Contents lists available at SciVerse ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Selective reduction of acetic acid to ethanol over novel Cu_2In/Al_2O_3 catalyst

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A R T I C L E I N F O

Article history: Received 4 March 2013 Received in revised form 30 April 2013 Accepted 31 May 2013 Available online xxx

Keywords: Acetic acid reduction Copper catalyst Indium co-catalyst Ethanol Ethyl acetate

ABSTRACT

Volatile fatty acids (VFAs) can be produced efficiently by simple thermochemical or biological biomass degradation. For the processing of these organic acids in hydrogen atmosphere, the consecutive reactions of acetic acid (AA) hydroconversion were studied in details looking for conditions of selective ethanol production over a novel and advantageous bimetallic composite applying indium as co-catalyst. The reactions were investigated in vapor phase at 240-380 °C, 7-21 bar hydrogen and 0.5-3.5 bar acetic acid partial pressures in a fixed bed flow-through reactor using supported copper catalysts. In₂O₃ admission can significantly increase AA hydroconversion activity of copper catalysts supported on various oxides and the yield of the produced ethanol. Efficient hydrogenating catalysts, containing finely dispersed metal particles were obtained by in situ reduction with H_2 at 450 °C. In the catalysts modified with In₂O₃ additive, formation of an intermetallic compound (Cu₂In) was strikingly observed resulting in a different, more advantageous catalytic behavior as of pure copper particles supported on different oxide supports. On comparing a commercial, conventionally used catalysts (Adkins: 72 wt% CuCr₂O₄ + 28 wt% CuO) with the bimetallic alumina supported composite (Cu_2In/Al_2O_3) the new catalyst proved to be much more active and selective for producing ethanol. A schematic representation of reactions involved in the hydroconversion of acetic acid was explored and verified. The activity dependence on the reactant partial pressures denotes rate-controlling surface reaction according to Langmuir-Hinshelwood mechanism. © 2013 Elsevier B.V. All rights reserved.

1. Introduction

A major 21st century goal of governments, academia and industry is the efficient and economic utilization of biomass resources for production of fuels and chemicals [1–6]. The key trend today is to move away from food crops to nonfood ones. For this transition, it is vital that low-cost processing technologies should be developed for conversion of low-cost biomass. The future success of "biorefineries" will require fundamental understanding of the types of processes best suited for converting the various biomassderived constituents into chemical moieties. Hence, the evolution of a broad range of conversion technologies including various catalytic processes is needed.

Direct and indirect methods are accessible for the production of bio-fuel from biomass. The indirect methods are based on Fischer–Tropsch (FT) technology. The direct methods improve the economy of the biomass-to-fuel conversion by preserving the possible highest fraction of C–C and C–H bonds in constituents of the organic biomass. Instead of the very simple, but seriously disadvantageous thermochemical routes (as pyrolysis), a novel way, a favorable biochemical destruction (branching from the biogas process: i.e., stopped before the slow methanogenesis step proceeding the rapid anaerobic acidogenic digestion stage) is suggested utilizing volatile fatty acids (VFAs) for production of biofuels and biochemicals [7–9]. It should be remarked that species of anaerobic bacteria, including members of the genus Clostridium, can convert directly sugar building units to AA from less expensive feeds, without converting to conventional ethanol as an intermediate and the formation of which is accompanied by CO₂ evolution. The overall chemical reaction conducted by these bacteria may be represented as:

 $C_6H_{12}O_6 \rightarrow 3 CH_3COOH$

The microorganisms anaerobically digest the biomass and convert it into mixture of volatile (short-chain) carboxylic acids (VFAs).







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⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.apcata.2013.05.042



Fig. 1. A schematic figure of the high-pressure fixed bed flow reactor system.

