

Short Communication

Acetic acid hydroconversion to ethanol over novel InNi/Al₂O₃ catalystsGyörgy Onyestyák^a, Szabolcs Harnos^{a,*}, Alexander Kaszonyi^b, Magdalena Štolcová^b, Dénes Kalló^a^a Institute of Materials and Environmental Chemistry, Research Centre for Natural Sciences, Hungarian Academy of Sciences, Pusztaszeri u. 59-67, Budapest, H-1025, Hungary^b Department of Organic Technology, Slovak University of Technology, Radlinského 9, Bratislava, SK-81237, Slovak Republic

ARTICLE INFO

Article history:

Received 30 May 2012

Received in revised form 17 July 2012

Accepted 20 July 2012

Available online 27 July 2012

Keywords:

Acetic acid reduction

Nickel catalyst

In₂O₃ doping

Ethanol

Ethyl acetate

ABSTRACT

Consecutive reduction of acetic acid (AA) to ethanol was studied looking for an advantageous catalyst for the processing of VFAs (volatile fatty acids) that can be produced by thermochemical or biological biomass degradation. A fixed bed flow-through reactor was applied with hydrogen stream at 21 bar total pressure in the temperature range of 220–380 °C. AA hydroconversion activity of the parent alumina supported Ni catalyst and the yield of selectively produced alcohol can be increased drastically by In₂O₃ addition. Efficient catalysts, containing finely dispersed metal particles were obtained by reduction with H₂ at 450 °C. In the catalysts modified with In₂O₃ additive formation of indium metal and/or an intermetallic compound (InNi₂) was observed resulting in a different catalytic behavior as for pure nickel particles supported on alumina. Appearance of metallic indium can direct the step by step catalytic reduction to ethanol formation inhibiting decarbonylation, decarboxylation, and additional dehydration. On comparing the commercial, conventionally used catalysts with the bimetallic alumina supported composite (InNi/Al₂O₃) the novel catalyst proved to be much more active and selective for producing ethanol.

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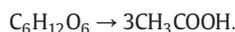
1. Introduction

Properties of practically used hydrogenation catalysts like copper or nickel are improved by various co-catalysts. Recently, we discovered highly efficient novel bimetallic supported catalysts which are exceedingly active and selective in the hydrodeoxygenation (HDO) of octanoic acid to octanol at moderate pressure and temperature [1]. The catalysts contained indium as co-catalyst and another metal of high hydrogenation activity, such as, copper or nickel, on various supports. Appearance of InCu₂ or InNi₂ phases, intermetallic compounds in the novel catalysts result in significant increase of desired hydrogenation activity, i.e., in stepwise hydrogenation of carboxylic acids (reactions 1, 2 in Scheme 1) stopped at alcohol formation and in inhibiting hydrodecarbonylation of carboxylic acids (loss of one carbon atom, reaction 7 in Scheme 1) and hydrogenolysis of hydrocarbon products (loss of further carbon atoms from longer hydrocarbons than methane) compared to mono-metallic forms. Moreover, in the presence of mobile indium atoms or of indium containing nano clusters, mono- or bimolecular alcohol dehydration capability of the support is suppressed selectively.

The production technologies of fuels and much in demand chemicals on various biomass platforms involve combinations of mechanical, thermal, chemical, and biochemical processes including separation operations [2–4]. Numerous biomass conversion pathways generate carboxylic acids as intermediates. Regarding the need of transportation

and industrial sectors for chemicals, the selective catalytic hydroconversion of bio-acids to alcohols, ethers, and esters is a process of high commercial interest.

Up to 150 °C, the distillate of the bio-oil, obtained from lignocellulose pyrolysis contains lower carboxylic acids and aldehydes in relatively high concentration. Fuel alcohol can be obtained by selective reduction of these components. Instead of the less advantageous thermochemical routes, a novel and favorable microbiological destruction/MixAlco/process has been developed [5]. In principle, the biogas process is suggested to be stopped after the rapid anaerobic acidogenic digestion stage to produce volatile fatty acids (VFA), mainly acetic acid [6,7], not followed by the slow methanogenesis step when mainly CH₄ and CO₂ are formed. The overall chemical reaction without loss of any part of biomass conducted by species of anaerobic bacteria, including members of the genus Clostridium may be represented as:



