO_2 in [7] and [15].

Alumina or silica supported nickel catalysts are not active in selective addition of hydrogen to carbon-oxygen bonds; however, they are very active in hydrogenolysis producing CH_4, H_2O and (fast methanized) CO (Fig. 3a and 3b). The appearance of higher reduced
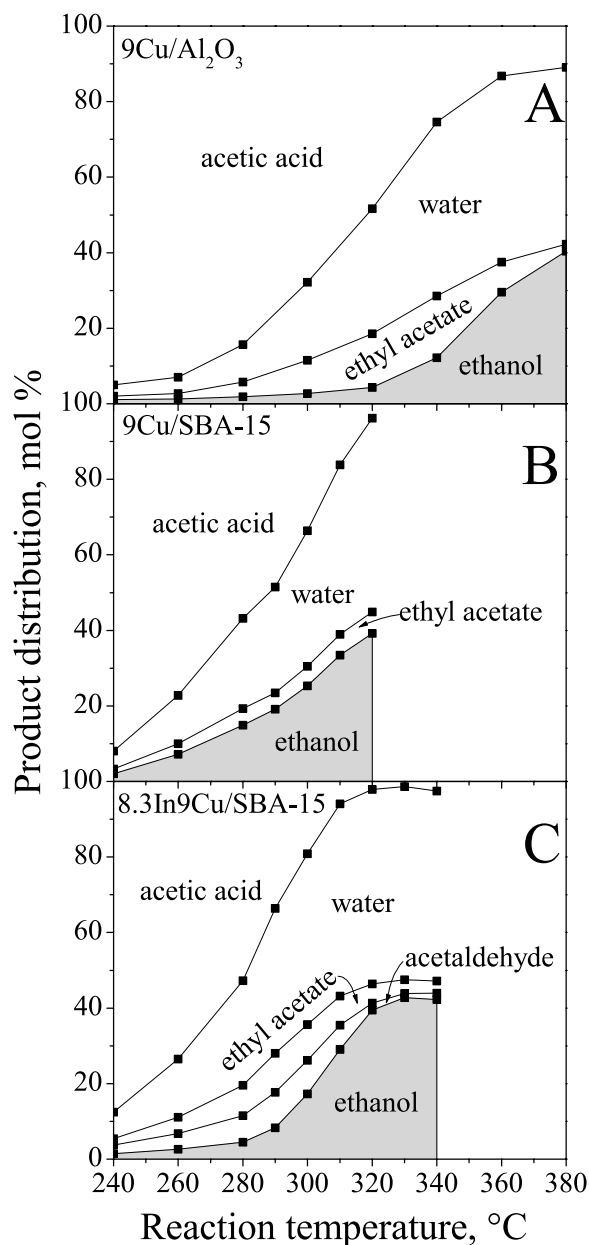
Figure 1: Stacked area graphs of product distribution of AA hydroconversion as a function of reaction temperature over monometallic (a) Cu/Al_2O_3, (b) Cu/SBA-15 and bimetallic (c) InCu/SBA-15 catalysts at 21 bar total pressure and $1 \, g_{AA}/g_{cat.} \times$ h WHSV.
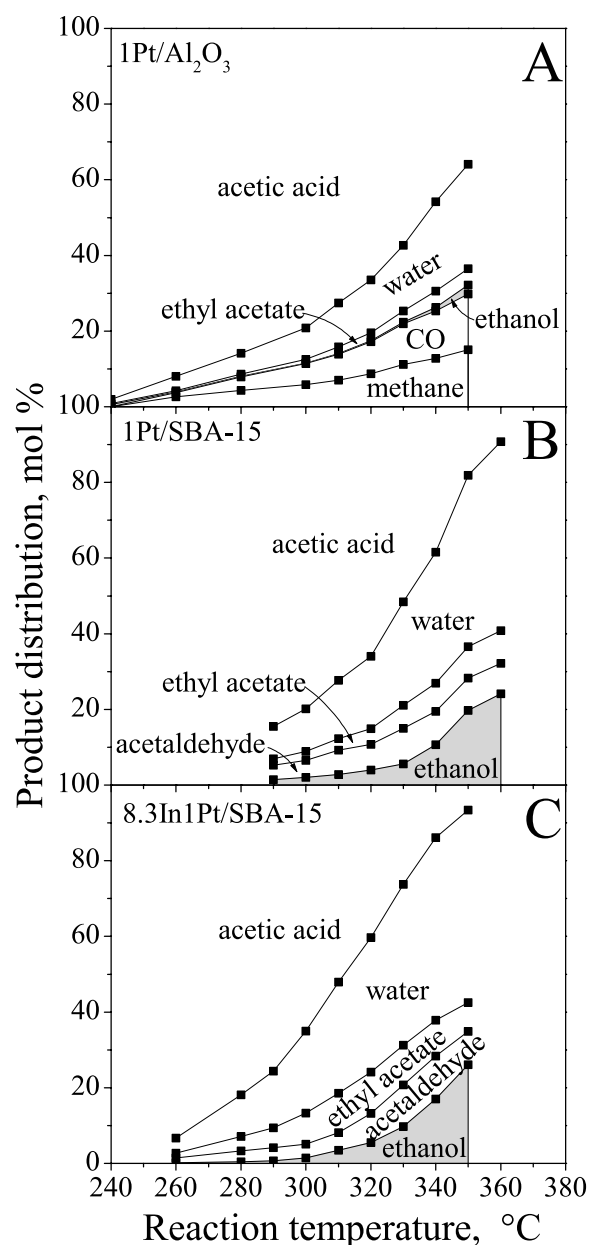
Figure 2: Product distribution of AA hydroconversion as a function of reaction temperature over monometallic (a) Pt/Al_2O_3, (b) Pt/SBA-15 and bimetallic (c) InPt/SBA-15 catalysts at 21 bar total pressure and $1 \, g_{AA}/g_{cat.} \times$ h WHSV using stacked area graphs.

