Article

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

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Abstract: Direct catalytic valorization of bioethanol to 1-butanol over different alumina supported catalysts was studied. Thirteen (13) heterogeneous catalysts were screened in search for the optimal material composition for direct one-pot conversion of ethanol to 1-butanol. For the most promising catalyst, a 25% ethanol conversion with 80% selectivity (among liquid carbon products) to 1-butanol could be reached at 250 °C. Additionally, the reaction kinetics and mechanisms were further investigated upon use of the most suitable catalyst candidate.

1. Introduction

Ethanol is currently the biggest liquid biofuel contributor worldwide. The first generation bioethanol production often employs edible food crops as raw materials and thus gives rise to increased food prices by competing with human food and animal feed production. In order to overcome this problem, the second generation biofuels are increasingly prepared from non-edible raw materials, e.g., wood, agricultural waste and other lignocellulosic materials [1–3]. In Nordic countries, the biofuel research focuses heavily on the use of woody biomass as a raw material for bioethanol and other biofuels. Finland and Sweden have the largest wood resources in Europe per capita, which makes wood a natural choice of raw material. However, there are still many problems associated with the use of ethanol fuel in internal combustion engines, e.g., its water solubility, corrosivity and the differences in its fuel properties compared to modern gasoline. These problems have to be overcome before the full potential of bioethanol can be utilized.

In order to overcome the disadvantages of ethanol as a fuel, catalytic valorization of ethanol to higher alcohols, e.g., 1-butanol can be carried out. Compared to ethanol, 1-butanol (or *n*-butanol) has several advantages: it can be burned in the existing gasoline engines without practically any engine or car modifications and it has higher energy content and air-to-fuel ratio than ethanol making 1-butanol an excellent green replacement for a modern gasoline. In summary, the properties of 1-butanol closely resemble the properties of modern gasoline (Table 1).

Table 1. Chemical and physical properties of gasoline, diesel, 1-butanol and ethanol. Data is reproduced from reference [4].

Fuel	Energy density/ MJ L^{-1}	Air-to-fuel ratio	Energy content/ Btu/USgallon	RON [a]	Water solubility/%
Gasoline	32	14.6	114,000	81–89	negligible
Diesel	35.5	14.7	130,000	-	negligible
1-butanol	29.2	11.12	105,000	78	7
Ethanol	19.6	8.94	84,000	96	100

[a] Research octane number.

Furthermore, another advantage of 1-butanol is the fact that it can be distributed via the existing pipelines for gasoline. In the end, it is an advantage if the consumer does not notice a difference when using 1-butanol as a fuel instead of modern gasoline in a gasoline driven vehicle.

1-Butanol is an important chemical feedstock and around 2.9 million tons was utilized by the industry in 2005. 1-Butanol can be synthesized by several routes such as the oxo-process [5–10], the acetaldehyde method or by fermentation.

In the open literature, only a few reports describe the direct catalytic dimerisation or conversion of ethanol to 1-butanol and other hydrocarbons [11–16]. These described technologies suggest a two-phase process where ethanol vapor is passed through a solid catalyst packed in a fixed bed. The

reaction temperatures vary from 200 °C up to 450 °C, with a relatively low conversion (10–20%) and selectivity approaching 70%. In the recent literature, a novel catalytic process utilizing a non-stoichiometric hydroxyapatite was found to be very promising [11,15]. In addition, solid bases [15], some zeolites [14], and supported metals (e.g., Ni, Co) [12] have been reported to convert ethanol to 1-butanol. To the best of our knowledge, until today no reports exist that describe a liquid-phase process for this particular reaction.

The conversion of biomass to valuable chemicals is a multi-step processes containing both chemical and catalytic reaction steps. By applying traditional approach and carrying out these conversions in separate reactors followed by subsequent separation, purification and drying steps would become complicated and expensive to realize in practice. Furthermore, in such a multi-step process, a lower yield of the end product with large amount of waste would be expected. One-pot reactions are capable of addressing these issues which involve multiple catalytic reaction steps in a single reactor unit. In this work, we demonstrate that conversion of ethanol to 1-butanol in one-pot manner is possible with high selectivity and conversion. The reaction was carried out in one pot without additional solvents in the absence of any catalyst pretreatments. For the most promising catalyst, a 25% ethanol conversion with 80% selectivity (among liquid carbon products) to 1-butanol could be reached.