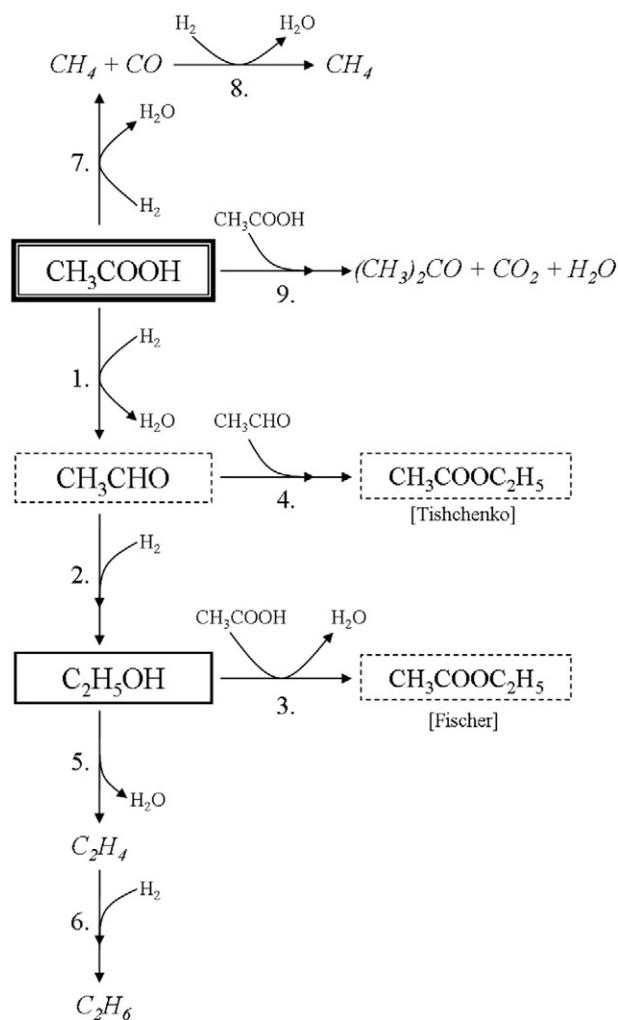
The selective hydrogenation of fatty acids to alcohol in a continuous flow system working in vapor phase under mild conditions seems to be still a problematic step.

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. For example, Rachmady and Vannice have shown related results for catalysts loading platinum on TiO₂, SiO₂, Al₂O₃ and Fe₂O₃ supports [8].

Recently, in a previous paper [1] the applicability of Ni/Al₂O₃ with co-catalyst In₂O₃ was tested with octanoic acid as model reactant.

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Scheme 1. Schematic diagram of reactions involved in the conversion of acetic acid on the base of detected products.

Indium doping of Ni/Al₂O₃ catalyst proved to be highly efficient for the reduction of the long chain fatty acids to aliphatic alcohols opening a novel route for catalyst development.

The present work relates to the application of the same catalyst systems for the selective reduction of VFAs, short chain carboxylic acid homologues to alcohols, using acetic acid (AA), the most easily available platform material obtainable from non edible biomass degradation, as model reactant.

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 hydrogen pressure of 18.9 bar and AA pressure of 2.1 bar in the temperature range of 220–380 °C, i.e., under similar conditions as in [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 1 h 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) equipped for AA products with a HP-Plot/U 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)

with thermal conductivity detector (TCD) on Carboxen 1006 PLOT capillary column. The results are represented as stacked area graphs where the distance between two neighboring curves represents the concentration of a given product at a given temperature in mole percents.

An activated γ -Al₂O₃ (Ketjen CK 300, Akzo-Chemie, BET: 199 m²/g) was impregnated with NH₄OH solution (Reanal Finechemical Co.) of Ni(acetate)₂ (Aldrich), dried, and calcined at 550 °C. The sample designation, e.g., 9Ni/Al₂O₃ formula represents a catalyst preparation containing 9 wt.% Ni. For comparison, an Adkins catalyst (consisting of 72 wt.% CuCr₂O₄ and 28 wt.% CuO) and a commercial HDS catalyst (containing 9 wt.% Mo and 2.5 wt.% Ni on alumina: 9Mo2.5Ni(P,Si)/Al₂O₃) were applied. Composite catalysts were prepared by adding indium (III) oxide to the samples in various amounts and grinding the mixture in agate mortar.