nickel concentration on SBA-15 silica than on alumina or (see later) using the same amount of precursor and reduced under identical conditions (at 450°C for an hour) is in line with the drastically different AA hydroconversion activity (Fig. 3a and 2b). Indium admission can completely eliminate the hydrodecarbonylation activity as found earlier [10,13], and can efficiently enhance the ethanol selectivity and yield over the silica supported Ni catalysts

(Fig. 3c), too. The selectivity change is very pronounced (bimetallic active surface appears instead of monometallic one, *vide infra*) while the influence on the activity is not observable. Main product ethanol and reactant acid can form ethyl acetate presumably in a non-catalytic route. The yield of intermediate product acetaldehyde and by-product ethyl acetate can be suppressed at more severe reaction conditions. At higher reaction temperatures, the ester yield
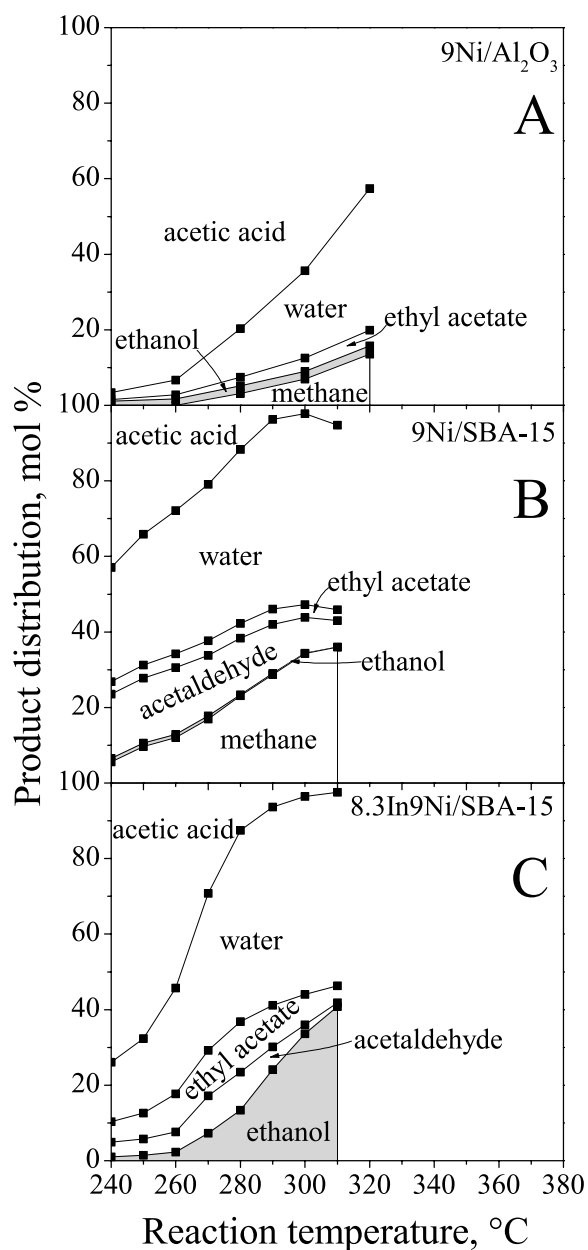
Figure 3: Product distribution of AA hydroconversion as a function of reaction temperature over monometallic nickel on (a) Al$_2$O$_3$, (b) SBA-15 and bimetallic nickel-indium on (c) SBA-15 catalysts at 21 bar total pressure and 1 g$_{AA}$/g$_{cat.}$× h WHSV using stacked area graphs.