For the catalytic conversion of liquid ethanol to 1-butanol several alumina supported heterogeneous catalysts were screened by applying a direct one-pot approach using only ethanol, catalyst and heating of the stirred mixture to carry out the reaction. The desired overall reaction scheme is presented in Scheme 1. The results from kinetic and mechanistic studies including catalyst characterization results will be presented here. Reaction schemes are presented in supplementary material.

Scheme 1. Dimerisation of ethanol to 1-butanol.
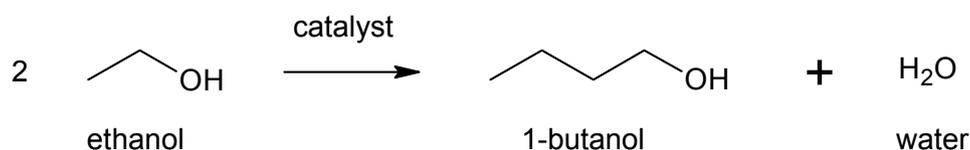
2. Results and Discussion

A large selection of heterogeneous alumina supported catalysts were screened for direct one-pot conversion of ethanol to 1-butanol at 250 °C as described in the experimental section. Catalyst characterization details are reported in Table 2 and preparation procedures in supplementary material. The best catalyst was studied in more detail employing kinetic and mechanistic experiments.

2.1. Catalyst Screening

The main products were acetaldehyde, diethyl ether, ethyl acetate, 1-butanol, 1,1-diethoxy ethane, 1-hexanol and 1-octanol which typically accounted for over 90% of the formed products. Their relative amounts varied depending on the choice of the catalyst. Also traces of other hydrocarbons were formed during some screening experiments. The higher C-6 and C-8 alcohols could be detected during prolonged experiments indicating that the reaction can proceed further from dimers of ethanol as well as to tri- and tetramers of ethanol. No odd number (C-3, C-5, C-7) alcohols were detected in the

screening experiments (based on GC-MS analysis). This kind of product distribution may be related to so called Guerbet reaction which produces branched alcohols from primary ones [15]. The product composition varied greatly over various tested catalysts. Mini-reactor experiments were used to find out the most selective catalyst (Table 2) for ethanol to 1-butanol production. Typical conversion of ethanol (after 3 h of reaction) in the mini-reactor screening experiments was approximately 2–5%. In control experiments without a catalyst, the conversion of ethanol remained around 1% and only acetaldehyde and diethyl ether were formed.

Table 2. Summary of the catalyst characterization results.

	Catalyst	Code	Metal dispersion (%) [a]	Metal particle size (nm), H_2 chemisorption [a]	Metal particle size (nm) [b], TEM	Metal particle size (nm) [c], XRD	Surface Area (m^2/g) [d]
1	5% Ru/Al$_2$O$_3$	H213B	37.88	3.49	2.5 ± 1.1	n.m.	105
2	5% Rh/Al$_2$O$_3$	G214RA	54.21	2.03	2.6 ± 1.3	n.m.	308
3	5% Pd/Al$_2$O$_3$	E213R	17.51	6.40	3.5 ± 1.7	4.2 ± 0.2	127
4	5% Pt/Al$_2$O$_3$	F214 XSP/D	n.m.	n.m.	2.5 ± 1.9	2.8 ± 0.2	n.m.
5	0.8% Au/Al$_2$O$_3$	MINTEK1/BC3	n.m.	n.m.	n.m.	n.m.	n.m.
6	Ni/Al$_2$O$_3$	Crossfield/ HTC-500	n.m.	n.m.	8.2	n.m.	n.m.
7	20% Ni/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	3.5 ± 0.2	n.m.	289
8	2% Ag/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	5.2 ± 2.1	n.m.	289
9	4% Ag/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	1-5 and 10-40	n.m.	289
10	6% Ag/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	n.m.	n.m.	289
11	1% Ru/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	n.m.	n.m.	289
12	2% Ru/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	n.m.	n.m.	289
13	5% Ru/Al$_2$O$_3$	Self-prepared	n.m.	n.m.	1-7 and 100	n.m.	289

[a] From hydrogen chemisorptions; [b] Based on transmission electron microscopy (TEM); [c] Based on X-ray diffraction (XRD); [d] Obtained from nitrogen physisorption; n.m. = not measured.