The carbon atom of carboxylic group is in a relatively high oxidation state. Removal of oxygen atoms by catalytic hydrogenation is extensively applied in industry. Catalysts like copper or nickel are promoted e.g., by chromium or molybdenum. Recently, we discovered novel highly efficient supported bimetallic catalysts, which are more active and selective in the hydrodeoxygenation (HDO) of octanoic acid to octanol at moderate pressure and temperature than conventional contacts [10-13]. Proper catalysts contain indium as co-catalyst and another metal of high hydrogenation activity, such as, copper or nickel, on various supports. Appearance of Cu₂In or Ni₂In intermetallic compounds as detectable phases result in significant increase of desired hydrogenation activity, i.e., the stepwise hydrogenation of carboxylic acids is stopped at alcohol formation and the hydrodecarbonylation of carboxylic acids (loss of one carbon atom) is inhibited. Moreover, in presence of mobile indium atoms or of indium containing nano clusters, monoor bimolecular alcohol dehydration capability of the support is suppressed.

The selective hydrogenation of short chain carboxylic acids to alcohol in a continuous flow system working in vapor phase under mild conditions seems to be still a problematic step. Only a few studies of such reactions have been carried out. The patent literature describes numerous catalysts for acetic acid hydrogenation comprising of one or more noble metals of Group VIII dispersed on Group III or IV metal oxides. Rachmady and Vannice published at the beginning of this century a series of papers [14–18] related to platinum catalysts supported on TiO₂, SiO₂, Al₂O₃ and Fe₂O₃ and the results are compared with that obtained without support [14]. Acetic acid was the model to test the carboxylic acid adsorption and its conversion kinetics because of molecular simplicity and wide range commercial application. Decarbonylation and decomposition reactions dominated on Pt powder, Pt/SiO₂ and Pt/Al₂O₃ similarly to Ni/Al₂O₃ catalysts shown in our recent studies [19,20]. Pt/Fe₂O₃ working at much higher temperature has particularly high selectivity for formation of acetaldehyde, i.e., to the less reduced intermediate. Pt/TiO₂ catalysts were the most active and selective in acetic acid hydrogenation to ethanol [14]. It has been strongly evidenced that both metal (Pt) and oxide support are involved in conversions. Thus, the interaction of acetic acid with the oxide support plays a major role in determining the hydroconversion kinetics and the principal role of Pt in this case is to provide mobile, activated hydrogen atoms. In present work, various supports are also

tested however, the catalytic properties were found to be controlled principally by modification of the metallic phases.

Recently, the highly active Ni₂In/Al₂O₃ composite catalyst has been already tested on comparing the hydroconversion of octanoic (C8) and acetic (C2) acid under similar conditions. The difference of the length of alkyl-chains resulted in significantly different product distributions [21]. The reduction of NiO formed from supported nickel salt can be observed near below 450 °C, at the routine temperature of pretreatment and became complete only far above 450 °C depending on the loading [19]. This means that NiO and active metallic phases are present and their partition may influence the catalytic properties. Therefore, a detailed study seemed to be promising with the less active Cu/Al₂O₃ catalysts, which are completely reduced at the routine temperature of pretreatment being near to the reaction temperature. Because of practical reasons, AA hydroconversion to ethanol was studied over catalysts containing copper in metallic form.

2. Experimental

The catalytic hydrogenation of AA (96%, from Reanal) (model compound with the shortest aliphatic chain) was studied in a high-pressure fixed bed flow-through reactor at 21 bar total pressure, 240-380 °C, 7-21 bar hydrogen and 0.5-3.5 bar acetic acid partial pressures, i.e., under similar conditions as in Refs. [10,21]. The Fischer esterification of AA and ethanol (absolute, from Molar Chemical) and ethylacetate (>99%, from Merck) hydrogenation were also studied over the investigated catalyst samples to follow the secondary reactions. The experimental setup is illustrated in Fig. 1. In general, the catalysts were pretreated in hydrogen flow in situ in the reactor at 450 °C and 21 bar for 1 h in order to obtain active metallic surfaces for carboxylic acid reduction. The reaction was allowed to run one hour at each condition to attain steady state. Before sampling, the effluent during the second hour was collected, depressurized and cooled to room temperature. The liquid product mixture at ambient conditions was analyzed by gas chromatograph (Shimadzu 2010) for AA products equipped with a Restek Rt-U-BOND capillary column, and a flame ionization detector. The gaseous reactor effluent was analyzed for CO₂, CO, CH₄ and light hydrocarbons using an on-line gas chromatograph (HP-5890) having Carboxen 1006 PLOT capillary column and thermal conductivity detector (TCD). The results are represented as stacked area

Table 1	1
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Specific surface areas of the supports and the particle diameters of copper formed on the catalysts after reductive pretreatment.

