

**Bio-Ethanol Valorization Towards C4s Including
1-Butanol over Metal Modified Alumina
and Zeolite Catalysts**



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ABSTRACT

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Keywords: bio-ethanol, bio-butanol, heterogeneous catalyst, alumina, zeolite.

Bio-ethanol has been used as a fuel additive in modern society aimed at reducing CO₂-emissions and dependence on oil. However, ethanol is unsuitable as fuel supplement in higher proportions due to its physico-chemical properties. One option to counteract the negative effects is to upgrade ethanol in a continuous fixed bed reactor to more valuable C4 products such as 1-butanol providing chemical similarity with traditional gasoline components. Bio-ethanol based valorization products also have other end-uses than just fuel additives. E.g. 1-butanol and ethyl acetate are well characterised industrial solvents and platform chemicals providing greener alternatives.

The modern approach is to apply heterogeneous catalysts in the investigated reactions. The research was concentrated on aluminium oxide (Al₂O₃) and zeolites that were used as catalysts and catalyst supports. The metals supported (Cu, Ni, Co) gave very different product profiles and, thus, a profound view of different catalyst preparation methods and characterisation techniques was necessary.

Additionally, acidity and basicity of the catalyst surface have an important role in determining the product profile. It was observed that ordinary determination of acid strength was not enough to explain all the phenomena e.g. the reaction mechanism. One of the main findings of the thesis is based on the catalytically active site which originates from crystallite structure. As a consequence, the overall evaluation of different by-products and intermediates was carried out by combining the information. Further kinetic analysis was carried out on metal (Cu, Ni, Co) supported self-prepared alumina catalysts. The thesis gives information for further catalyst developments aimed to scale-up towards industrially feasible operations.

REFERAT

Toni Riittonen

Uppgradering av bioetanol till C4-komponenter, speciellt 1-butanol på metallmodifierade zeolit- och aluminiumoxidkatalysatorer

Nyckelord: bioetanol, biobutanol, heterogen katalysator, aluminiumoxid, zeolit

Bioetanol har använts som bränslekomponent i vårt moderna samhälle som eftersträvar en minskning av koldioxidutsläpp och beroende av olja. Etanol är dock olämplig som bränsletillsats i högre kvantiteter p.g.a. ofördelaktiga fysikaliska och kemiska egenskaper. Ett sätt att övervinna de negativa effekterna är att uppgradera etanol i en reaktor med fast bädd så att värdefullare C4-produkter såsom 1-butanol bildas. Dessa molekyler påminner mera om traditionella bränslekomponenter. Bioetanolbaserade uppgraderingsprodukter har även andra tillämpningar än som tillsatsämnen i bränslen. T.ex. 1-butanol och etylacetat är väletablerade industriella lösningsmedel och plattformskemikalier som utgör gröna alternativ.

Det moderna sättet att angripa problemet är att tillämpa heterogena katalysatorer på omvandlingsreaktioner, som behövs för uppgradering av bioetanol. Forskningen fokuserades på aluminiumoxid och zeoliter som användes både som katalysatorer och katalysatorbärare. De metaller som studerades (Cu, Ni, Co) gav mycket varierande produktprofiler, vilket innebär att djupgående insikter i katalysator-tillverknings- och karakteriseringsmetoder blir nödvändiga.

Katalysatorytans surhet och alkalinitet har ett stort inflytande på produktfördelningen. Det observerades att en standardbestämning av syrastyrkan inte kunde förklara alla fenomen, som upptäckts experimentellt, t.ex. reaktionsmekanismen. En av de viktigaste upptäckterna i doktorsavhandlingen baserar sig på förståelsen av det katalytiskt aktiva sätet som kan förklaras med ämnets kristallinitet, vilken förklarar det observerade syra-basbeteendet. Olika biprodukters och reaktionsintermediärers roll avslöjades genom att kombinera information från olika källor. En djupare kinetisk analys tillämpades på experimentella data som erhållits för metallkatalysatorer (Cu, Ni, Co) på aluminiumoxidbärare. Doktorsarbetet ger information för vidare katalysatorutveckling med tanke på uppskalning av processen till praktiska industriella dimensioner.

LIST OF PUBLICATIONS

I One-Pot Liquid-Phase Catalytic Conversion of Ethanol to 1-Butanol over Aluminium Oxide—The Effect of the Active Metal on the Selectivity.

Catalysts **2012**, 2, 68-84.

Riittonen, T.; Toukoniitty, E.; Madnani, D.K.; Leino, A.-R.; Kordas, K.; Szabo, M.; Sapi, A.; Arve, K.; Wärnä, J.; Mikkola, J.-P.

Ib Extract from Pro Gradu (Riittonen, T.: 2009, University of Turku, Finland) as supplementary material.

II Continuous Liquid-phase Valorization of Bio-Ethanol Towards Bio-Butanol over Metal Modified Alumina.

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III Microporous Solid Acid and Ni modified H-Beta and H-Y Catalysts for the Synthesis of Diethyl Ether.

(Submitted to *Journal of Renewable Energy*, Hindawi Publishing Press)

Riittonen, T.; Kumar, N.; Mikkola, J.-P.

IV Direct Synthesis of 1-Butanol from Ethanol in a Plug Flow Reactor: Reactor and Reaction Kinetics Modeling.

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Riittonen, T.; Salmi, T.; Mikkola, J.-P.; Wärnä, J.

OTHER PUBLICATIONS RELATED TO THE TOPIC

Book Chapter

Riittonen T., Eta V., Hyvärinen S., Jönsson L.J., Mikkola J.-P. Advances in Chemical Engineering, Chemical Engineering for Renewables Conversion, Engineering Aspects of Bioethanol Synthesis, Bioethanol Valorization Over Inorganic Heterogeneous Catalysts: Classical Liquid and Gaseous Products. Vol. 42, pages 1-73, 2013. Elsevier, 2013, ISSN: 0065-2377.

Oral Conference Presentations

- Dechema, Karlsruhe, Germany, 2010.
- Finnish-Indian-Swedish Symposium on Heterogeneous Catalysis, Turku, Finland, 2012.
- Organic Reactions Catalysis Society, Tucson, US, 2014.

Poster presentations

- Catalysis for Biorefineries, Torremolinos, Spain, 2010.
- Catalysis on Multiphase Reactors, Naantali, Finland, 2011.
- Nordic Symposium on Catalysis, Åland, Finland, 2012.
- European Congress on Catalysis, Lyon, France, 2013.
- Organic Reactions Catalysis Society, Tucson, US, 2014.

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Preface

The work was carried out at the Laboratory of Industrial Chemistry & Reaction Engineering, Department of Chemical Engineering at Åbo Akademi University between 2009 and 2014. The research was a part of the Process Chemistry Centre (PCC) activities. The PhD work was a continuation on the M. Sc. thesis, which was completed in 2009.

I would like to express my gratitude to all the professors in our laboratory for their assistance over the years, especially to professor Salmi and professor Wärnå for providing help with kinetic modelling. Professor and supervisor Jyri-Pekka Mikkola deserves a special mention for his passion for promoting a scientific way of living and working, especially in late evenings. In addition, I want to thank all my co-authors, colleagues, TTO-personnel and parents. I am also grateful for Docent Kari Eränen and Docent Narendra Kumar for their unlimited patience and willingness to help. Professors Riitta Keiski and Lars Pettersson are acknowledged for their work in evaluating the thesis.

The years spent in the lab taught me a lot.

Turku/Åbo, May 2014

Toni Riittonen

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1.

Introduction

1.1 Lignocellulosic Biorefinery Concept

It is well recognized that there is a global need to diminish CO₂ and other greenhouse gas emissions resulting from the burning of fossil fuels. Additionally, the decreasing amount of potential existing fossil reserves suggests another perspective. One option to change our current practices is to increase the amount of renewable energy. Thus, based on the geographical location of a country, there are several possibilities available. For example, Nordic countries are known to possess wide forest reserves that are today, as in the past, used in the production of pulp and paper products. However, due to the changing world economy the traditional processes have become threatened and other applications for forest based material are becoming vitally important.

One advantage over forest based material is that this source is a non-edible feedstock meaning that the origin of biomass feedstock is not competing with human related food production. It can be well understood that agricultural based production of bioenergy is unsustainable in the long term. The classification between these two sources is denoted as 2nd and 1st generation bioenergy strategies, respectively. Based on this advantage, Nordic pulp and paper mills can be converted to modern biorefineries taking advantage of the

lignocellulosic biomass. In general, wood can be divided into four main components in these refineries; cellulose, hemicellulose, lignin and extractives. Each of the components have special characteristics with this work focusing on the application of biobased ethanol, also known as ethyl alcohol, resulting from the fermentation of generated sugars. In fact, there is a possibility to combine traditional pulp and paper industry with e.g. the production of bio-ethanol [1-3].

1.2 Bio-Ethanol as a Source for Biofuels & Biochemicals

Despite several other bio-based options [4], bio-ethanol is relatively attractive due to its existing and well-known public picture (95E10, 98E5). However, the public is not so well aware of some disadvantages regarding ethanol as a supplementary fuel. For instance, ethanol has a lower energy content in comparison to the traditional gasoline and it is also relatively corrosive in its nature. In addition, the modern storage tanks and delivery systems have not been designed for high ethanol blending [5,6]. Ethanol can nowadays be blended with traditional gasoline with 5 to 10 vol-% proportions. However, to be able to achieve higher blending ratios, some new compounds should be investigated to compensate for the negative aspects of ethanol.

One possible product or valorization candidate is 1-butanol that provides many advantages over bio-ethanol. It constitutes four carbon atoms, thus doubling the amount of carbon in comparison to ethanol. By evaluating possible chemical structures suitable for blending with traditional gasoline, it should be understood that the mixture should resemble fossil based fuel when considering its physico-chemical properties. Thus, 1-butanol containing longer hydrocarbon chains can be expected to deliver a better performance. In fact, butanol can be relatively well mixed with gasoline up to 20 % [6]. Furthermore, 1-butanol has an energy content relatively close to that of gasoline and it is almost immiscible in water [5,6]. It is also known to be much less corrosive than ethanol which

provides support for better storage and handling capabilities. Additionally, 1-butanol has also many other possible end-users than the ordinary car industry. 1-Butanol is a well known solvent in the overall industry, in the synthesis of vitamins, herbicides, antibiotics, and, as a component in brake fluid [6]. Traditionally, 1-butanol has been manufactured by chemical means (main processes: Oxo synthesis, Reppe synthesis and crotonaldehyde hydrogenation), whereas biological pathways have included e.g. ABE-fermentation by micro-organisms [5,6].

However, the products obtained from bio-ethanol are not only limited to 1-butanol. There are many other valuable products available such as diethyl ether and ethyl acetate. In addition, different ethanol derivatives may have a different impact on the environment and people and, thus, some studies have evaluated sustainability issue [7] and life cycle analysis [8] providing interesting views. On the diesel fuel sector, it can be assumed that diethyl ether [9] might possess similar potential as 1-butanol in gasoline [10].