decreases indicating that the activation energy of ester hydrogenolysis is higher than that of ester formation.

Comparing the monometallic Cu and the bimetallic InCu catalyst supported on the highly ordered SBA-15 of a distinct pore diameter (6 nm) or fumed silica CAB-O-SIL of a wide mesopore distribution, very important differences could not be observed, although silica supports are of very different textures (comparative figures are not presented). Metallic nickel particles are formed in hydrogen flow at

much higher reduction temperature than copper. The support may influence the reduction of the Ni precursor hence SBA-15 supported Ni (Fig. 3b) is more active than Ni/CAB-O-SIL (Fig. 4A). Probably the highly ordered SBA-15 support with limited microporosity can give higher and more homogenous nickel surface inside the regular channels of very narrow mesopore distribution during the formation of the catalytically active nickel particles. This difference is eliminated by indium admission when a totally different bimetallic active surface should be formed (Figs. 3c and 4B). Regarding the hydrodeoxygenating activity over monometallic, catalysts of originally lower activity can be increased much more efficiently with indium admission as observed already in numerous former studies [12]. Among non-precious metals, indium doped nickel seems to be much more efficient as noble metal hydrodeoxygenating catalyst preferred in the literature. Promising to focus only on Ni-In catalysts as the properties can be further improved (e.g. applying more suitable supports, sophisticated preparation techniques, etc.).

The lowest activity can be observed for both the mono- and bimetallic catalysts by applying a microporous silica gel support (Sylobead) without any significant meso- or macroporosity (see Fig. 4a and 4b). Indium admission improves only the selectivity by mechanism change without any observable activity increase (Fig. 4b). It seems probable that mass transport may control the reaction rate in this microporous silica. An activity increase can only be attained using bimodal silicas with adjustable mesopore diameters [19].

For easier comparison, activities and ethanol selectivities are plotted in Fig. 5 for different metals and supports together. Upon varying the supports, catalytic behavior is highly influenced and the effects cannot be simply correlated with the specific surface areas (e.g. alumina and CAB-O-SIL silica have exactly identical BET surfaces). Mesoporous (amorphous or highly ordered) silicas seem to be more efficient supports than alumina. The commercial Adkins catalyst (72 wt.% CuCr$_2$O$_4$ and 28 wt.% CuO) is less active in ethanol formation than copper on SBA-15 silica support (Figs. 5d and 5a). Mesoporous silicas loaded with the novel InNi composite exceed the conventional catalyst even more (Figs. 5d and 5c).