	Al ₂ O ₃ (Akzo)	TiO ₂ (Degussa)	TiO ₂ (Aldrich)	SiO ₂ (Cabot)	SiO ₂ (Grace)	SiO ₂ (Sylobead)
BET (m ² /g)	199	55	12	200	291	563
ØCu ⁰ (nm)	20	43	123	34	30	165

graphs where the distance between two neighboring curves represents the concentration of a given product at a given temperature in mole percent.

Activated γ -Al₂O₃ (Ketjen CK 300, Akzo-Chemie, BET: 199 m²/g), SiO₂ (CAB-O-SIL M-5, Cabot Corp., BET: 200 m²/g; Grace, BET: 291 m²/g; Grace Sylobead, BET: 563 m²/g) and TiO₂ (Aeroxide P25, Degussa, BET: 55 m²/g (anatase); Aldrich, BET: 12 m²/g (rutile)), were impregnated with NH₄OH solution (Reanal) of Cu (acetate)₂ (Aldrich), dried, and calcined at 550 °C in air stream. The sample designation, e.g., 9 Cu/Al₂O₃ formula represents a catalyst preparation containing 9 wt% Cu. For comparison, an Adkins catalyst (consisting of 72 wt% CuCr₂O₄ and 28 wt% CuO) was applied. Composite catalysts were prepared by adding indium(III) oxide (Aldrich) to the samples in various amounts and grinding the mixture in agate mortar.

X-ray patterns were recorded by a Philips PW 1810/1870 diffractometer with monochromatic Cu K_{α} radiation at elevated temperatures using a high-temperature XRD cell (HT–XRD). The

mean crystallite size of the copper particles was estimated by the Scherrer equation. Nitrogen physisorption measurements were carried out at -196 °C using Quantochrome Autosorb 1C instrument for determining the specific surface area. Specific surface area of the supports and particle diameters of copper formed after reductive pretreatment are collected in Table 1. Very similar surface and diameter values are obtained after loading.

3. Results and discussion

Ni₂In/Al₂O₃ catalyst was proven more active in both octanoic [10,11] and acetic acid hydroconversion [21] than Cu₂In/Al₂O₃ since the conversion and alcohol yield curves are shifted by 20–30 °C to higher temperatures for Cu₂In/Al₂O₃. The product distributions are similar with some small, however, not negligible differences for the two bimetallic catalysts. Aside from



Fig. 2. XRD patterns of 9 wt% Cu on (a) Al₂O₃ (Akzo-Chemie), (b) TiO₂ (Degussa), (c) TiO₂ (Aldrich), (d) SiO₂ (Cabot) and (e) SiO₂ (Grace) supports doped with 10 wt% of In₂O₃. In the case of (f) SiO₂ (Grace-Sylobead) InCl₃ is applied containing the same amount of indium. The diffractograms were recorded at the indicated temperatures after 30 min treatment at each temperature in H₂ flow.



Fig. 3. AA hydroconversion over 9 wt% Cu on (a) Al₂O₃ (Akzo-Chemie), (b) TiO₂ (Degussa), (c) TiO₂ (Aldrich), (d) SiO₂ (Cabot), (e) SiO₂ (Grace) and (f) SiO₂ (Grace-Sylobead) catalysts characterized by the distribution of the main products between 240 and 380 °C at 21 bar total pressure, represented by stacked area graphs. Each sample was admixed with 10 wt% of In₂O₃ before the reductive pretreatment with exception (f) SiO₂ (Grace-Sylobead) applied InCl₃ containing the same amount of indium. The WHSV of AA was $1.0 h^{-1}$. Partial pressures of AA and H₂ were 2.1 and 18.9 bar.

the different hydrogenation activity of the main metals (Ni or Cu) similarity of catalytically active alloy phases seems probable (Ni₂In and Cu₂In).