1.3 Scope of the Research

The aim of this research was to demonstrate the production of bio-ethanol derivatives in biorefineries. The work presents the chemical way of manufacturing 1-butanol (as main product) in a simple continuous operating fixed bed reactor (liquid phase). The actual research has mainly been carried out in preparation, evaluation and characterisation of suitable heterogeneous catalysts candidates. 1-Butanol and ethyl acetate production have been investigated over commercial and in-house modified heterogeneous alumina (Al_2O_3) catalysts. Manufacture of diethyl ether is evaluated by means of heterogeneous zeolite catalysts in the similar manner as with alumina in small-scale batch reactors. The overall description of the research is depicted in **Figure 1**.



Bio-Ethanol



Diethyl ether



1-Butanol



Ethyl acetate

Figure 1. Manufacturing of ethanol derivatives in modern biorefineries.

2.

Experimental

2.1 Catalyst Preparation

2.1.1 Commercial Catalysts

Catalyst screening for 1-butanol synthesis was concentrated on metal supported alumina catalysts. Several [**I**, **Ib**] commercial metal/alumina catalysts were screened according to the procedures described in chapter 2.2. Commercial HTC-500 (Ni/Al₂O₃ 20.7 wt-%, Crossfield Inc.) was used as a reference and model catalyst over the entire bio-butanol project [**I**, **Ib**, **II**].

In addition, two commercial zeolite catalysts (Zeolyst International) were used after minor modification in the evaluation of bio-ethanol conversion to diethyl ether [**III**] (NH₄-Beta-25 and NH₄-Y-12).

2.1.2 Self-Prepared Catalysts

Research concentrated on understanding the behaviour of tailor-made alumina materials on a commercial support (A 201, provided by Euro Support). The effect of different metals and preparation methods were studied in detail [**I**,

Ib, II]. The incipient wetness impregnation method [**I, Ib**] was applied in the preparation of silver and ruthenium based alumina catalysts [**I, Ib**] whereas the deposition-precipitation method with urea was preferred over gold [**Ib**], nickel [**I, Ib, II**], copper [**II**] and cobalt [**II**] supported catalysts.

Zeolite-based catalyst preparation was focused on two aspects. Na-ZSM-12 zeolite was prepared in the laboratory by varying synthesis time (72, 96 and 144 h). Na-ZSM-12-72 h, Na-ZSM-12-96 h and Na-ZSM-12-144 h zeolites were transformed to their corresponding NH_4 forms by repeated ion-exchange with 1 M NH_4Cl solution for 48 h. The H-ZSM-12-72 h, H-ZSM-12-96 h and H-ZSM-12-144 h catalysts were obtained after calcination of NH_4 form catalysts in a muffle oven. Additionally, commercial NH_4 -Beta-25 and NH_4 -Y-12 zeolites were calcined to obtain protonic form zeolites which were further impregnated with nickel nitrate solution providing nickel forms of these zeolites [**III**].

2.2 Catalyst Evaluation

2.2.1 Isobaric Mini-Reactors

As the first stage, qualitative (all products) and quantitative (mainly diethyl ether) catalyst screening was carried out in small, 2 ml isobaric mini-reactors equipped with magnetic stirring (**Figure 2**). The purpose of this first step was to provide fast and relatively reliable results which were further expanded to batch- and continuous operating reactors over alumina based catalysts. The screening of catalysts aiming at diethyl ether (zeolite catalysts) was limited to this stage. The catalyst testing procedure was as follows: the reactor was loaded with the catalyst and ethanol (Etax Aa, 99.5%, 1.5 mL) under inert atmosphere (He) in a glove bag. The reactors were closed and placed in the heating unit allowing 8 reactors to be run simultaneously. The reactors were heated to 250

°C with a heating rate of 20 °C/min. The reaction was allowed to proceed for 3 h. After reaction, the reactors were rapidly quenched (cooled down) in a water bath and the liquid contents were analyzed by gas chromatography (GC).



Figure 2. Isobaric mini-reactors for catalyst pre-screening.

2.2.2 Laboratory-Scale Batch-Reactor

As the second stage, commercial HTC-500 alumina catalyst (20.7 wt-% Ni/Al₂O₃, Crossfield Inc.) was used as our model catalyst for quantitative screening of reaction products and determination of preliminary reaction kinetics in the production of bio-butanol from bio-ethanol. In addition, the performance of several other metals were also evaluated as incorporated in self-prepared catalysts and taking advantage of the commercial alumina support. Experiments were carried out in a 300 ml high pressure Parr autoclave equipped with a mechanical Rushton turbine. The ethanol reactant (100 mL) was flushed with helium gas inside the reactor before commencing the reaction. The reactor was heated rapidly to 250 °C and the course of the reaction monitored by taking

small liquid samples. The semi-quantitative gas-phase composition was analyzed at the end of the reaction after cooling with a quadrupole mass spectrometer (Balzers). The stirring rate applied throughout the matrix of catalytic experiments was 1,500 rpm thus ensuring that we resided in the kinetic regime. Due to the fact that only liquid reactants (ethanol) were used and that the reaction rates were rather slow, the danger of external mass transfer limitations can be regarded as negligible.



Figure 3. Laboratory-scale batch-reactor applied for the determination of preliminary kinetics and reaction mechanism over alumina catalysts.

2.2.3 Continuous Fixed-Bed Reactor

As a third stage, the performance of alumina supported metal catalysts was carried out in a laboratory-scale continuous stainless steel fixed bed reactor operated in liquid-phase (**Figure 4**). In a typical experiment, 2 gram of 150-250 mesh (0.15-0.25 mm) metal/alumina catalyst was placed in the reactor followed by heating to 240 °C, setting the reactor pressure to 70 bar (Ar) and switching on the HPLC-pump (ethanol). The overall process scheme is presented in **Figure 5**, while the packing of the reactor is depicted in **Figure 6**. The sampling was carried out by a special valve capable of draining 1 ml sample and analyzed by means of GC-FID (see **2.2.4**).



Figure 4. Continuous liquid-phase fixed bed reactor setup for the determination of performance of the alumina catalysts.

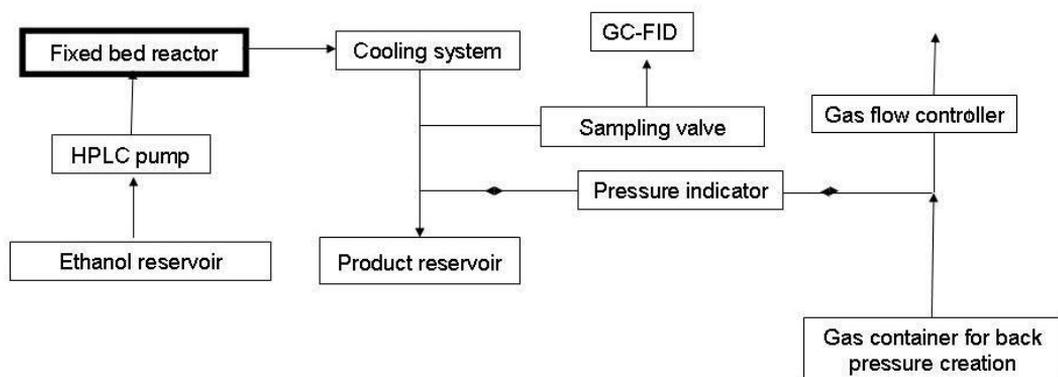


Figure 5. Flowsheet of the experimental equipment.

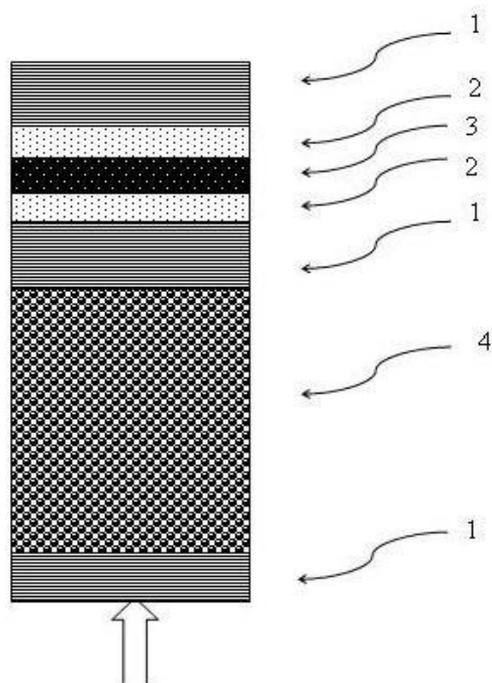


Figure 6. Reactor packing; 1 = quartz wool, 2 = quartz sand, 3 = catalyst, 4 = silica beads.

2.2.4 Product Analysis by GC-FID (Gas Chromatography - Flame Ionization Detector)

The reaction product analysis was carried out by dissolving 0.5 ml (from sampling valve) of product to 1 ml of tetrahydrofuran (Sigma Aldrich 33709) and subjected to gas chromatography. The samples were analyzed by means of GC-FID (Agilent Technologies 6890 N; column: DB-Petro 122-10A6, 100 m, i.d. 0.250 mm; flame ionization detector) calibrated with analytes.

2.3 Catalyst Characterization

2.3.1 XRD (X-Ray Diffraction) & TEM (Transmission Electron Microscopy)

Energy-filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB₆ filament, 120 kV) was used to assess the particle sizes and reveal the microstructure of the samples. The crystal phases of the support and catalyst particles were evaluated by X-ray diffraction (Bruker D8 Discover, Cu K α).

2.3.2 FT-IR (Fourier Transform Infrared Spectroscopy)

FT-IR (ATI Mattson) was used to determine the Brønsted and Lewis acid sites of the prepared catalysts, using pyridine as the probe molecule. A self-compressed disc of alumina catalyst was placed into the FTIR cell followed by evacuation. The temperature was raised to 450 °C for one hour and decreased to 100 °C for the measurement of the background spectrum. Pyridine was adsorbed to the catalyst for 30 min by sparging helium through a pyridine solution followed by subsequent desorptions at 250 °C, 350 °C and 450 °C, respectively. Moreover, sample spectra were recorded between each temperature ramp. The

measurement was carried out under vacuum at 100 °C. Spectral bands at 1545 cm^{-1} and 1450 cm^{-1} were used to identify the corresponding Brønsted- and Lewis acid sites.

2.3.3 XPS (*X-Ray Photoelectron Spectroscopy*)

To determine the abundance of metal oxide and aluminate type of structures of nickel, cobalt and copper species XPS spectra were collected with a KRATOS Axis Ultra DLD electron spectrometer under monochromatic Al Ka radiation (1486.6 eV). A pass energy of 160 eV with a step size of 1 eV was used for survey scans. For separate photoelectron lines, a pass energy of 20 eV was used with a step size of 0.1 eV.