3. Results and discussion

X-ray diffraction patterns recorded and evaluated [1] proves that in the novel InNi/Al₂O₃ composite catalysts, activated at 450 °C in H₂ flow before the reaction, In₂O₃ is reduced and indium metal far above its melting point (156.4 °C) is present under the reaction conditions and finely dispersed bimetallic InNi₂ particles are formed. Consequently, the appearances of these two characteristic components in the samples containing initially admixed In₂O₃ are responsible for the drastic changes of catalytic properties. In general, the modification by indium changes the hydrogenation activity of the nickel catalyst for the C–O or C=O bonds and controls the extent of side reactions.

The catalytic activity and selectivity of the various catalyst preparations are characterized by the product distribution as a function of reaction temperature (see Figs. 1, 2 and 3). Main valuable products formed from acetic acid (marked by double line frame) are acetaldehyde, ethyl acetate (both marked by dotted line frame) and ethanol (highlighted by simple line frame). As by-products, acetone, ethane, methane, carbon dioxide, carbon monoxide and water were determined in various amounts depending on the composition of the catalysts. All the reactions responsible for the found products are summarized in Scheme 1. Carboxylic acid can be converted first to

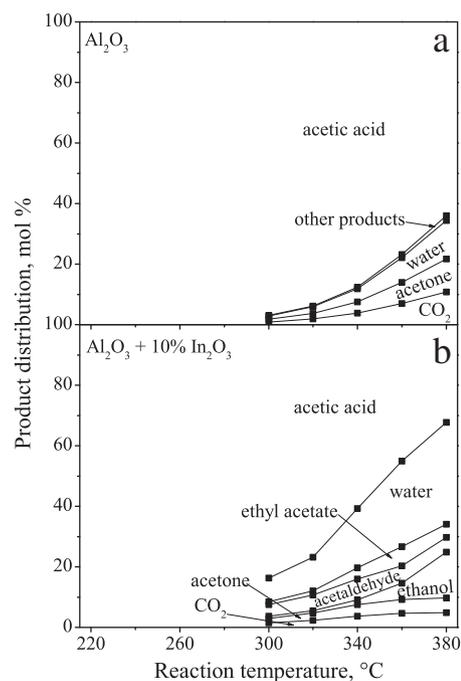


Fig. 1. Product distribution on (a) Al₂O₃ and (b) Al₂O₃ + 10% In₂O₃ in the hydroconversion of AA as a function of reaction temperature at 21 bar total pressure. Partial pressures of AA and H₂ were 2.1 and 18.9 bar. WHSV of AA was 1.0 h⁻¹.

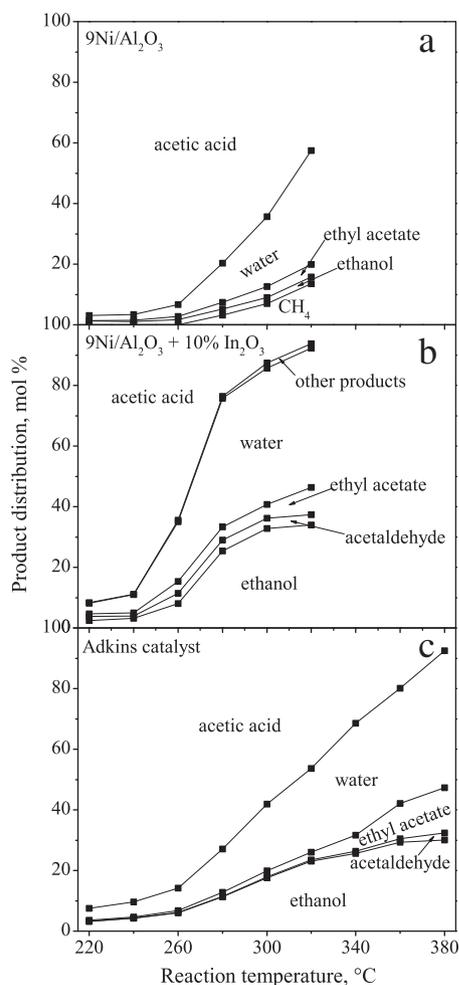


Fig. 2. Product distribution on (a) 9Ni/Al₂O₃, (b) 9Ni/Al₂O₃ + 10% In₂O₃ and (c) conventional Adkins catalysts in the hydroconversion of AA. Reaction conditions as in Fig. 1.