The following qualitative conclusions can be drawn for the formed liquid hydrocarbon products from the catalyst screening experiments which give valuable guidelines for the future catalyst development:

Ru: Commercial 5% Ru on alumina and self-prepared 1-, 2- and 5% Ru on alumina were tested (Table 3). 1-butanol selectivity was 30% when the commercial catalyst was evaluated. The self-prepared Ru-catalysts showed lower selectivity towards 1-butanol when compared to the commercial one but the conversion was much higher. One possible explanation might be the formation of gaseous products over the self-prepared catalysts. A reduced catalyst promoted the formation of diethyl ether. The same catalyst reduction effect was observed for Ni on alumina catalyst as well. For all catalyst screening experiments, the commercial supported metal catalysts were used as received in unreduced state. TEM and XRD were measured over the self-prepared 5% Ru on alumina catalyst (Figure 1).

Table 3. Results obtained with alumina supported Ru catalysts.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Degussa	5% Ru/Al$_2$O$_3$	H213 B/D	2	8	1	0	**30**	19
La Roche	1% Ru/Al$_2$O$_3$ (self-prep.)	A 201	8	50	18	0	**0**	33
La Roche	2% Ru/Al$_2$O$_3$ (self-prep.)	A 201	11	54	8	0	**4**	33
La Roche	5% Ru/Al$_2$O$_3$ (self-prep.)	A 201	12	54	3	2	**9**	31

Figure 1. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) images of self-prepared 5 wt% Ru/Al$_2$O$_3$ catalyst. XRD shows the existence of RuO$_2$ and the particle size distribution varies between 1–7 nm. In addition, particles up to 100 nm were also found.
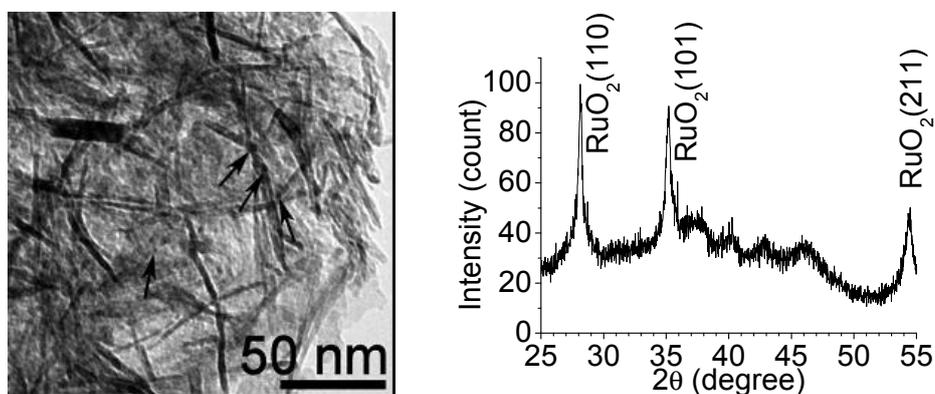
Rh: Commercial 5% Rh on alumina was tested (Table 4). Rh on alumina produced diethyl ether (S = 30%) and 1-butanol (S = 35%). In comparison to ruthenium (Degussa H 213 B/D), rhodium might have a promoting effect on alumina leading to an increase in the catalyst acidity and, thus, higher diethyl ether formation.

Table 4. Results obtained with alumina supported Rh catalyst.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Degussa	5% Rh/Al$_2$O	G214 RA/D	5	4	41	0	**35**	4

Pd: Commercial Pd on alumina was screened (Table 5) and the results (S$_{butanol}$ = 21%) follow almost similar behavior with the rhodium, promoting the formation of diethyl ether.