2.3.4 ICP-OES (*Inductively Coupled Plasma Optical Emission Spectroscopy*)

ICP-OES measurements were performed over self-prepared alumina catalysts with Perkin Elmer Optima 5300 DV instrument. The samples were weighed into Teflon bombs followed by addition of acid mixture. Thereafter, a microwave oven (Anton Paar, Multiwave 3000) was applied in the digestion and appropriate dilutions were performed prior to the ICP analysis.

3.

Results & Discussion

3.1 Alumina Catalysts in the Production of Bio-Butanol & Ethyl Acetate

The preliminary screening of suitable heterogeneous catalysts in the production of 1-butanol from bio-ethanol was carried out in mini-reactors (Section 2.2.1). Based on these results [I, Ib], the clear advantage of alumina supported metal catalysts was verified. Additionally, a more comprehensive alumina based catalyst screening was investigated with the help of a batch-reactor (2.2.2), including a study of possible reaction mechanisms, by-products and thermodynamics [I, Ib]. The final stage aimed at simulating industrial conditions and the fixed bed continuous reactor was applied in combination with alumina based catalyst (Ni, Co, Cu). In all these experiments, commercial HTC-500 (Ni/Al₂O₃) catalyst was used as the reference material.

From an engineering point of view, alumina may not offer any significant advantages but from a chemical point of view, the outcome may be totally different. The reason for this is based on the fact that alumina itself contains a heterogeneous surface structure [11] consisting of e.g. crystalline and amorphous regions. If a metal cation (e.g. Ni, Co, Cu) is brought into contact with this type of surface by chemical and physical means, several phenomena

can occur leading to the formation of entirely new surface structures (Section 3.3).

Batch reactor studies were performed over Ni-, Ag- and Au-supported alumina catalysts [I, Ib]. Commercial HTC-500 catalyst (**Figure 6**) demonstrates that 25 % conversion and 80 % selectivity (liquid products) were generally observed under the studied reaction conditions. Additionally, by-products formed suggest that reaction is dependent on formed acetaldehyde, supporting the general concept of Guerbet reaction (also known as aldol condensation).

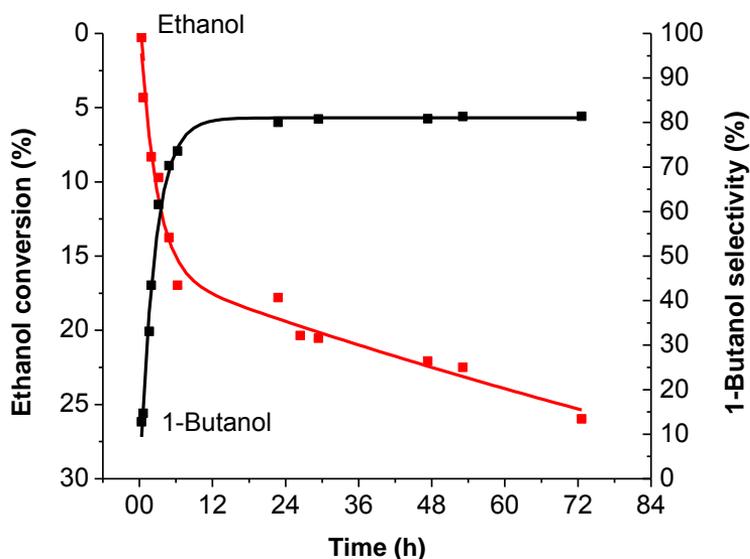


Figure 6. Batch-experiment with commercial HTC-500 catalyst (250°C 70 bar).

The literature concerning the investigated reaction is mainly based on hydrotalcite- and hydroxyapatite-type catalyst structures [12-21] but also basic MgO [22,23], alkali cation zeolites [24], CeO₂ [25], ZrO₂ [26], cobalt powder [27] and γ -alumina [28] have been reported. Nevertheless, only one study has been reported of on a similar type of a catalyst support [28] to the one described here. Evidently, metal oxides have a crucial role in the reaction. Furthermore,

the current metal oxides are also recognized as basic or acid-base bi-functional (ZrO_2) catalyst materials. Thus, based on the available literature on the topic, highly acidic materials do not favour the production of 1-butanol from ethanol.

The continuous operating tests [III] were performed with Co, Ni and Cu supported on commercial alumina (A 201, Euro Support). The metals chosen reflect the large scale screening effort over several different transition metals, calcination or reduction temperatures and metal loading procedures. Nickel was investigated in two forms as the commercial HTC-500 and self-prepared Ni-19 (19 wt-% nickel loading, **Figure 8**), whereas copper was evaluated with 1.8 wt-% (Cu-1.8) and 4.5 wt-% (Cu-4.5) loadings (**Figure 9**). Additionally, cobalt was studied with 16 wt-% loading providing interesting results (**Figure 10**).

The conversions of each five catalysts are depicted in **Figure 7**. Consequently, it can be observed that Co- and Ni-catalysts have a relatively similar profile in terms of conversions of around 25 to 30 %, whereas Cu-catalysts reach a stable level at 12-14 %. Commercial HTC-500 demonstrated a similar initial level as the copper catalyst but clear deactivation is evident.

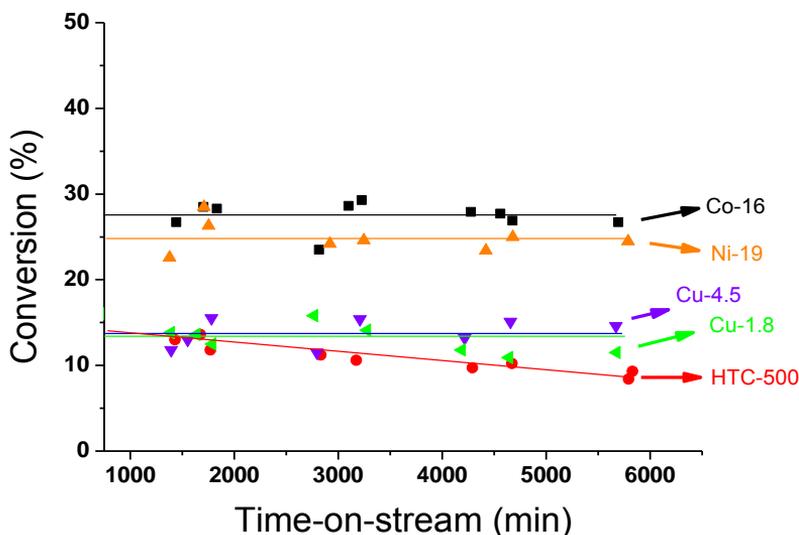


Figure 7. Conversion as a function of time for five of the investigated catalysts.

The selectivity profiles of both nickel catalysts (**Figure 8**) provide rather similar results with 1-butanol and gaseous products being the main outcome of the reaction. However, on a self-prepared catalyst, approximately 10 % selectivity towards 1-hexanol was observed which is absent for the HTC-500 catalyst. It can be proposed that the difference results from more advanced Guerbet reaction providing C₆-alcohols (1-butanol + ethanol).

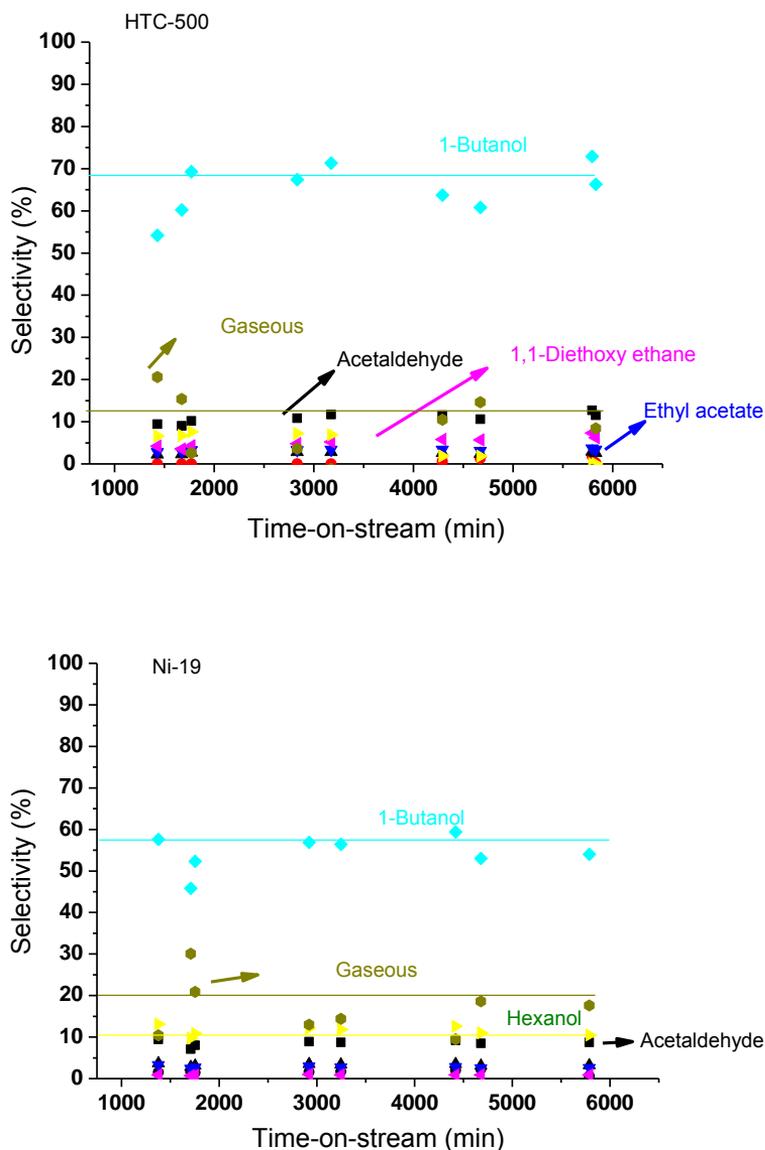


Figure 8. Selectivity profiles for self-prepared HTC-500 and Ni-19.