X-ray diffraction patterns evidence that in the novel indium containing composite catalysts, activated at 450 °C in H₂ flow before the reaction, In₂O₃ is reduced (excepted when the support is Aldrich TiO₂ shown in Fig. 2c) and liquid indium metal should be present under the reaction conditions being the reduction temperature far above the melting point of indium (156.4 °C). Reduced copper reacts immediately with indium and Cu₂In particles are formed as shown in Fig. 2. Cu nanoparticles appear on various supports when copper oxide is fully reduced up to 350 °C, and the small copper particles do not change up to 650 °C without indium doping (not shown here). Reduction of admixed In_2O_3 (or $InCl_3$) can be observed at much higher temperature, i.e., between 350 and 450 °C (see Fig. 2) detected by disappearance of In_2O_3 diffraction lines (+) and appearance of the Cu₂In phase in the diffractogramms. This transformation is completed up to 450 °C. Mainly Cu₂In phase, but Cu₄In and Cu₉In₄ phases may also be present, however, in much lower concentration. These phases were identified on ICDD database [22], the corresponding ICDD numbers are Cu₂In: 42-1475, Cu₄In: 42-1477 and Cu₉In₄: 42-1476. 10 wt % In₂O₃ admitted to 9 wt % copper-containing samples corresponds to the Cu₂In stochiometric composition characteristic for the new intermetallic compound detected on all the samples excepted when a low surface area support as Aldrich TiO₂ was applied (Fig. 2c). On this support, In₂O₃ cannot be reduced at all. Exceptionally indium admission was also carried out with InCl₃ impregnation into the 9Cu/SiO₂ (Grace Sylobead), because the mixture of the oxides composing the catalyst bed cannot be pressed to pellets without binder. Although the presence of InCl₃ phase being finely distributed cannot be detected in Fig. 2f, the reduction to metallic indium takes place under similar conditions as for In₂O₃ resulting in similar nice signals for formation the Cu₂In phase as in Fig. 2d or e.

The catalytic activity and selectivity of the various supported catalyst preparations are characterized by the product distribution as a function of reaction temperature in stacked area graphs (see Fig. 3). Main valuable products formed from acetic acid are acetaldehyde, ethanol and ethyl acetate. As by-products, acetone, carbon dioxide (only when the samples do not contain copper) and water (over each catalyst) were determined as well. All the supports are of low activity for undesired catalytic reactions (e.g., Fig. 4a). Reduction of In₂O₃ results in liquid indium metal on the surface of support the catalytic activity of which is essentially lower and the selectivity poorer than for the composite catalyst containing both indium and copper (Fig. 4b and c). The activity and selectivity of supported Cu can be improved by In₂O₃ addition (Fig. 5). After reduction, the appearance of Cu₂In phase is detectable beside copper and excess indium. It seems thus likely that this new phase should probably be responsible for the drastic changes of catalytic properties. Similar effects of indium addition could be observed for supported nickel, i.e., the activity for C-O and C=O hydrogenation



Fig. 4. AA hydroconversion over (a) Al_2O_3 , (b) $Al_2O_3 + 10\%$ In_2O_3 and (c) $9Cu/Al_2O_3$ catalysts characterized by the distribution of the main products, represented by stacked area graphs. Reaction conditions as in Fig. 3.

increased while for undesired hydrogenolysis of C–C bond became negligible.

The Cu₂In active phase on Al₂O₃ and SiO₂ supports of 200-300 m²/g specific surface (Fig. 3a, d, e) demonstrate practically equal activities and very similar selectivities independently of the supports in a wide reaction temperature range (280–380 °C). Specific surface area of the supports does not play any role in activity the Cu₂In surface should be decisive. Cu₂In on Aldrich TiO₂ is not detectable and on the highly microporous Grace-Sylobead SiO₂ can be formed the largest metal crystals with relatively low surface in the meso- or macro-pores of support (Table 1 (size of the monoand bimetallic particles was found to be nearly the same in many cases)). This conclusion is supported by observations for Cu-zeolites [23]. On applying Cu-zeolites as catalyst precursors containing copper cations completely dispersed, the reduction results in complete destruction of zeolite structure, i.e., in a similarly low surface support (shown in Fig. 3c), however, the active metal appears in high dispersion and thus of high activity [12,24].