Over the indium modified nickel catalysts, the rate of AA hydroconversion increases linearly at low conversions with the hydrogen partial pressure (e.g., for Sylobead, Fig. 6) while the hydrogenation activity is suppressed by increasing AA pressures (by increased AA coverage). The found activity dependence on the reactant partial pressures can be in line with the Langmuir-Hinshelwood type kinetics and mechanism.
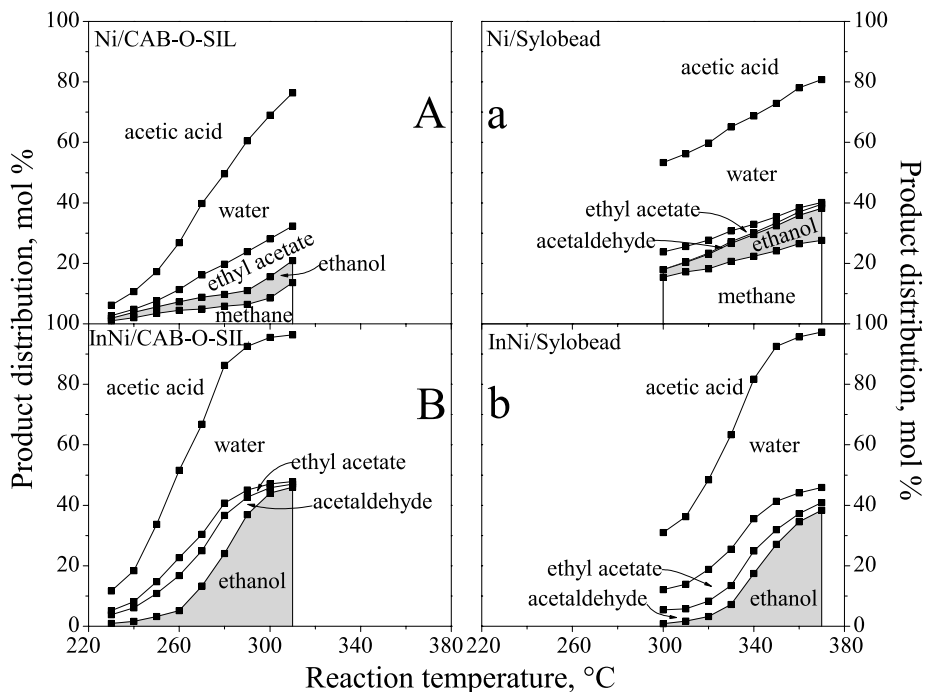
Figure 4: Stacked area graphs of product distribution of AA hydroconversion as a function of the reaction temperature at 21 bar and 1 g_{AA}·/ $g_{cat.}$×h WHSV over In-free (A, a) and In-doped (B, b) silica (A, B /CAB-O-SIL/), (a, b /Sylobead/) supported Ni-catalysts.
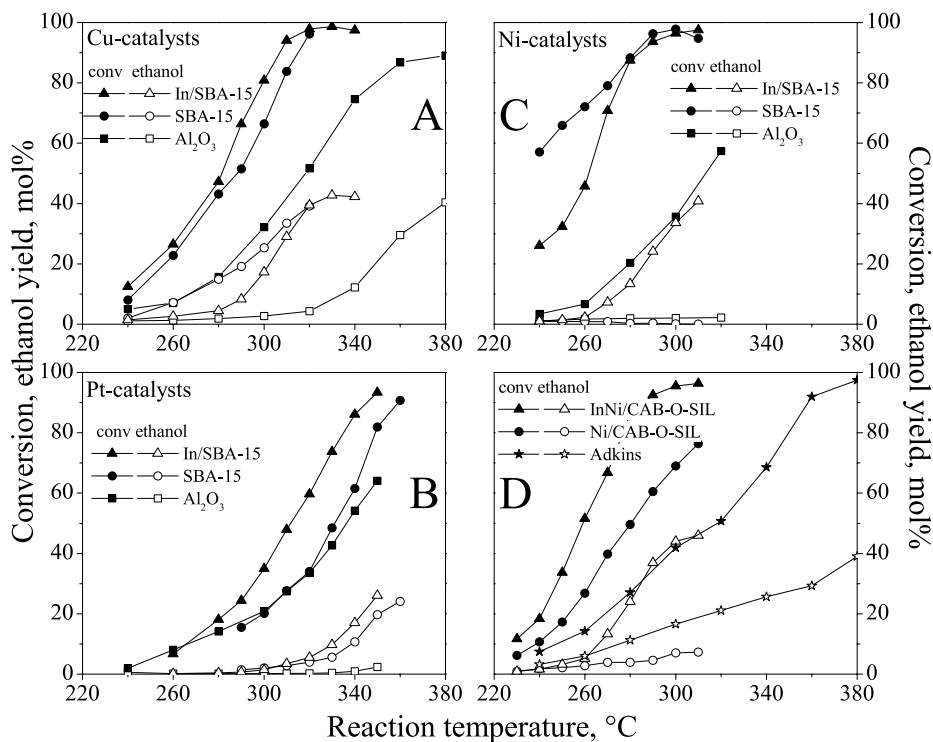