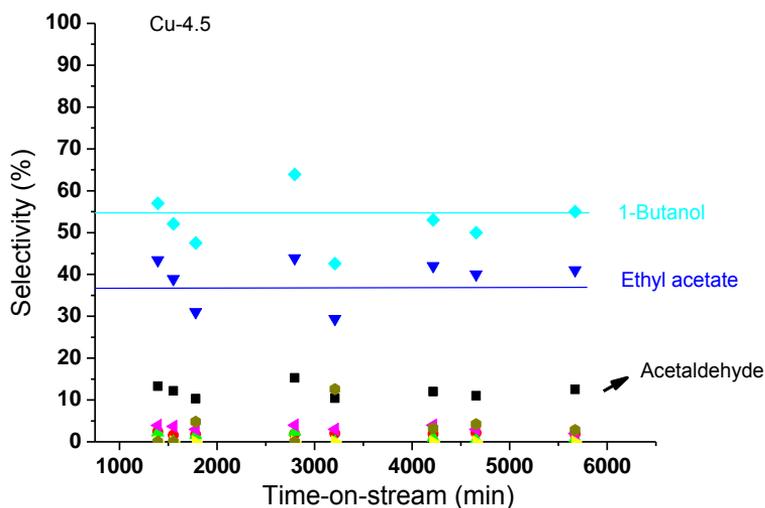
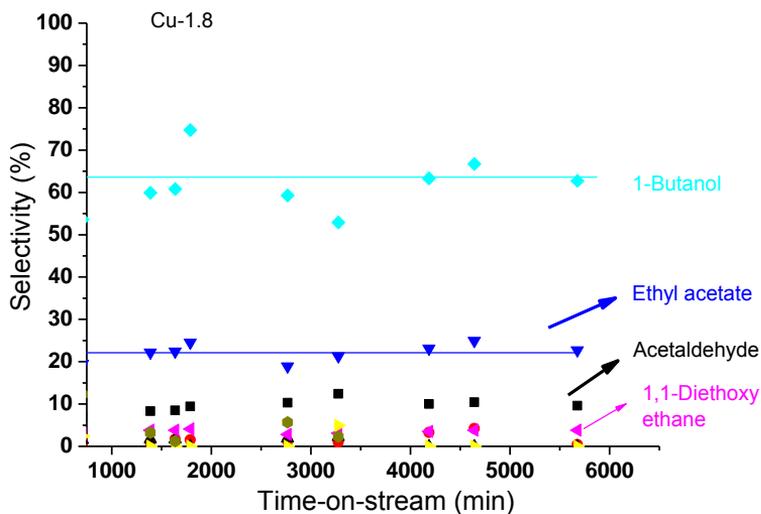


Figure 9. Selectivity profiles for Cu-1.8 and Cu-4.5 catalysts.

The experiments carried out on in-house prepared Cu-catalysts (**Figure 9**) provided rather similar picture as in the case of nickel catalysts, resulting in 65 % (Cu-1.8) and 55 % (Cu-4.5) selectivities towards the main product, 1-butanol. Surprisingly, ethyl acetate was observed as a new valorization candidate with selectivities approaching 25 % and 35 %. There seems to be a

clear tendency for copper to promote the formation of ethyl acetate. Thereafter, the rise in the copper content of the catalyst is followed by a decreasing trend in the formation of 1-butanol whereas ethyl acetate behaves in the opposite fashion. The detailed explanation is discussed in Section 3.3.

The production of ethyl acetate is rather well covered in the literature on Cu-Zn-Zr-Al-O catalysts [29-32]. As a consequence, these metal oxide type of catalyst structures seem to be relatively close to the structures presented above for the 1-butanol production. Further, the experiment on cobalt supported alumina catalyst (**Figure 10**) produced almost solely ethyl acetate with the selectivity of 85 %. By comparing nickel with cobalt on the alumina surface by means of relatively similar metal loading, an entirely different product distribution was observed. It is obvious that the phenomenon cannot be explained by the choice of the metal only on the alumina surface (Section 3.3).

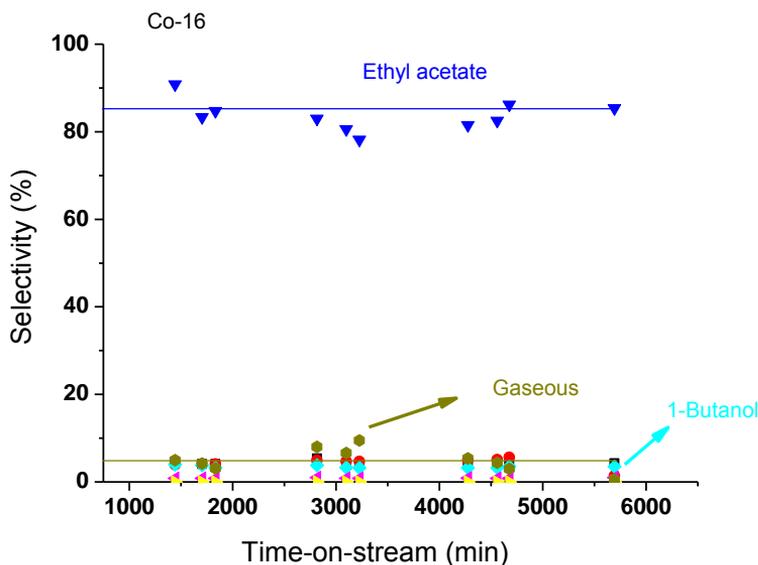


Figure 10. Selectivity profile for in-house prepared Co-16 catalyst.

3.2 Zeolite catalysts in the Production of Diethyl Ether

Our research included acid catalysts [III] which are known to form diethyl ether and ethylene at higher temperatures. Our aim was to investigate the effect of acidity, crystallite structure and synthesis time in the production of diethyl ether from ethanol over zeolite catalysts (**Table 1**) in mini-reactors (Section 2.2.1). In the literature, acid catalysis considering the reaction is widely covered [33-37]. Not only zeolitic materials but also acid resins [33] and transition metal oxides [35] are reported to be useful in the process. Thus, in comparison to butanol production, these catalyst types provide a wider option of different catalyst formulations.

The research covering the in-house prepared H-ZSM-12 catalyst was concentrated on three different synthesis times (72, 96 and 144 h), resulting in different conversions and yields towards diethyl ether. The higher conversion and yield towards diethyl ether was observed for materials prepared under prolonged synthesis time. Our observations favouring the efficient synthesis of diethyl ether from ethanol can be listed as:

- Increase in crystallite size
- Increase in Brønsted and Lewis acid sites
- Phase purity (structural purity)

Table 1. Conversion and yield of the investigated zeolites.

Catalyst	Conversion of ethanol mol %	Yield of diethyl ether mol %
H-ZSM-12-34 - 72 h	30.3	26.9
H-ZSM-12-34 - 96 h	68.9	61.4
H-ZSM-12-34 - 144 h	72.3	67.0
15 wt % Ni-H-Beta-25	61.6	53.7
5 wt % Ni-H-Y-12	34.5	26.4

In addition, commercial zeolite catalysts H-Beta-25 and H-Y-12 were ion exchanged by nickel in order to study whether it would possibly provide higher conversion of ethanol and yield towards diethyl ether. It was assumed that Ni²⁺ could act as an additional Lewis acid site thus providing additional catalytically active sites. Based on the results, there does not seem to be positive correlation in the investigated reaction. From an industrial viewpoint, protonic forms of zeolites are the most promising catalysts in the production of diethyl ether from bio-ethanol.

3.3 Crystallite Structure vs Acidic & Basic Nature of Active Sites

Based on the experiments utilizing continuous operating reactor (Section 3.1) over Ni-, Cu- and Co-supported alumina catalysts, an exceptional discovery considering the product distribution between ethyl acetate and 1-butanol was observed. Ni-catalysts were found to be relatively selective towards 1-butanol (as liquid product) while gaseous products were abundant by-products. It can be assumed that Ni has an ability, due to its acidic character, to break carbon-carbon bond of the ethanol molecule and, thus, facilitate the formation of gaseous molecules. Interestingly, cobalt provided an entirely different outcome by forming ethyl acetate with high selectivity. It was also observed that copper based alumina catalysts behaved between these two extremes by forming both products and having a low tendency towards gaseous species.

In general, it is evident that metal oxides are widely applied in these types of reactions. Thus, there must be something special involved in the oxide structures. In terms of catalysis, normally acidic and basic properties of a catalysts surface are measured and, furthermore, used as a source of explanation and conclusions. However, metal oxides are generally very heterogeneous

structures and need to be carefully addressed. In fact, the crystallite structure of a metal oxide has a huge importance when evaluating different catalytically active sites and reaction mechanisms. It should be understood that in many cases the fundamental understanding evolves from crystallite structure resulting in acidic and basic properties, not vice versa.

Alumina (Al_2O_3) [11] is known to consist of crystalline and amorphous regions thus providing a wide scale of different applications. However, particularly interesting changes on the catalyst surface can happen when other metals (e.g. Ni, Cu, Co) are brought into contact with alumina surface. In our study, it was observed that copper and nickel ions diffuse (during catalyst preparation procedure) into the alumina lattice, possibly through so called grain boundary or crystallite defect sites [38]. The outcome of the process is the formation of a new structure, known as spinel. These spinel structures were found to be the catalytically active sites in the investigated reaction and, additionally, were verified by XPS. Additionally, cobalt was found to form a surface spinel structure and, thus, not to diffuse into the alumina lattice.

Based on our literature survey [39-42], nickel aluminate spinels (NiAl_2O_4) are well known structures. Spinels were detected in both commercial (**Figure 11**) and in-house prepared (**Figure 12**) alumina catalysts by means of XPS. In addition, metallic Ni and NiO were also present on the catalyst surface. However, these findings do not explain the observed behavior between the formation of 1-butanol and ethyl acetate.

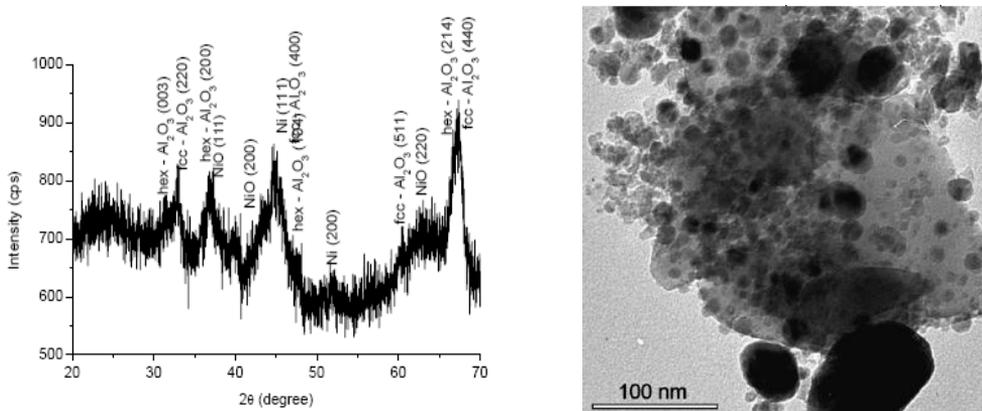


Figure 11. X-Ray powder diffraction patterns and Transmission electron microscope micrograph of 20.7 wt-% Ni/Al₂O₃ HTC-500 catalyst.