Grace–Sylobead SiO₂ support (BET: 563 m²/g) is a highly microporous material of high specific surface and the precursors cannot penetrate into the micropores to form metal nanoparticles during reduction. Therefore, copper atoms form big metal particles (165 nm) with very low active surface, which is reflected in the extremely low activity. Near this disadvantageous situation, the exceptional application of different indium source (InCl₃) further handicaps the catalyst creating a much lower activity than with the pure, monometallic Cu-catalyst. Although reduction of InCl₃ and the formation of Cu₂In particles seem to be undisturbed below the sublimation temperature of the salt (see Fig. 2f) something is wrong from catalytic point of view. To prove this effect, another but highly active Cu loaded silica gel, Grace (BET: 291 m²/g) was tested without In_2O_3 as indium source using InCl₃. Instead of the nice hydroconversion shown in Fig. 3e a similar low activity was observed than we can see in Fig. 3f. Instead of InCl₃ using the likewise water soluble In(NO₃) completely same results can be obtained than with In_2O_3 .

Regarding the comparison of the applied support of appropriate morphology in Fig. 3a, b, d, e, the chemical composition of the supports do not seem to be important, because the properties of the supported bimetallic particles are dominant in the acetic acid hydroconversion. Consequently the further studies can be carried out using only the activated γ -Al₂O₃ (Ketjen CK 300, Akzo-Chemie, BET: 199 m²/g), commercial support.

The metal free alumina is able to ketonize acetic acid at higher reaction temperature (Fig. 4a), however, this capability can be partly suppressed by indium admission (Fig. 4b) and completely eliminated by loading copper (see Fig. 4c). In hydrogen, copper on alumina enables attack only of the C–O bond (see Fig. 4) contrary to nickel [10,21] where the hydrogenolysis of C–C bond is dominant resulting in the hydrodecarbonylation of carboxylic acids. Indium doping can block this reaction route during hydrodeoxyganation over more active hydrogenating metals (e.g., Pt or Ni) resulting in drastic change of the product distribution, instead of chain shortening the step by step reduction toward alcohol dominates. Since only the last reaction route is characteristic for copper catalysts indium admission changes only the product distribution in this reaction way and increases the reaction rates (compare Fig. 4c and Fig. 3a. as well as Fig. 5).

The influences of indium doping can be seen in details in Fig. 5 and a comparison can be found with a commercial Adkins catalyst. $Cu_2In/alumina$ catalyst is significantly more active than monometallic alumina supported Cu or chromium containing industrial catalysts (see Fig. 5a) and the changes of the selectivity are different. In low temperature range, the high activity of the composite catalyst is ascertained by the high yield of acetaldehyde (see Fig. 5b) being the intermediate product of alcohol formation. At higher reaction temperature, the indium doped sample gives the highest yield of the most desired product ethanol (see Fig. 5c). On comparing Figs. 4c and 5d ethyl acetate is formed and is efficiently hydrogenated to ethanol.

The nascent ethanol reacts easily with the reactant acetic acid in the Fischer esterification reaction even without catalyst contrary to longer carboxylic acids (e.g., octanoic acid) [11] (see Fig. 6). The boiling points of these two main products (ethanol and its ester) are almost the same thus their separation is rather expensive. Using the product mixture as fuel the separation is not necessary. In order to obtain pure ethanol or ethyl acetate the reaction mechanism is to be explored and reaction conditions optimized accordingly. The acidic sites of the alumina support can effectively catalyze ester formation. Ethyl acetate yield is lower when SiO₂ is used as support. However, this kind of advantage of silica is masked in presence of metals active in ester hydrogenation. The yield of ethyl acetate is restricted by the presence of hydrogenating metals: similarly by indium or copper and more effectively by Cu₂In alloy. The genesis of the ester cannot be prevented and its hydrogenolysis



Fig. 5. Conversion (a) and the yield of acetaldehyde (b), ethanol (c) and ethyl acetate (d) over Adkins, 9Cu/Al₂O₃ and 9Cu/Al₂O₃ + 10 wt% In₂O₃ catalysts in AA hydroconversion as a function of reaction temperature. Reaction conditions as in Fig. 3.