Table 5. Results obtained with alumina supported Pd catalyst.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Degussa	5% Pd/Al$_2$O$_3$	E213 R/D	9	3	64	1	**21**	2

Pt: Commercial Pt catalyst was found to contain a positive impact ($S_{butanol}$ = 37%) on the desired product (Table 6) and, furthermore, the selectivity towards diethyl ether was much lower in comparison to Pd and Rh.

Table 6. Results obtained with alumina supported Pt catalyst.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Degussa	5% Pt/Al$_2$O$_3$	F 214 XSP/D	3	9	10	9	**37**	8

Ag: The self-prepared silver catalysts were rather inactive towards 1-butanol giving selectivities between 13–20%. However, also a rather high selectivity to acetaldehyde and 1,1-diethoxy ethane were observed (Table 7). TEM and XRD were measured over the self-prepared 4% Ag on alumina catalyst (Figure 2).

Table 7. Results obtained with alumina supported Ag catalysts.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
La Roche	2% Ag/Al$_2$O$_3$	A 201 (self-prep.)	1	48	12	4	**16**	20
La Roche	4% Ag/Al$_2$O$_3$	A 201 (self-prep.)	1	49	13	4	**13**	20
La Roche	6% Ag/Al$_2$O$_3$	A 201 (self-prep.)	2	45	11	6	**20**	16

Figure 2. TEM and XRD pictures of self-prepared 4 wt% Ag/Al$_2$O$_3$ catalyst. XRD reveals metallic silver with an average crystal size of ~13 nm. The particle size analysis based on TEM measurements shows a bimodal size distribution with ranges of 1–5 nm and 10–40 nm.
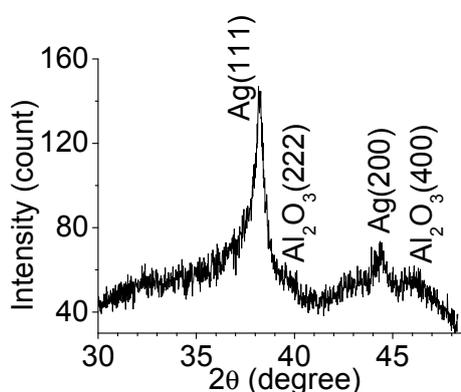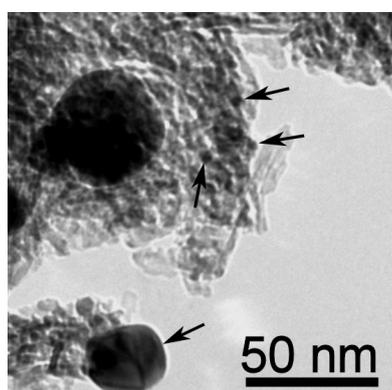

Ni: Two types of nickel catalysts were tested (Table 8). Overall, the commercial HTC-500 (20.7% Ni on alumina) was the best catalyst within the whole series of catalysts screened in terms of selectivity (62%). Also self-prepared 20% Ni on alumina (La Roche) showed moderate selectivity (37%) towards 1-butanol but the conversion was almost four times higher in comparison to the

HTC-500, producing a significant amount of acetaldehyde. Both nickel catalysts were characterized by means of XRD and TEM (Figures 3 and 4). Interestingly, the self-prepared catalyst shows a considerably smaller particle size distribution and it does not contain any aggregates which are presumed to be inactive parts.

Table 8. Results obtained with alumina supported Ni catalysts.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Crossfield	20% Ni/Al$_2$O$_3$	HTC-500	5	5	7	4	**62**	3
La Roche	20% Ni/Al$_2$O$_3$	Self-prepared	18	43	5	4	**37**	11