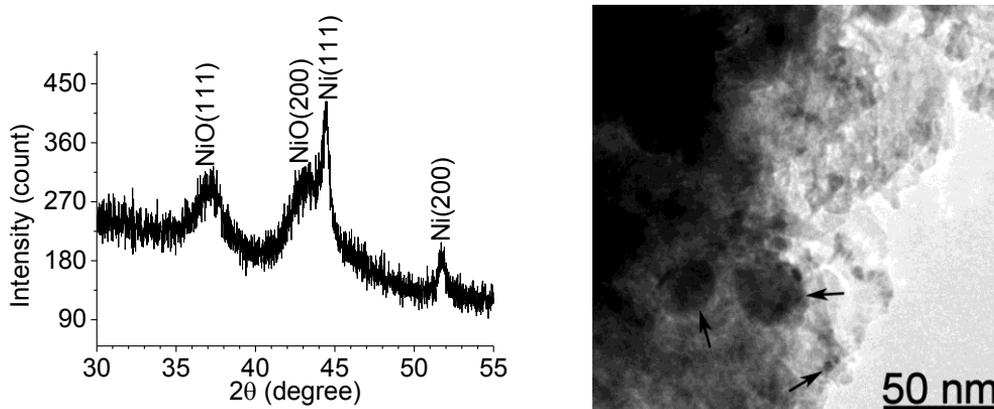


Figure 12. X-ray powder diffraction patterns and Transmission electron microscope micrograph of Ni-19 catalyst (Ni 13.7±0.2 nm; NiO 5.2±0.7 nm).

Further experiments carried out on copper catalysts (**Figures 13 and 14**) revealed interesting information. Catalysts with lower copper loading exhibited no CuO and other peaks, whereas higher copper loading demonstrates the existence of CuO. However, XPS results verified the existence of CuO in both copper catalysts. Based on the contradiction between XRD and XPS measurements, it can be proposed that a small amount of CuO may be needed

(1-butanol production) in close vicinity of copper aluminate structure that cannot be detected by XRD. By recalling previous experiments, lower copper loading produced higher selectivity towards 1-butanol. Based on the findings, copper aluminate structures are the active sites in the production of 1-butanol from ethanol whereas (higher emergence of) CuO shifts the reaction towards ethyl acetate. Literature study on alumina supported copper catalysts [43-45] is in line with the behavior observed.

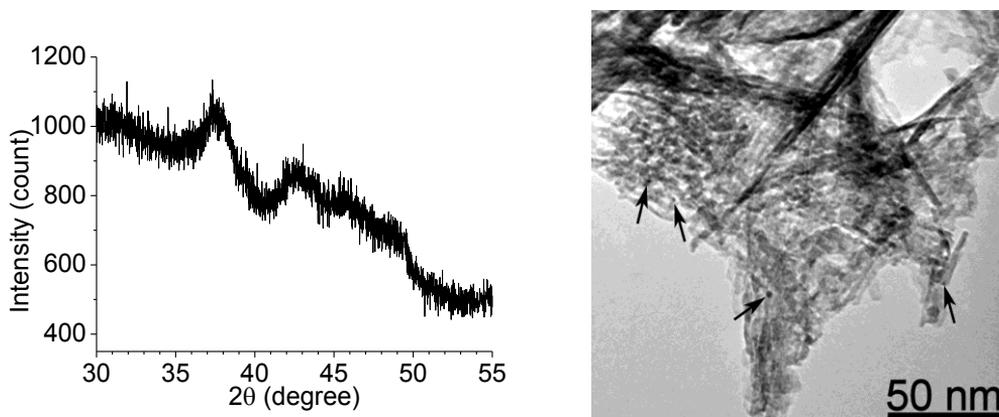


Figure 13. Characterization of Cu-1.8 catalyst using X-ray Powder Diffraction (no reflections) and Transmission Electron Microscopy.

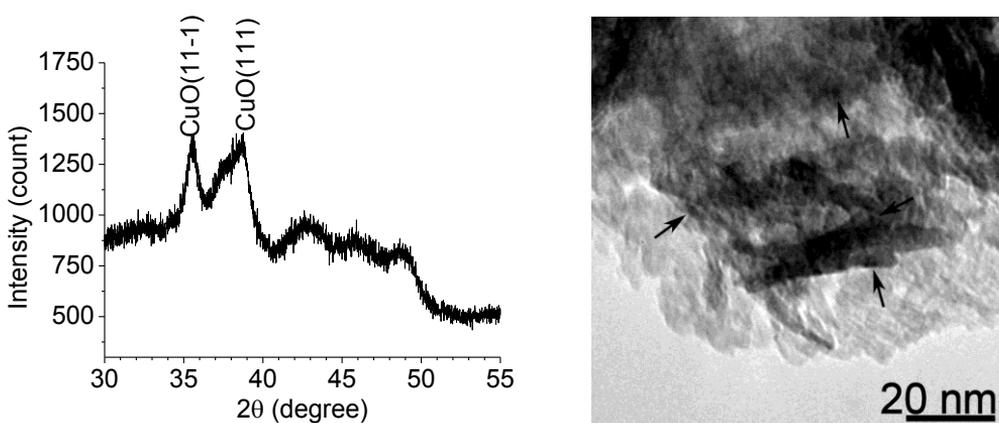


Figure 14. Characterization of Cu-4.5 (Cu 8.5 ± 0.7 nm) catalyst using X-ray powder diffraction and Transmission electron microscopy.

As previously discussed, cobalt provided the most interesting outcome by producing ethyl acetate with a high selectivity. However, a possible explanation related to the issue was still missing. By investigating the XRD and TEM results on cobalt catalysts (**Figure 15**), we can clearly notice an emergence of Co_3O_4 surface spinel structure. Surprisingly, by recalling supported Ni- and Cu-catalysts, formation of aluminates was verified (MAl_2O_4) which is different to that of cobalt. The literature view [46-47] supports the observed outcome and, additionally, the structure is known to consist of a similar spinel crystallite structure comparable to CuAl_2O_4 and NiAl_2O_4 .

There can be several reasons for the formation of ethyl acetate on the cobalt catalyst. For example, cobalt can work as a Lewis acid site ($\text{Co}^{2+}/\text{Co}^{3+}$) on the observed surface clusters (**Figure 15**) possibly providing similar tendency with the Cu-4.5 catalyst (small clusters). In addition, the use of high pressure [31] can also enhance the production of ethyl acetate. On the other hand, the reaction between ethanol and acetaldehyde can result in the formation of so called hemiacetal which may be involved in the reaction [30].

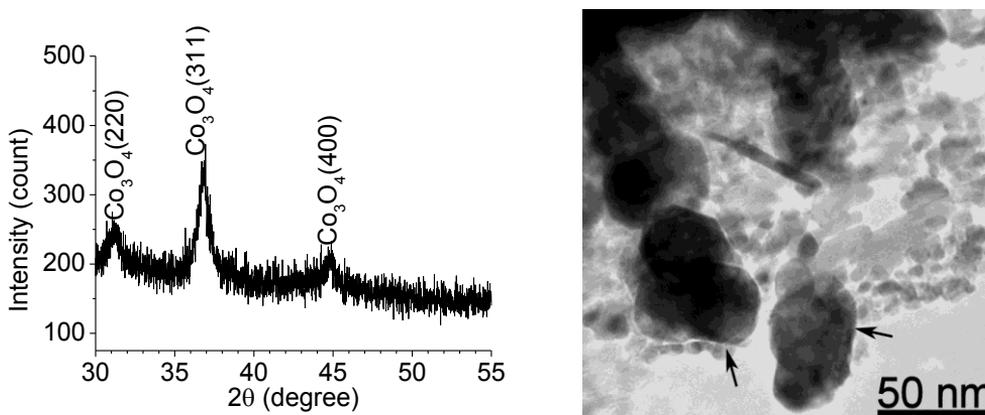


Figure 15. Characterization of Co-16 (Co_3O_4 10.0 ± 2.6 nm) catalyst using X-ray Powder Diffraction and Transmission Electron Microscopy.

All in all, we can suggest that spinel structures are the active sites in the production of butanol and ethyl acetate from ethanol. However, there is still a question among the spinels what determines the difference. Based on the literature [39-47], spinel can possess both tetrahedral and octahedral structures. The difference between these two structures is based on orientation of the corresponding metal (Ni, Cu). On octahedral sites, M^{2+} ions are located near the catalyst surface, whereas tetrahedral coordination results in a deeper location of M^{2+} ion. Additionally, tetrahedral coordination is known to cause strong metal support interaction between the investigated metal (Ni, Cu) and support resulting in higher acidity, whereas octahedral coordination results in an opposite effect. The phenomenon is clearly in line with the acidity measurements of nickel- and copper catalysts (**Table 2**).

Table 2. Determination of Brønsted - and Lewis acid sites of catalysts using FTIR-pyridine.

Catalyst	BAS (250 °C) (mmol/g _{cat})	BAS (350 °C) (mmol/g _{cat})	LAS (250 °C) (mmol/g _{cat})	LAS (350 °C) (mmol/g _{cat})
Ni-19	13	4	52	11
HTC-500	98	9	333	27
Co-16	0	14	73	3
Cu-1.8	11	5	52	88
Cu-4.5	16	9	87	138

Thus, as a conclusion, it can be suggested that octahedral spinel coordination is responsible for the production of 1-butanol whereas tetrahedral spinel coordination is observed upon formation of ethyl acetate. The graphical presentation on the issue is depicted in **Figure 16**. In addition, based on the atomic concentrations of recorded XPS spectra over Cu-catalysts, it can be concluded that relative abundance of $CuAl_2O_4/CuO$ is 7:1 on Cu-1.8 catalyst

and 2:1 on Cu-4.5 catalyst. Thus, it is obvious that surface spinels (Cu, Ni) are the catalytically active sites in the bio-ethanol valorization to bio-butanol. Thereafter, the difference observed between copper catalysts product profiles in comparison to nickel catalysts can be justified with the Jahn-Teller effect affecting the Cu^{2+} cations in the spinel structure. The phenomenon is known to promote octahedral copper aluminate spinel orientation in low loading of copper, whereas the opposite is noticed in higher loadings.

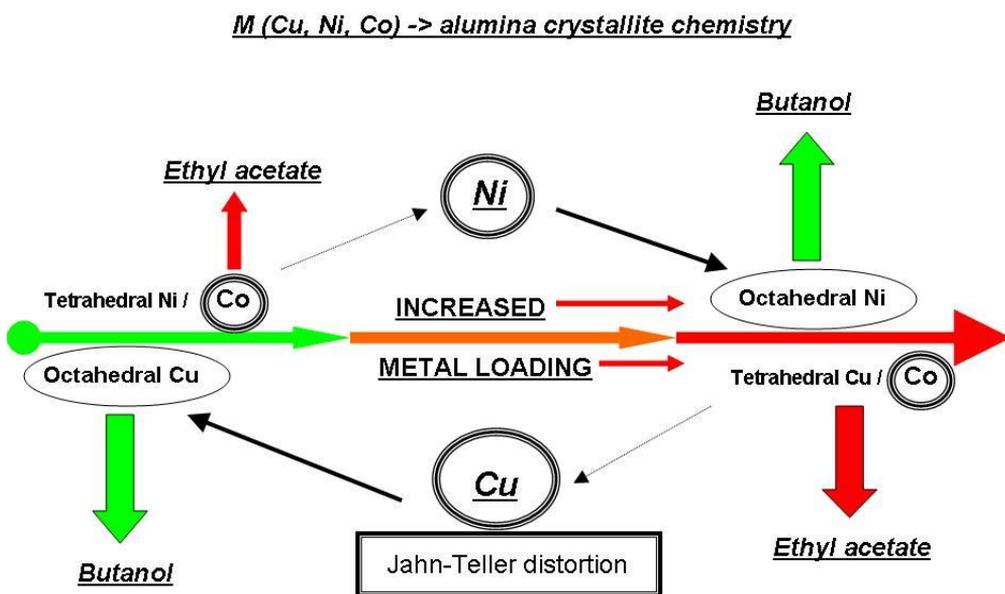


Figure 16. Suggested crystallite chemistry for the classification of Ni-, Cu- and Co-supported alumina catalysts. Relationship between tetrahedral-octahedral crystallite sites in comparison to 1-butanol and ethyl acetate.