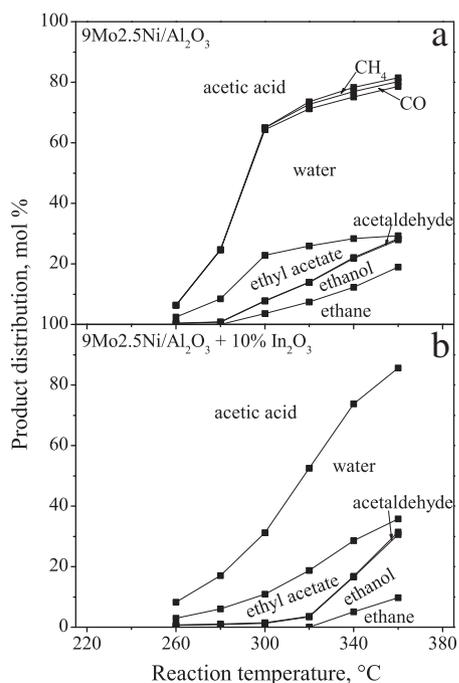


Fig. 3. Product distribution on (a) 9Mo_{2.5}Ni/Al₂O₃ and (b) 9Mo_{2.5}Ni/Al₂O₃ + 10% In₂O₃ in the hydroconversion of AA. Reaction conditions as in Fig. 1.

aldehyde and then to alcohol (reactions 1 and 2). Depending on the reaction conditions, fractions of the reactant acid and the product alcohol can form ethyl acetate according to the Fischer esterification mechanism (reaction 3). Ethyl acetate can however form directly from the intermediate acetaldehyde in the Tishchenko reaction (reaction 4) [9]. It would be of importance to enhance the selective formation of ethyl acetate when the expensive intermediate ethanol step in conventional two step process could be eliminated [9]. From acetic acid after AA-anhydride formation decarboxylation results in formation of acetone and CO₂ (reaction 9). Ethanol can be easily dehydrated in a monomolecular way to ethylene (reaction 5) (diethyl-ether formed in bimolecular dehydration cannot be detected). In similar catalytic system hydrodeoxygenation of octanoic acid and AA results with high selectivity in alcohol formation, however, the by-products are different (see later).

The catalytic behavior of Al₂O₃, Ni/Al₂O₃, In/Al₂O₃ and Ni,In/Al₂O₃ were determined in order to follow the contribution of the constituents of composite catalyst. Ni and In free alumina catalyze mainly acetone formation above 300 °C (Fig. 1a) according to reaction 9 in Scheme 1 (products of desired consecutive AA reduction cannot be detected) whereas composite Ni,In/Al₂O₃ catalysts are working at essentially lower temperature range.

AA hydroconversion on monometallic Ni/Al₂O₃ below 350 °C results in considerable methane formation beside ethyl acetate and ethanol (Fig. 2a). Appearance of methane proves the proceeding of reactions 7 and 8 in Scheme 1. It seems likely that for the formation of products shown in Fig. 2a mainly nickel particles are responsible.

Contrary the liquid indium metal (working highly above its melting point, 156.4 °C) presumably well dispersed on alumina support shows significant hydrogenating activity (Fig. 1b) producing all the compounds observable in consecutive AA reduction steps as main products but by 80–100 °C higher reaction temperature than over the In,Ni/Al₂O₃ composite (Fig. 2b). Besides this, a part of the original activity of alumina support is still preserved in the presence of indium since significant amounts of acetone and CO₂ are produced. It means that indium atoms at this concentration can poison only a part of such active sites all over the surface of alumina support.

On the composite catalyst (Fig. 2b) step by step reduction of acetic acid to ethanol seems to be dominant. Ethanol can be esterified with reactant acid (reaction 3 in Scheme 1) decreasing its yield. However, reaction 4 in Scheme 1 cannot be excluded either in ethyl acetate formation when intermediate acetaldehyde is involved. The role of alumina support in the presence of ethanol cannot be disregarded in ester formation (not examined for Al₂O₃ in Fig. 1a). Here is an exciting room for future research for understanding the reaction mechanism around the appearance of ethyl acetate.