Figure 5: Comparison of conversion (solid) and ethanol yield (open) curves grouped as Cu-catalysts (A), Pt-catalysts (B), Ni-catalysts (C) and Ni/silica (CAB-O-SIL) together with Adkins catalysts (D).
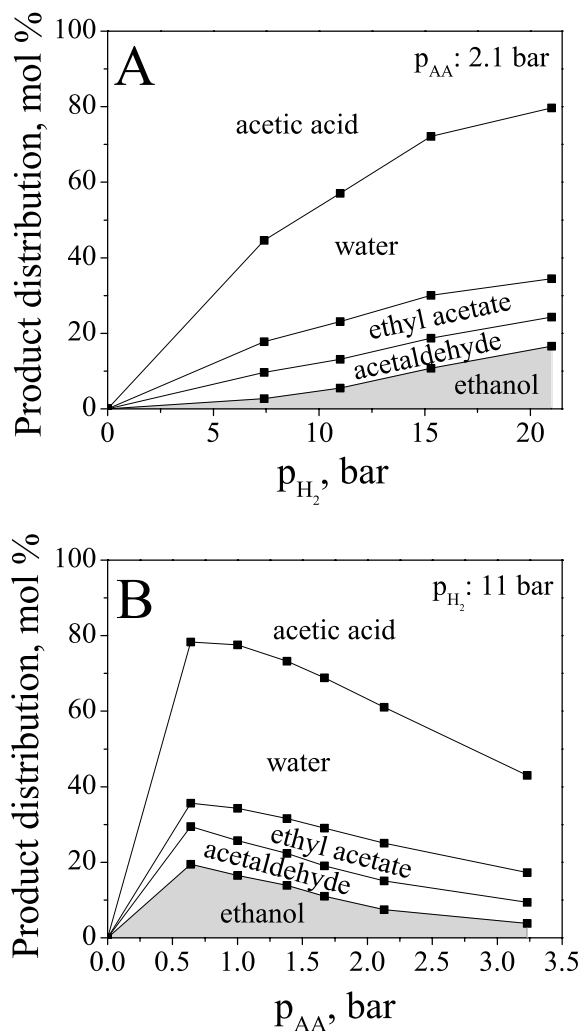
Figure 6: Stacked area graphs of AA hydroconversion as a function of hydrogen and acetic acid partial pressures at 340°C over NiIn/Sylobead catalyst.

As for the stability, hydroconversion activity gradually decreases with time on stream over monometallic catalysts (Ni and Pt) on which side reactions, e.g. hydrodecarbonylation can be a significant reaction route as shown above and in former papers, e.g. in [10]. In the case of catalysts where hydrodecarbonylation is the dominant reaction route, carbon deposition was probably the reason of activity decrease. Complete inhibition of C–C bond cleavage upon indium admission results in permanent activity level and selectivity checked for more than fifty hours operations. After measurements under varying conditions, results for doped catalysts were also reproducible (Figs. 1c, 2c, 3c, 4b, 4b).

After having reviewed the most significant catalytic properties of mono- and bimetallic contacts, some structural characteristics are to be surveyed. Different

textural features of the applied supports for Ni and Ni_2In particles are reflected by the nitrogen adsorption and desorption isotherms shown in Fig. 7. The isotherms of Sylobead sample (∇, $\blacktriangledown$) loaded with Ni or Ni_2In particles (*vide infra*) are of typical Type I indicating a clearly microporous adsorbent without any detectable mesoporosity. Without metals, approx. double the adsorbed nitrogen amount and consequently approx. double BET value (563 m^2 g^{-1}) were determined (this curve is not shown). Most of metal particles are present in micropores; thus, hardly accessible due to high diffusion resistance. Ad- and desorption isotherms of Ni and Ni_2In containing samples are also practically overlapping for SBA-15 support.

In the case of the mesoporous silica having regular, well ordered, uniform pore structure, all isotherms of the measured triad are shown in Fig. 7. SBA-15 isotherms are of the form well known in the literature (as type IV with H2 hysteresis loop). The mean mesopore diameter in all the three samples is approx. the same (6 nm). Inserting nickel particles results in blocking of significant fractions of mesopores, thus decreasing the accessible mesopore surface. Appearance of the second, guest metal indium does not change the adsorption properties. It enhances, most probably, only the length of cylindrical metal particles in the channels as supported by TEM (see later).

CAB-O-SIL M-5 fumed silica seems to be particular. The isotherms of all the three derivatives are overlapping. The Ni_2In loaded sample is the only one shown in Fig. 7 (the situation is the same as for alumina which has similar specific surface are). The mono- or bimetal particles do not influence the texture. The agglomerates of extremely small silica particles are forming pores in a wide range between 10 and 50 nm, i.e., dominantly in the mesopore range.