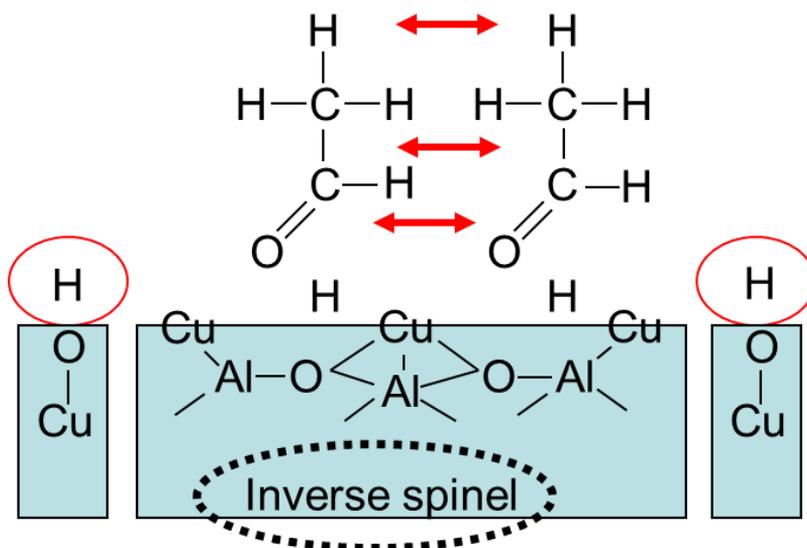


Figure 17 B. Oxidation of ethanol to acetaldehyde and aldol condensation between them. Accommodation of hydrogens on metal oxides.

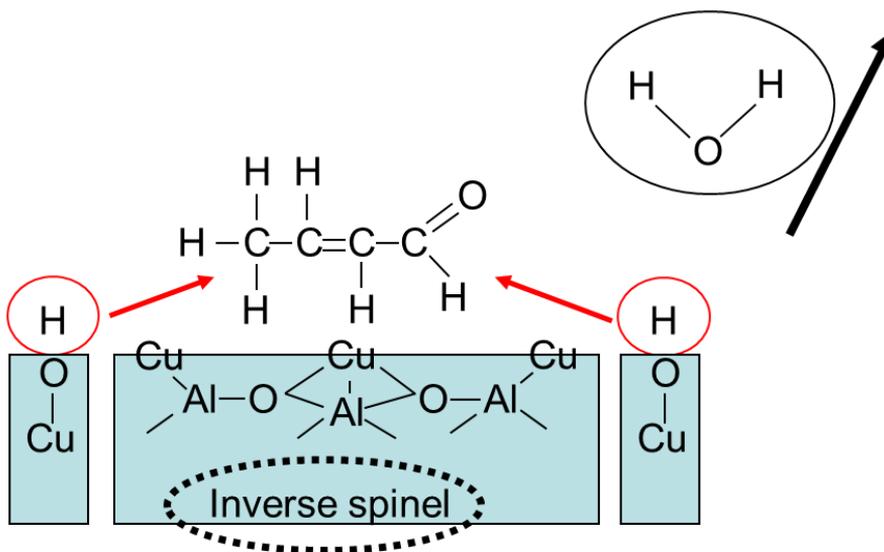


Figure 17 C. Hydrogenation of formed crotonaldehyde intermediate to 1-butanol

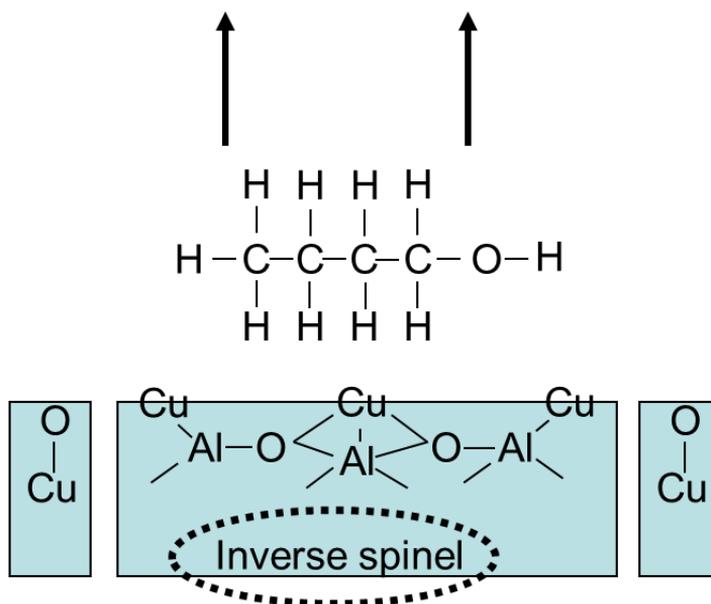


Figure 17 D. Desorption of 1-butanol from the catalyst surface.

Figure 17 A-D. Suggested reaction mechanism for aldol condensation of bio-ethanol to bio-butanol.

As previously discussed, the effect of crystallite structure is of utmost importance in the ethanol chemistry. However, from the engineering point of view, acid and base properties should also be addressed (**Figure 18**). It is generally recognized that close interaction between acid and base sites results in the formation of 1-butanol and other C_4 -products. Additionally, basic sites are known to be responsible for the formation of acetaldehyde and, thus, involved in aldol condensation reaction. Diethyl ether and ethylene are well investigated reaction products promoted by acid sites.

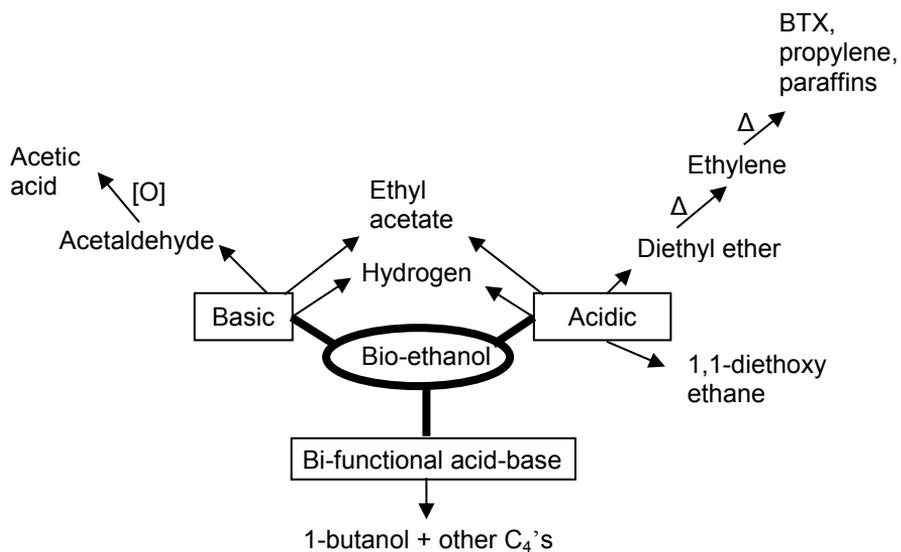
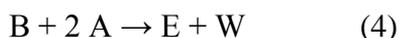


Figure 18. Schematic presentation of possible bio-ethanol based products.

3.4 Kinetics of Bio-Ethanol Valorization to Bio-Butanol

Kinetic modelling [IV] of ethanol valorization was based on acetaldehyde (1), 1-butanol (2), ethyl acetate (3), 1,1-diethoxy ethane (4) and diethyl ether (5) as described below.



where A = ethanol, B = acetaldehyde, C = **1-butanol**, D = ethyl acetate, E = 1,1-diethoxyethane, F = diethyl ether, H₂ = hydrogen and W = water.

It should be emphasized that the reaction scheme (1-5) does not represent the molecular mechanism on the catalyst surface, but just the overall reactions. The scheme above is based on the experimentally observed and identified chemical species in the experimental data.

The simplest way to approach the reaction kinetics is to use the law of mass action for reactions (1-5). This can be justified for the case that the amounts of adsorbed species are minor on the catalyst surface. Since the amount of experimental data is limited, the use of a more sophisticated model is unrealistic. The rate expressions are listed below:

$$R_1 = k_1 c_A \quad (6)$$

$$R_2 = k_2 c_A^2 \quad (7)$$

$$R_3 = k_3 c_A^2 \quad (8)$$

$$R_4 = k_4 c_A^2 c_B \quad (9)$$

$$R_5 = k_5 c_A^2 \quad (10)$$

For describing of the laboratory-scale fixed bed reactor, the pseudo-homogeneous plug flow model was used. Since the catalyst particles were small (150-250 micrometer) and the reaction rates relatively slow, the internal diffusion resistance in the porous catalyst particles was neglected. Calculation of the Thiele modulus gave a value of 0.07 or less which also confirms that the reaction conditions are clearly in the kinetic regime.

The feed to the reactor consisted of pure ethanol (A), which diminishes the role of external mass transfer resistance at the outer surfaces of the catalyst particles. Thus, the use of the pseudo-homogeneous reactor model is justified. The model is written as follows,

$$dc_i/d\tau = \rho_B r_i \quad (11)$$

where τ =the liquid residence time in the reactor, ρ_B is the catalyst bulk density (=mass of catalyst/reactor volume) and r_i is the component generation rate calculated from the stoichiometry:

$$r_i = \sum v_{ij} R_j \quad (12)$$

where the index j refers to the reaction ($R_1 \dots R_5$). Application of the stoichiometric relations (1-5) on eq. (12) gives the component generation rates as follows:

$$r_A = -R_1 - 2R_2 - 2R_3 - 2R_4 - 2R_5 \quad (13)$$

$$r_B = R_1 - R_4 \quad (14)$$

$$r_C = R_2 \quad (15)$$

$$r_D = R_3 \quad (16)$$

$$r_E = R_4 \quad (17)$$

$$r_F = R_5 \quad (18)$$

$$r_H = R_1 + 2R_3 \quad (19)$$

$$r_W = R_2 + R_4 + R_5 \quad (20)$$

The model thus consists of eight ordinary differential equations for A...W. The objective function for parameter estimation was the sum of squares equation.

$$Q = \sum (c_{i,\text{exp}} - c_{i,\text{model}})^2 \quad (21)$$

where *i* denotes the values of the organic components A, B, C, D, E, F. The concentrations predicted from the model were obtained from numerical solutions of eq. (11).