Modification with a co-catalyst, adding plus 10 wt.% In₂O₃ of the mass of monometallic Ni/Al₂O₃ catalyst highly increases the activity (Fig. 2b) and strikingly changes the selectivity. Hydrodecarbonylation (reactions 7, 8 in Scheme 1) is completely eliminated thus governing the process clearly to the consecutive deoxygenating reaction pathway, i.e., a step by step reduction with H₂ and stopping this hydrogenation reaction series at ethanol formation allowing esterification only to a limited extent. The boiling points of these two main products are almost the same causing an expensive separation. However if the product mixture is used as transportation fuel then the separation is not necessary. In order to obtain pure ethanol or ethyl acetate the reaction mechanism is to be explored.

Comparing the commercial, conventionally used Cu-chromite Adkins catalyst (Fig. 2c) with the bimetallic alumina supported composite (InNi/Al₂O₃) the novel catalyst system (Fig. 1d) seems to be much more active and selective for producing ethanol.

Comparison of the octanoic acid and the acetic acid hydroconversions over 9Ni/Al₂O₃ + 10% In₂O₃ catalyst results in significant differences (different by-products), but important similarities can also be observed (cf. Figs. 2b and 4B in Ref. [1]). In the case of octanoic acid, formed alcohol is dehydrated to ether and octene, while, in the case of

AA, intermediate aldehyde can be detected and ester formation is observable, however, the course of main reaction, i.e., the selective hydrogenation of carboxylic acids to alcohols, is very similar. The conversions are practically the same when mass rates are the same but in this case the molar feed rate of AA is at least 2 times higher than that of octanoic acid; it means that the conversion rate in moles/s \times g_{cat} is at least 2 times higher for AA than for OA.

Ni,Mo(P,Si)/Al₂O₃ commercial hydrotreating catalyst was tested in the AA hydroconversion with or without indium doping under the same conditions as that with the other catalysts (Fig. 3). In spite of the lower Ni content the industrial NiMo/Al₂O₃ catalyst shows hardly lower activity than the novel InNi(P,Si)/Al₂O₃ composite (cf. Figs. 3a and 2b). However a whole of difference can be observed in the product distributions supposing to be controlled by the different co-catalysts (MoO₃ or In₂O₃ added approx. in the same concentration). From acetic acid the commercial Ni,Mo(P,Si)/Al₂O₃ catalyst produces mainly ethyl acetate. It seems likely that AA hydroconversion is not followed by Fischer esterification (reaction 3 in Scheme 1) but by direct formation of the ester from aldehyde over the molybdena as a heteropolyacid catalyst according to Tishchenko reaction (reaction 4 in Scheme 1) [9]. (Understanding of this mechanism is not a subject of the present work studying influences of indium admission.). Fischer esterification is less presumptive since initial formation rate of ethyl acetate is higher than that of ethanol. The molybdenum component of the 9Mo2.5Ni(P,Si) catalyst seems to be more efficient and at the low nickel content the influence of indium doping is weak.

It was found lately that, at a fixed Ni-loading (9 wt.%) decreasing the amount of added indium oxide in a wide range down to 10 wt.% hardly affects the selectivity of the catalyst composites in octanoic acid hydroconversion [1]. Hence it seems likely to apply in low concentration the expensive, but strongly efficient In₂O₃ co-catalyst. It was estimated that both active metal components can be used in about 10 wt.% to attain high carboxylic acid conversion with high and stable alcohol yield. Therefore, the conversion of the practically more important acetic acid on the same catalyst is studied only in this low In₂O₃ co-catalyst range. In Fig. 4 product distributions as a