Alumina has a much narrower pore size distribution, around 8 nm. Alumina contains mesopores of similar sizes as SBA-15; however, this pore system is three-dimensional, excluding the disadvantage of pore blocking of SBA-15.

By metal loading, a significant loss of supporting surface was observed for Sylobead (not shown) and SBA-15 (Fig. 7). Applying SBA-15, any improvement of the conventional incipient wetness capillary impregnation method in the near future to avoid formation of metal plugs in the parallel channels can result in much more active catalysts.

Formation of active metallic phases on the three different silicas used in this study can be followed in Fig. 8 using HT-XRD technique. NiO ($\bullet$) formed during calcination of impregnated Ni-acetate can be fully reduced to nickel up to 450°C (the routine pretreatment
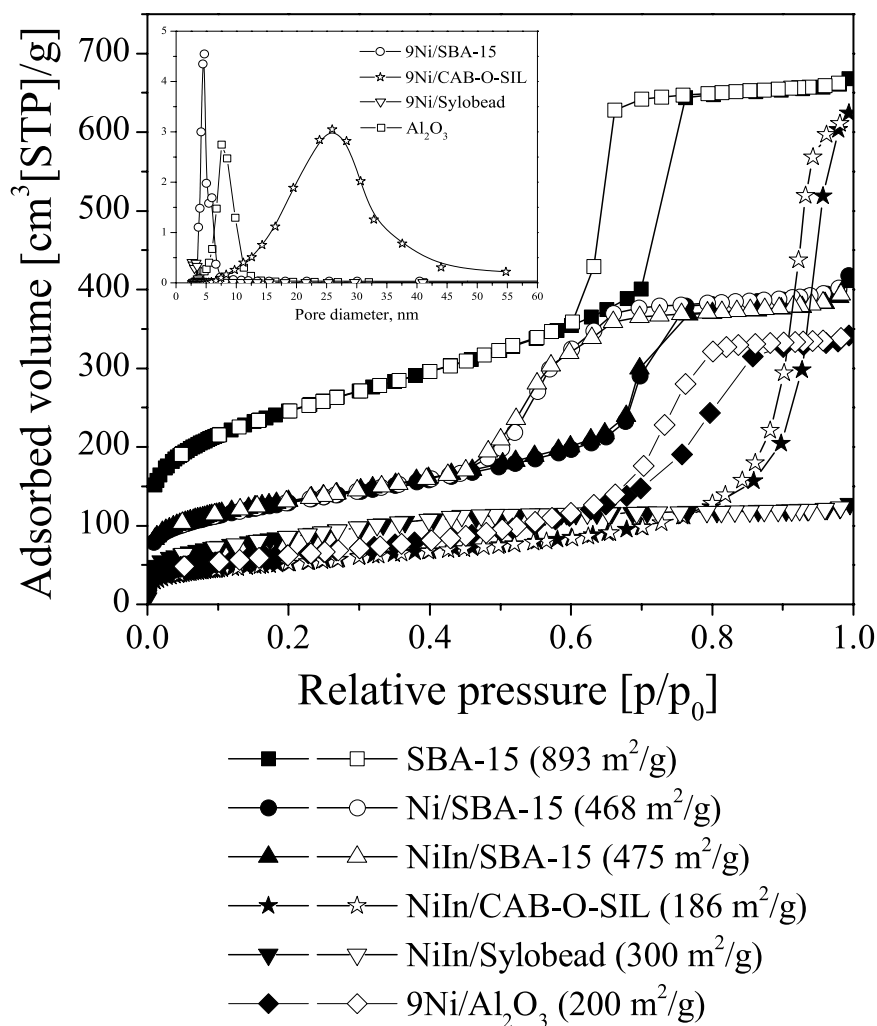
Figure 7: Adsorption and desorption isotherms of nitrogen at -196°C of unloaded, Ni loaded SBA-15, alumina and Ni+In loaded SBA-15, Sylobead and CAB-O-SIL.

temperature before reaction) in all silica supports (Fig. 8 diffractograms a and b) in contrast with alumina [10]. HT-XRD measurements were carried out in H_2 flow with linearly increasing the temperature to values shown in Fig. 8 then keeping constant for 30 min. The time was sufficient for total reduction of investigated samples. Ni^0 nanoparticles particles (*) formed in Sylobead having average size of 7 nm with no change in the size at elevated temperature. In SBA-15, the particle size of Ni is 21 nm estimated using the Scherrer equation which means, presumably, that in cylindrical channels of 6 nm diameter, Ni prisms are formed instead of spheres because of steric constraint. In CAB-O-SIL M-5 fumed silica, 17 nm nickel particles were determined from the XRD patterns. These may be spherical (see later).