The temperature dependence of the rate constants (*k*) are taken into account with the Arrhenius equation.

$$k_j = k_{0j} e^{-\frac{E_{Aj}}{R} \left(\frac{1}{T} - \frac{1}{T'} \right)} \quad (22)$$

The backward difference method was used to solve the mass balances (system of ordinary differential equations ODE) and a hybrid method involving Simplex and Levenberg-Marquardt methods was used for estimation of the kinetic parameters, i.e. in the minimization of the objective function, eq. (21). The distribution and sensitivity of the parameters were controlled with the Markov-Chain Monte Carlo method (MCMC) [48]. In addition, the equilibrium constant was calculated to be 1800 at 250 °C in the investigated reaction.

Parameter estimation results

In the evaluation of the kinetic parameters, the frequency factors k_{01} - k_{04} and activation energies E_{A1} - E_{A4} were estimated. Reaction 5 was omitted, since diethylether (F) was formed in small amounts in the experiments.

The estimated parameter values, based on rate equations (6-10) are fitted of the model to the experimental data as depicted in **Figure 19** as a parity plot, model predicted concentrations (mol/m^3) vs. experiment concentrations (mol/m^3). **Figures 20-22** show the fit of the model to experimental data as function of residence time. **Figures 20-22** also show the confidence interval (95%, grey area in the figures) for the model. For the calculation of the probability regions of the model the Markov-Chain-Monte-Carlo (MCMC) method is used (Modest software). The formation of 1,1-diethoxy ethane (E) is low, and therefore, it is difficult to estimate the frequency factor and activation energy for reaction (4). The frequency factor k_{04} was identified with Simplex and Levenberg-Marquardt methods, but with a high error (77%), but the activation energy (E_{A4}) was estimated to be close to zero with a very large error. The reason for this is probably the low concentration of 1,1-diethoxyethane and/or larger experimental data error for this compound. The activation energy $E_{A,4}$ for reaction (4) predicted with the MCMC method is not as well identified as $E_{A,1-3}$ but has a broader optimum range = 10-25 kJ/mol.

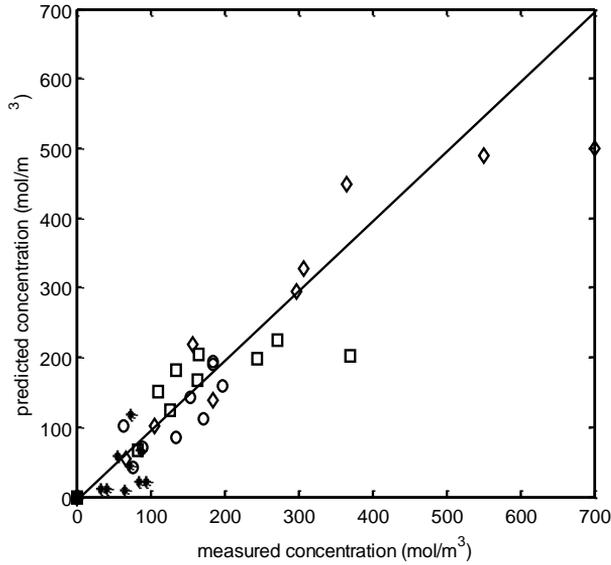


Figure 19. Parity plot model prediction vs. experimental data, concentration in mol/m³, (o acetaldehyde, □ butanol, ◇ ethyl acetate, * 1,1-diethoxy ethane)

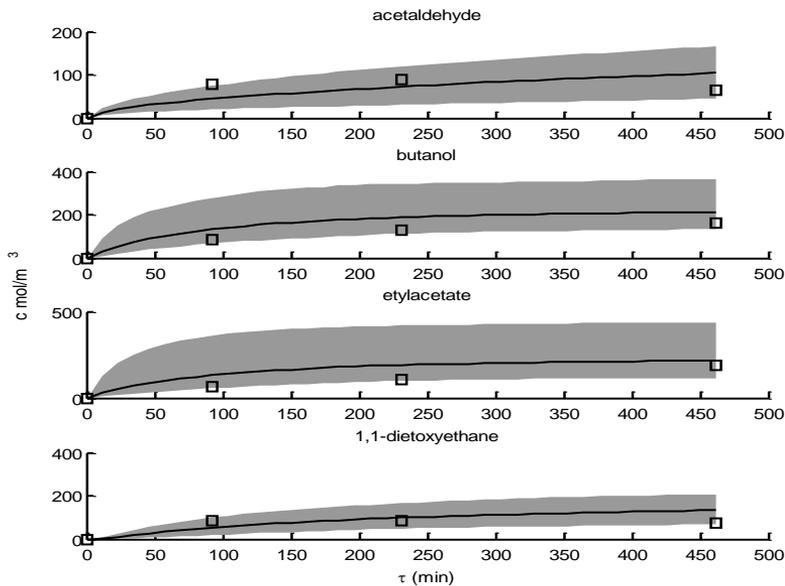


Figure 20. Fit of model prediction (-) to experimental data (□) at 200 °C, concentration (mol/m³) vs. residence time (min). The grey area shows the 95% confidence interval for the model.

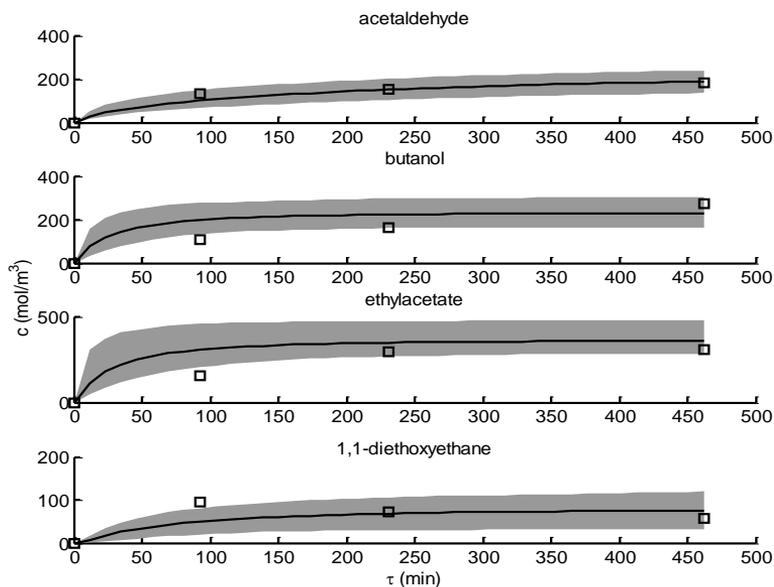


Figure 21. Fit of model prediction (-) to experimental data (\square) at 220 °C, concentration (mol/m^3) vs. residence time (min). The grey area shows the 95% confidence interval for the model.

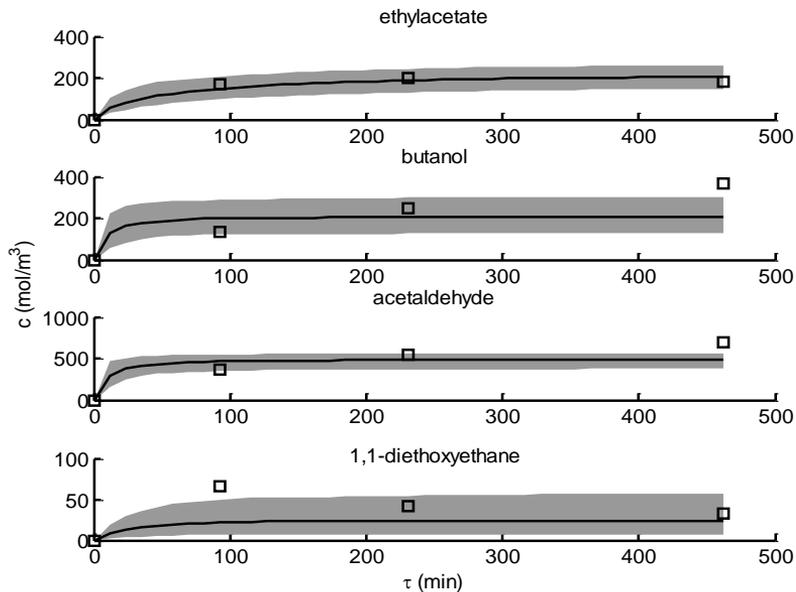


Figure 22. Fit of model prediction (-) to experimental data (\square) at 240 °C, concentration (mol/m^3) vs. residence time (min). The grey area shows the 95% confidence interval for the model.

4.

Conclusions

Consequently, we can conclude that bio-ethanol itself is not a chemical of the future, but instead, the derivatives of it can provide much more valuable bio-products for the society. Especially interesting products are 1-butanol and diethyl ether which may find some applications in automotive and (basic) industrial purposes.

In addition, there are also challenges which must be overcome before any large-scale biorefinery strategies become truly feasible in economic sense. Indeed, chemical reactors and heterogeneous catalysts are part of the biorefinery concept. However, the structures and preparation methods of heterogeneous catalysts in industrial scale are still big challenges.

The main findings of the thesis were based on the complex nature of the different crystallite structures and sensitivity of them in the determination of the bio-ethanol valorization product profile. In the synthesis of 1-butanol from ethanol, copper and nickel aluminates were found to be the active sites. The aluminate structure can possess tetrahedral or octahedral spinel coordinations, the former improving the synthesis of ethyl acetate and the latter one leading to the formation of 1-butanol. In addition, cobalt was observed to produce solely ethyl acetate because of the tetrahedral spinel coordination. Diethyl ether was formed on zeolite catalysts and factors affecting positively on it were the

increase in synthesis time, catalyst acidity and crystallite purity. The reaction kinetics was measured experimentally in a laboratory-scale tube reactor and a kinetic model was developed for the main and side reactions. The model described the system behaviour rather well.

A lot of research still lies ahead before bio-ethanol can be declared as the base-chemical of the future. In these types of operations, additional research considering e.g. aqueous ethanol solutions, the effect of feedstock impurities (e.g. sulfur) and catalyst deactivation should be carefully addressed. From an industrial viewpoint, aqueous 85 vol-% ethanol solution should be the main target since higher ethanol concentrations demand remarkably higher energy input and, thus, are not economically feasible processes. Overall, metal oxides such as alumina and zeolites with highly precise crystallite structures might provide a very useful platform for the future development work. It is also worth mentioning that hydrotalcite type catalyst structures may not be as successful as alumina in the synthesis of 1-butanol due to their limited process stability.