Figure 3. TEM and XRD pictures of self-prepared Ni/Al$_2$O$_3$ catalyst. Based on the results it can be seen that both Ni and NiO are found with average particle sizes of ~4 nm for both phases.
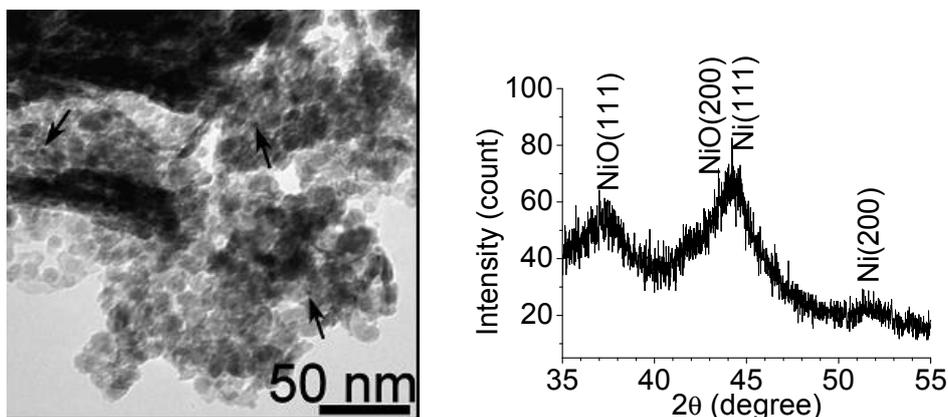
Figure 4. TEM and XRD images of the commercial model catalyst 20.7 wt% Ni/Al$_2$O$_3$ HTC-500. The average particle size was found to be about twice as much as for the self-made Ni-catalyst and showed considerably broad size dispersion.
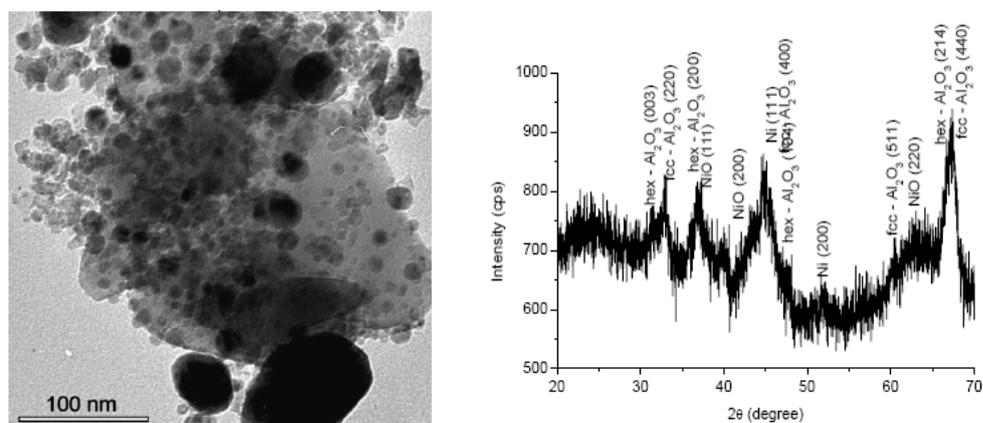
Au: The commercial gold catalyst showed an interesting behavior by producing a moderate selectivity to 1-butanol (35%) and also some amounts of acetaldehyde, ethyl acetate and diethyl

acetate (Table 9). This might be due to the ability of gold to promote different and simultaneous reaction pathways.

Table 9. Results obtained with alumina supported Au catalyst.

Manufactured	Catalyst	Product code	Conversion (%)	Selectivity (%)				
				acetaldehyde	diethyl ether	ethyl acetate	1-butanol	1,1-diethoxy ethane
Mintek	0.8% Au/Al$_2$O$_3$	BC3	6	18	31	15	**35**	0

2.2. Validation of the Bomb Reactor Screening Experiments

The reproducibility of the experiments was controlled by repeating experiments with same catalyst at least twice. For each and every test batch of eight (8) mini-bomb reactors, a reference catalyst was used to control the experimental reproducibility. When the product distribution obtained in mini-bomb reactors was compared with the products obtained in the Parr autoclave, under similar conditions and with the same catalyst, it was evident that analogous results were obtained, *i.e.*, the process is scaleable.

Out of all screened catalysts, the catalyst HTC-500 (20.7% Ni on alumina) was clearly the best one giving a good conversion (X = 5%) and highest selectivity (S$_{butanol}$ = 62%) in the whole series. Nevertheless, it is expected that after optimizing catalyst properties and reaction conditions, the selectivity, activity and ethanol conversion could be notably improved.