In the presence of indium, the formation of Ni-In alloy, specified as Ni_2In intermetallic compound particles (×), can form up to 450°C. In the case of CAB-O-SIL, formation of both Ni and Ni_2In phases can be observed simultaneously, i.e., Ni does not transform quantitatively to Ni_2In up to 650°C even in presence of liquid indium. This mesoporous silica of wider pores and pore distribution has the lowest diffusion resistance. Consequently, it enables fast transportation of metal atoms resulting in faster build up of metal ensembles with different phase composition (even pure Ni particles in presence of indium). However, from a catalytic point of view, it is satisfactory that the outer surface of the metal particle is covered with In atoms forming the desired phase composition as reflected by the identical product distributions shown in Figs. 3c and 4B.
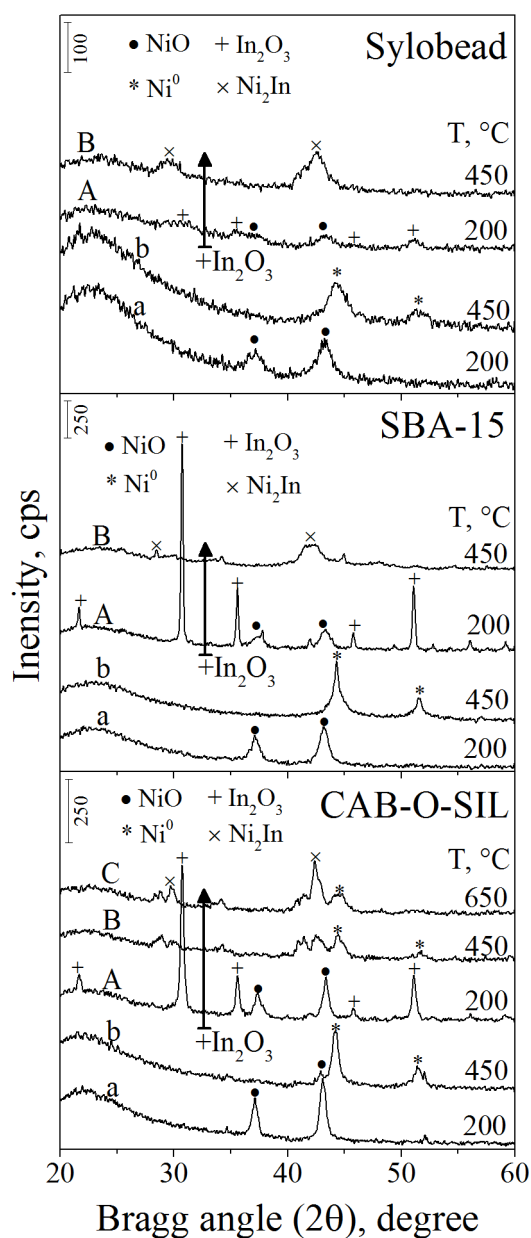
Figure 9: H$_2$-TPR of NiO particles supported on alumina and silicas.

Figure 8: The evolution of active metallic phases reflected by the selected HT-XRD patterns of indium free Ni/SiO$_2$ catalyst precursors (a, b) and of Ni/SiO$_2$ admixed with 10% In$_2$O$_3$ (A, B, C) reduced in H$_2$ flow step by step for 30 min at 200 (a, A), 450 (b, B) and 650°C (C).
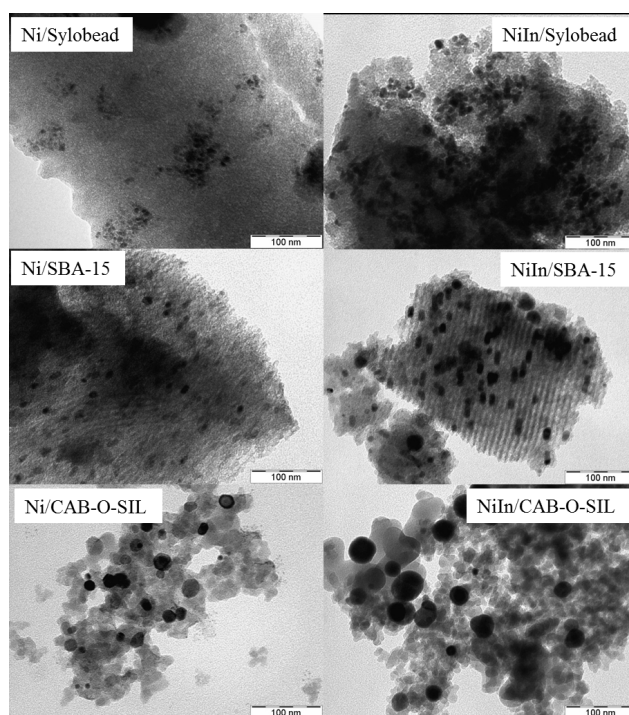
Figure 10: TEM images of the mono- and bi-metallic catalysts after treated in H$_2$ flow for 30 min at 450°C.