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References

- [1] S. Liu, H. Lu, R. Hu, A. Shupe, L. Lin, B. Liang, A sustainable woody biomass biorefinery, *Biotechnol. Adv.* 4 (2012) 785-810.
- [2] A. Limayem, S.C. Ricke, Lignocellulosic biomass for bioethanol production: Current perspectives, potential issues and future prospects, *Prog. Energy Combust. Sci.* 4 (2012) 449-467.
- [3] R.B. Phillips, H. Jameel, H.M. Chang, Integration of pulp and paper technology with bioethanol production, *Biotechnol. Biofuels* 13 (2013) 1-12.
- [4] B.L. Salvi, K.A. Subramanian, N.L. Panwar, Alternative fuels for transportation vehicles: A technical review, *Renew. Sust. Ener. Rev.* 25 (2013) 404-419.
- [5] O.I. Shapovalov, L.A. Ashkinazi, Biobutanol: Biofuel of second generation, *Russ. J. Appl. Chem.* 81 (2008) 2232-2236.
- [6] S.B. Pankar, S.A. Survace, H. Ojamo, T. Granström, Biobutanol: the outlook of an academic and industrialist, *RSC Adv.* 3 (2013) 24734-24757.
- [7] J.A. Posada, A.D. Patel, A. Roes, K. Blok, A.P.C. Faaij, M.K. Patel, Potential of bioethanol as a chemical building block for biorefineries: Preliminary sustainability assessment of 12 bioethanol-based products, *Bioresour. Technol.* 135 (2013) 490-499.

- [8] R. Thompson, M. Behnam, J. Swana, Y. Yang, An analysis of net energy production and feedstock availability for biobutanol and bioethanol, *Bioresour. Technol.* 102 (2011) 2112-2117.
- [9] D.C. Rakopoulos, C.D. Rakopoulos, E.G. Giakoumis, A.M. Dimaratos, Studying combustion and cyclic irregularity of diethyl ether as supplement fuel in diesel engine, *Fuel* 109 (2013) 325-335.
- [10] S. Szwaja, J.D. Naber, Combustion of n-butanol in a spark-ignition IC engine, *Fuel* 89 (2010) 1573-1582.
- [11] M. Trueba, S.P. Trasatti, γ -Alumina as a support for catalysts: A review of fundamental aspects, *Eur. J. Inorg. Chem.* (2005) 3393-3403.
- [12] E. Diaz, M. Leon, S. Ordonez, Ethanol catalytic conversion over Mg-Al mixed oxides derived from hydrotalcites, *Catal. Today* 164 (2011) 436-442.
- [13] L.C. Appel, L.E.P. Borges, R.R. de Avillez, D.L. Carvalho, M.T. Rodrigues, Mg and Al mixed oxides and the synthesis of n-butanol from ethanol, *Appl. Catal., A* 415-416 (2012) 96-100.
- [14] S. Ordonez, A. Auroux, E. Diaz, M. Leon, A. Vega, Consequences of the iron-aluminium exchange on the performance of hydrotalcite-derived mixed oxides for ethanol condensation, *Appl. Catal., B* 102 (2011) 590-599.
- [15] N. Tanchoux, F. Fajula, I.-C. Marcu, D. Tichit, Catalytic valorization of bioethanol over Cu-Mg-Al mixed oxide catalysts, *Catal. Today* 147 (2009) 231-238.

- [16] A. Onda, S. Ogo, K. Yanigisawa, Selective synthesis of 1-butanol from ethanol over strontium phosphate hydroxyapatite catalysts, *Appl. Catal., A* 402 (2011) 188-195.
- [17] D.L. Carvalho, L.E.P. Borges, L.G. Appel, P.R. de la Piscina, N. Homs, In situ infrared spectroscopic study of the reaction pathway of the direct synthesis of n-butanol from ethanol over MgAl mixed-oxide catalysts, *Catal. Today* 213 (2013) 115-121.
- [18] J.J. Bravo-Suárez, B. Subramaniam, R.V. Chaudhari, Vapor-phase methanol and ethanol coupling reactions on CuMgAl mixed metal oxides, *Appl. Catal. A* 455 (2013) 234-246.
- [19] I.-C. Marcu, N. Tanchoux, F. Fajula, D. Tichit, Catalytic Conversion of Ethanol into Butanol over M–Mg–Al Mixed Oxide Catalysts (M = Pd, Ag, Mn, Fe, Cu, Sm, Yb) Obtained from LDH Precursors, *Catal Lett* 143 (2013) 23-30.
- [20] T. Tsuchida, J. Kubo, S. Sakuma, T. Takeguchi, W. Ueda, T. Yoshioka, Reaction of ethanol over hydroxyapatite affected by Ca/P ratio of catalyst, *J. Catal.* 259 (2008) 183-189.
- [21] S. Ogo, A. Onda, Y. Iwasa, K. Hara, A. Fukuoka, K. Yanagisawa, 1-Butanol synthesis from ethanol over strontium phosphate hydroxyapatite catalysts with various Sr/P ratios, *J. Catal.* 296 (2012) 24-30.
- [22] N.J. Coville, A.S. Ndou, N. Plint, Dimerisation of ethanol to butanol over solid-base catalysts, *Appl. Catal., A* 251 (2011) 337-345.

- [23] T.W. Birky, J.T. Kozlowski, R.J. Davis, Isotopic transient analysis of the ethanol coupling reaction over magnesia, *J. Catal.* 298 (2013) 130-137.
- [24] C. Yang, Z. Meng, Bimolecular condensation of ethanol to 1-butanol catalyzed by alkali cation zeolites, *J. Catal.* 142 (1993) 37-44.
- [25] K. Shimura, K. Kon, S.M.A. Hakim Siddiki, K.-I. Shimizu, Self-coupling of secondary alcohols by Ni/CeO₂ catalyst, *Appl. Catal. A* 462–463 (2013) 137-142.
- [26] J.T. Kozlowski, R.J. Davis, Sodium modification of zirconia catalysts for ethanol coupling to 1-butanol, *J. Energ. Chem.* 1 (2013) 58-64.
- [27] X. Zhanbg, Z. Liu, X. Xu, H. Yue, G. Tian, S. Feng, Hydrothermal synthesis of 1-butanol from ethanol catalyzed with commercial cobalt powder, *ACS Sustainable Chem. Eng.* 1 (2013) 1493-1497.
- [28] X.Z. Jiang, K.W. Yang, W.C. Zhang, One-step synthesis of n-butanol from ethanol condensation over alumina-supported metal catalysts, *Chin. Chem. Lett.* 15 (2004) 1497-1500.
- [29] K. Inui, N. Ichikawa, T. Kurabayashi, S. Sato, Effective formation of ethyl acetate from ethanol over Cu-Zn-Zr-Al-O catalyst, *J. Mol. Catal. A: Chem.* 216 (2004) 147-156.
- [30] A.B. Gaspar, F.G. Barbosa, S. Letichevsky, L.G. Appel, The one-pot ethyl acetate syntheses: The role of the support in the oxidative and the dehydrogenative routes, *Appl. Catal. A* 1–2(2010) 113-117.

- [31] K. Inui, T. Kurabayashi, S. Sato, Direct synthesis of ethyl acetate from ethanol carried out under pressure, *J. Catal.* 2 (2002) 207-215.
- [32] K. Inui, T. Kurabayashi, S. Sato, Direct synthesis of ethyl acetate from ethanol over Cu-Zn-Zr-Al-O catalyst, *Appl. Catal. A* 1–2 (2002) 53-61.
- [33] G.A. Olah, T. Shamma, G. K. S. Orakash, Dehydration of alcohols to ethers over Nafion-H, a solid perfluoroalkanesulfonic acid resin catalyst, *Catal. Lett.* 1-2 (1997) 1-4.
- [34] I. Takahara, M. Saito, M. Inaba, K. Murata, Dehydration of ethanol in ethylene over solid acid catalysts, *Catal. Lett.* 3-4 (2005) 249-252.
- [35] T. Zaki, Catalytic dehydration of ethanol using transition metal oxide catalysts, *J. Colloid Interface Sci.* 2 (2005) 606-613.
- [36] F.F. Madeira, N.S. Gnep, P. Magnoux, S. Maury, N. Cadran, Ethanol transformation over HFAU, HBEA and HMF1 zeolites presenting similar Brønsted acidity, *Appl. Catal. A* 1–2 (2009) 39-46.
- [37] S. Arenamnar, W. Trakarnpruk, Ethanol conversion to ethylene using metal-mordenite catalysts, *Int. J. Appl. Sci. Eng.* 4 (2006) 1, 21-32
- [38] B.H. Bolt, F.H.B.M. Habraken, J.W. Geus, Formation of nickel, cobalt and iron aluminates from α - and γ -alumina-supported oxides: A comparative study, *Solid State Chem.* 135 (1998) 59-69.

- [39] Y. Li, R. Shi, R. Wang, M. Yang, Effect of metal-support interaction on the catalytic performance of Ni/ Al₂O₃ for selective hydrogenation of isoprene, *J. Mol. Catal. A: Chem.* 344 (2011) 122-127.
- [40]] M. Absi-Halabi, K. Al-Dolama, A. Stanislaus, Effect of nickel on the surface acidity of γ -alumina and alumina-supported nickel-molybdenum hydrotreating catalysts, *Appl. Catal.* 50 (1989) 237-245.
- [41] K.V.R. Chary, P.V.R. Rao, V.V. Rao, Catalytic functionalities of nickel supported on different polymorphs of alumina, *Catal. Commun.* 9 (2008) 886-893.
- [42] J.E. Sueiras, J.L.G. Fierro, F. Medina, P. Salagre, Characterization of nickel species on several γ -alumina supported nickel samples, *J. Mol. Catal. A: Chem.* 106 (1996) 125-134.
- [43] K. Shimizu, H. Yoshida, T. Hattori, H. Maeshima, A. Satsuma, Spectroscopic characterisation of Cu-Al₂O₃ catalysts for selective catalytic reduction of NO with propene, *Phys. Chem. Chem. Phys.* 2 (2000) 2435-2439.
- [44] J.S. Ledford, P.W. Park, The influence of surface structure on the catalytic activity of alumina supported copper oxide catalysts. Oxidation of carbon monoxide to methane, *Appl. Catal., B* 15 (1998) 221-231.
- [45] P.K. Rao, Ch. Sivaraj, ESCA characterization of copper/alumina catalysts prepared by deposition-precipitation using urea hydrolysis, *Appl. Surf. Sci.* 51 (1991) 27-33.

[46] B. Jongsomjit, J.G.Jr Goodwin, J. Panpranot, Co-support compound formation in alumina-supported cobalt catalysts, *J. Catal.* 204 (2001) 98-109.

[47] J.G.Jr Goodwin, A. Horvath, R. Oukaci, A. Sirijaruphan, Cobalt aluminate formation in alumina-supported cobalt catalysts: effects of cobalt reduction state and water vapor, *Catal. Lett.* 91 (2003) 89-94.

[48] Modest User's Guide, Profmath Oy, Helsinki 2002



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