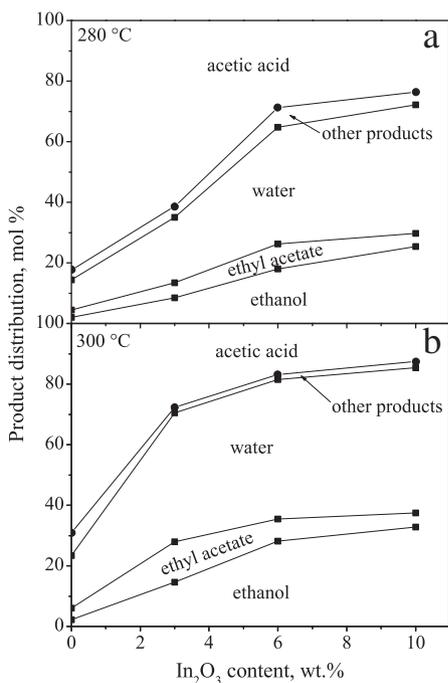


Fig. 4. Comparison of the yields of main products (■) and the conversions (●) on 9Ni/Al₂O₃ catalysts with various amounts of In₂O₃ admission in the hydroconversion of AA at 280 and 300 °C at 21 bar. Reaction conditions as in Fig. 1.

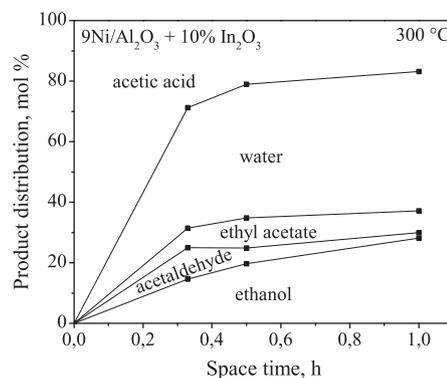


Fig. 5. Hydroconversion of AA over 9Ni/Al₂O₃ + 10% In₂O₃ catalysts as a function of space time at 21 bar total pressure and 300 °C.

function of the admixed indium content can be compared at high conversions at 280 and 300 °C. Acetaldehyde concentration is negligible in the full range of indium loadings. The first step of acetic acid reduction should give acetaldehyde, as a highly reactive intermediate, which can produce ethanol through reduction or directly ethyl acetate in the bimolecular Tishchenko reaction (Scheme 1). The last route seems to be more dominant at lower reaction temperature and lower indium content. At higher indium loading the reduction of acetaldehyde can be faster on the active sites of increased number or/and the hydrogenation of ethyl acetate to two ethanol molecules can be more complete. Around 300 °C and 10 wt.% In₂O₃ loading ethanol can be produced with high selectivity.

The increasing space time does not favor the accumulation of the acetaldehyde intermediate (Fig. 5) which can be the reactant of two parallel reaction routes: ester formation or reduction.

The AA conversion to ethanol and ethyl acetate increases roughly linearly with increasing hydrogen partial pressure over 9Ni/Al₂O₃ + 6% In₂O₃ composite catalyst. The acetaldehyde selectivity is the highest at lowest hydrogen partial pressures (at low conversions). The hydrogenation activity is suppressed by an increased AA coverage (higher AA partial pressures). The found activity dependence on the reactant partial pressures is the same as in our previous work [1] and it is in line with the Langmuir–Hinshelwood type kinetics and mechanism.

4. Conclusions

Hydroconversion of aliphatic carboxylic acids over a Ni/Al₂O₃ catalyst and the yield of selectively produced alcohols (octanol or ethanol) can be increased drastically by In₂O₃ doping. Appearance of metallic indium near nickel can effectively direct the step by step catalytic reduction to alcohol formation over partly reduced Ni catalysts instead of hydrodecarbonylation. Indium doping has been found to be highly efficient also for the reduction of acetic acid with hydrogen to ethyl alcohol.

On comparing the hydroconversion of octanoic and ethanoic acids over InNi/Al₂O₃ composite catalyst under similar conditions the conversion rate of ethanoic acid is twice as high that of octanoic acid. It suggests that the molecular reduction rate of the carboxylic group on the bimetallic surface (perhaps only to a formyl group) is higher for lighter carboxylic acid than for heavier one. However, the product compositions are different: after hydroconversion of octanoic acid either aldehyde or ester cannot be detected but there are some alcohol dehydration, while for acetic acid, ester formation is considerable and aldehyde formation can be observed but no dehydroxylation.

The activity dependence on the reactant partial pressures denotes the rate-controlling Langmuir–Hinshelwood kinetics.

Combining relatively simple pyrolytic (or biochemical) technologies resulting in the production of acetic acid with the catalytic transformations shown, bioethanol and chemicals, such as ethyl acetate, can be obtained from biomass, e.g. from lignocellulosic raw material.

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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