The significantly lower activity of alumina supported catalysts compared with different metal loaded SBA-15 samples can be attributed to lower degree of NiO reduction (Fig. 9). A stronger interaction is presumed between the support and NiO in the case of alumina than for silicas.

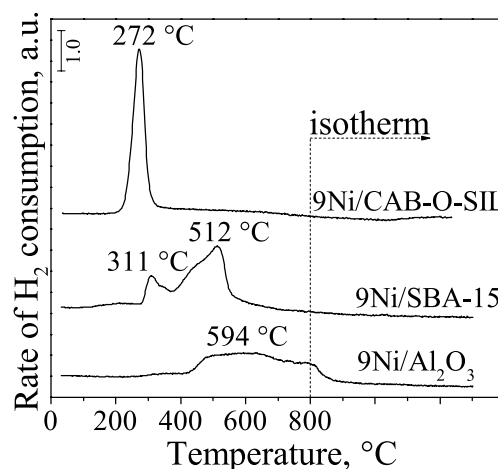In order to compare the metallic particle distribution over six different silica supported reduced hydrogenating catalysts (three monometallic, three bimetallic samples), TEM micrographs are presented in Fig. 10 at identical magnification (36000). Well-shaped metal nanoparticles of uniform distribution can be observed. In all the samples, Ni particle sizes agree well with the particle diameters obtained from XRD patterns. In SBA-15, the particles are located inside the 6 nm channels and shaped to these tubes. The bimetallic particles are significantly larger

(approx. two times). In SBA-15, only longer bimetallic particles could form because of steric constraints. In CAB-O-SIL, both the small silica and the metal particles have unhindered access; here the diffusional mass transfer resistance of reactants and products are presumably negligible.

4 Conclusion

Outstanding significance of proper support optimization for metal catalysts is demonstrated. Application of SBA-15 as a highly ordered mesoporous silica support instead of alumina drastically increased AA hydroconversion activity of Cu catalysts and the yield of selectively produced alcohol over Pt catalysts by changing the reaction pathway. The most active nickel catalysts do not enable the selective addition of hydrogen to carbon-oxygen bonds independently of supports. However, the support exchange from alumina to silica results in an extremely high increase of the activity. Indium doping can already completely eliminate the hydrodecarbonylation activity applying various silica supports as found in earlier studies. Since indium co-catalyst applied with nickel is extremely efficient in selective reduction of AA with hydrogen to ethanol, indium modification thus results in a fundamental change of the reaction mechanism on the active metallic surface using significantly different silica supports. Direct interaction between the metallic and silica surfaces was not observed. The efficiency of bimetallic Ni_2In particles is highly influenced by the texture of various silica supports. High surface area of mesoporous catalyst support can also provide high active metal surface. However, the unimodal microporous silica results in poor diffusion of reactants and products and consequently, low, supposing deeply diffusion controlled activity. Well-ordered mesoporous silica (SBA-15) has the highest support surface area, consequently attained the highest metallic surface and activity; however, the active metal particles are formed as plugs in the channel; consequently silica and metal surfaces are less accessible. Fumed silica (CAB-O-SIL) with the lowest specific surface area but the larger and easily accessible polimodal mesopores gives the same activity as the unimodal mesoporous SBA-15 due to the less diffusion resistance and the free access of metallic surface. Such bimetallic preparations are promising catalysts for the industry of fine chemicals. An improvement can be still attained by improved loading techniques of metals with high dispersion over silicas and by development on bimodal silicas with adjustable pore diameters.

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