can be catalyzed by all the metals applied although with different effectiveness. These differences are demonstrated in Fig. 7 for alumina supported indium, copper, and Cu₂In. The ethyl acetate hydrolysis over Cu₂In/alumina producing ethanol and acetic acid seems to be hardly detectable since acetic acid formed is immediately converted to ethanol. Thereafter diethyl ether and water are produced by dehydration of ethanol proceeding on alumina support. Ethanol can form via ester hydrolysis catalyzed by alumina (as shown in Fig. 6 for the reverse reaction) and by multistep hydrogenolysis of ester. Former way results in AA formation hardly observable on the composite catalyst (Fig. 7c) which indicates that hydrogenolysis activity surpasses the acidic activity of the support. Ethanol formation is higher for supported Cu than for supported In pointing to higher hydrogenolysis activity of Cu than that of In. Thus a sequence of increasing activity In < Cu < Cu₂In seems probable.

Fig. 8 shows the conversion curves determined on the monoand the bimetallic catalysts at 320 °C, which demonstrate the



Fig. 6. Ethyl acetate yield in the reaction of acetic acid:ethanol (1:1 mol) mixture as a function of reaction temperature. Reaction conditions as in Fig. 3.

complexity of the reaction network. On monometallic catalyst, acetaldehyde can hardly be detected while on bimetallic sample acetaldehyde seems to be a primary product and ethanol a secondary one. Acetaldehyde as an intermediate has a maximum concentration as a function of space time (Fig. 8b). Ester formation rate increases both with aldehyde concentration and ethanol concentration hence both Tishchenko and Fischer reactions seem probable (Scheme 1). The kinetics results would be captured as rate equations in which the Arrhenius parameters (normalized pre-exponential factor, apparent activation energy) could be compared with those obtained in other laboratories. Fig. 9 demonstrates different activities of the investigated alumina supported mono- and bimetallic copper catalysts obtained from initial slopes of conversion curves similar as shown in Fig. 8. Formation of the indium containing bimetallic catalytically active metal phase results in approx. 1.5 times higher apparent activation energy (108 kJ/mol instead of 70 kJ/mol determined on the monometallic copper surface) reflecting a new quality of the active alloyed surface resulting in a different reaction mechanism. A similarly 1.5 times higher pre-exponential factor reflects a high increase in the reaction rate of the step-by-step reduction of acetic acid to ethanol. Although in this paper the apparent activation energy was determined only for the overall hydrogenation reaction the values obtained are comparable with Ref. [14] for the monometallic Pt catalyst supported by titania.

Hydroconversion of acetic acid to ethanol and ethyl acetate increases roughly linearly with increasing hydrogen partial pressure over $Cu_2In/alumina$ composite catalyst (Fig. 10). Acetaldehyde selectivity is high at low hydrogen partial pressures (where the conversions are low). The hydrogenation activity is suppressed by increased AA partial pressures (i.e., at higher AA coverages) (see Fig. 11). The found concentration changes are in accordance with earlier conclusions. As for the activity dependence on the reactant partial pressures, it is in line with the Langmuir–Hinshelwood kinetics and mechanism.

Above observations concerning the reaction routes in acetic acid hydroprocessing are summarized in Scheme 1.



Fig. 7. Stacked area graphs of ethyl acetate hydrogenolysis over (a) $Al_2O_3 + 10$ wt% In_2O_3 , (b) $9Cu/Al_2O_3$ and (c) $9Cu/Al_2O_3 + 10$ wt% In_2O_3 catalysts as a function of reaction temperature at 21 bar total pressure. WHSV of ethyl acetate was $1 h^{-1}$. The partial pressure of ethyl acetate and H_2 were 2.1 and 18.9 bar.

Comparison of the octanoic acid and the acetic acid hydroconversions over $9Cu/Al_2O_3 + 10\% In_2O_3$ catalyst significant differences (different by-products), but important similarities can also be observed (cf. Fig. 3a and Fig. 4d in Ref. [11]). In the case of octanoic acid, formed alcohol is dehydrated to ether and octene, while in the case of acetic acid intermediate aldehyde can be detected in much higher concentration, ether yield is much less, ethylene or ethane is not formed at all and ester formation is significant. However, the courses of main transformations, i.e., the selective hydrogenation of carboxylic acids to alcohols are very similar. The conversions are practically the same at the same temperature when the molar feed rates of different carboxylic acids are equal. It means that the reactivity of carboxylic group hardly depends on the length of alkyl chains.

All the reactions responsible for the formation of products are shown in Scheme 1. Acetic acid can be hydroconverted first to acetaldehyde and then to ethanol (reactions 1 and 2). Depending on the reaction conditions, fractions of unconverted reactant acetic acid and the product ethanol can form ethyl acetate according to the Fischer esterification mechanism (reaction 3). Ethyl acetate could however be formed directly from



Fig. 8. Stacked area graphs of AA hydroconversion over (a) $9Cu/Al_2O_3$ and (b) $9Cu/Al_2O_3 + 10$ wt% In_2O_3 catalysts as a function of space time at 320 °C and 21 bar total pressure.

the intermediate acetaldehyde in the Tishchenko reaction [25] (reaction 4). Ethyl acetate can be hydrogenated directly to two ethanol molecules most efficiently on the composite catalyst (reaction 5). Monomolecular ethanol dehydration to ethylene has not been detected under the reaction conditions applied. Diethyl-ether can be formed in bimolecular dehydration at higher ethanol coverage (reaction 6). From acetic acid after AA–anhydride formation decarboxylation results in formation of acetone and carbon dioxide (reaction 7) but this reaction is characteristic only for some kind of supports at high reaction temperature.



Scheme 1. Schematic diagram of the reactions of AA hydroconversion on the basis of detected products.



Fig. 9. Comparison of the reaction rates over In-free and In doped 9Cu/Al₂O₃ catalysts in Arrhenius plots for the hydroconversion of acetic acid related for the catalyst mass at 21 bar total pressure.



Fig. 10. Stacked area graph of AA/H₂/He hydroconversion over 9Cu/Al₂O₃ + 10% In₂O₃ catalysts as a function of H₂ partial pressure at 320 °C and 21 bar total pressure. WHSV of AA was 1.0 h⁻¹. Constant partial pressure of AA was 2.1 bar. The H₂ partial pressure was changed by changing the H₂/He ratio.



Fig. 11. Stacked area graph of AA/H₂/He hydroconversion over 9Cu/Al₂O₃ + 10 wt% In₂O₃ catalysts as a function of AA partial pressure at 320 °C and 21 bar total pressure. WHSV of AA was 1.0 h⁻¹. Constant partial pressure of H₂ was 11.0 bar. The AA partial pressure was changed by changing the AA/He ratio.

4. Conclusions

Indium doping has been found to be efficient in the reduction of acetic acid with hydrogen to ethyl alcohol. Hydroconversion of acetic acid over alumina or silica supported Cu catalysts the ethanol yield can be increased significantly by indium metal formed by reduction of the admixed In₂O₃. This efficient promotion can be correlated with appearance of a new alloy phase or intermetallic compound (Cu₂In), which can also be generated perfectly from InCl₃ as precursor, but in this case the composite catalysts are practically inactive.

On comparing hydroconversion of octanoic (C8) and acetic (C2) acid over Cu_2In/Al_2O_3 composite catalyst under similar conditions the molar conversion rates are practically the same. It suggests that the molecular reduction rate of the carboxylic group to aldehyde group on the bimetallic surface is approximately equal for lighter carboxylic acid than for heavier one. However, the product compositions are different reflecting the differences in the succeeding reaction steps: After hydroconversion of octanoic acid ester formation cannot be detected, but alcohol dehydration is more significant, while for acetic acid ester formation is considerable and acetaldehyde intermedier formation can be detected.

The activity dependence on the reactant partial pressures denotes the rate-controlling surface reaction in terms of Langmuir–Hinshelwood kinetics.

Combining relatively simple pyrolytic (or biochemical) technologies resulting in production of acetic acid with the catalytic transformations shown, bioethanol and chemicals, such as ethyl acetate or acetaldehyde, can be obtained from biomass, e.g., from lignocellulosic raw material more efficiently over a novel supported bimetallic catalyst system.

Acknowledgments

The authors wish to express their appreciation to Mrs. Ágnes Farkas Wellisch for her technical assistance. Thanks is due to the Hungary-Slovakia Cross-border Co-operation Program (Project registration number: HUSK/1101/1.2.1/0318) for supporting this research.

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