2.3. Kinetics and Mechanistic Studies with HTC-500 (20.7% Ni on Alumina)

Based on the results from the screening experiments (Tables 3–9) commercial Ni/Al$_2$O$_3$ (HTC-500) was chosen for further studies in batch reactor.

The reaction kinetics was investigated in the 300 mL Parr autoclave using the identical catalyst-to-ethanol ratio as in the miniature bomb reactors. Commercial (Crosfield HTC-500, 20.7% Ni on alumina) catalyst was used in the experiments. The temperature profile in the larger batch reactor during the reaction was similar consisting of 15–20 min heating period after which an isothermal reaction was carried out at 250 °C. Analysis of samples taken at time zero and at the time when the desired reaction temperature was reach revealed that negligible ethanol conversion took place during the short (15–20 min) reactor heating step. A representative kinetic plot is illustrated in Figure 5 which shows the conversion of ethanol and the selectivity of 1-butanol among liquid carbon products as a function of time. Moreover, the behavior of side products concentration evolvement is illustrated in Figures 6 and 7, respectively. Interestingly, the behavior of acetaldehyde and 1,1-diethoxy ethane follow a different pattern than that of ethyl acetate, butyraldehyde, diethyl ether and 1-hexanol. Concentrations of the later mentioned by-products illustrate a stable upward trend whereas acetaldehyde and 1,1-diethoxy ethane concentrations seem to peak in early stages of the reaction followed by a sharp decrease. It might be that acetaldehyde and 1,1-diethoxy ethane have a remarkable effect on the reaction in question. The larger scale (300 mL instead of 2 mL) autoclave allowed sampling of the liquid-phase during the course of the reaction under controlled temperature and pressure. The gas-phase composition could be analyzed by MS after the reaction. When the

experiments were repeated over the same catalyst it was observed that the reproducibility of the results was within 1%.

Figure 5. Valorization kinetics of ethanol to 1-butanol over a Ni catalyst (HTC-500) in the batch reactor. Reaction conditions: 250 °C, 70 bar. Selectivity calculated among liquid carbon products.
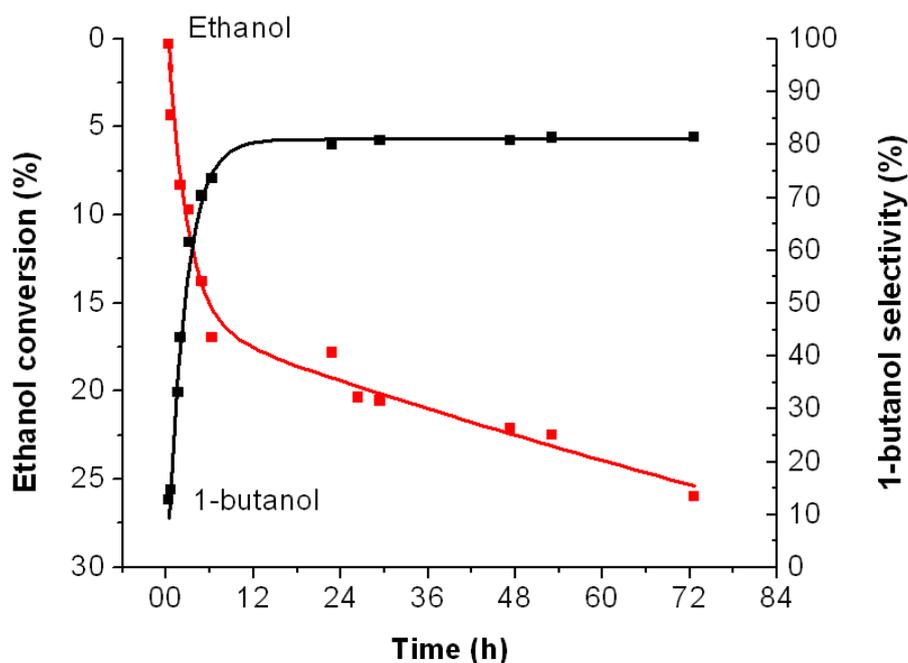
Figure 6. Ethyl acetate, 1-hexanol, diethyl ether and butyraldehyde concentrations as a function of time.
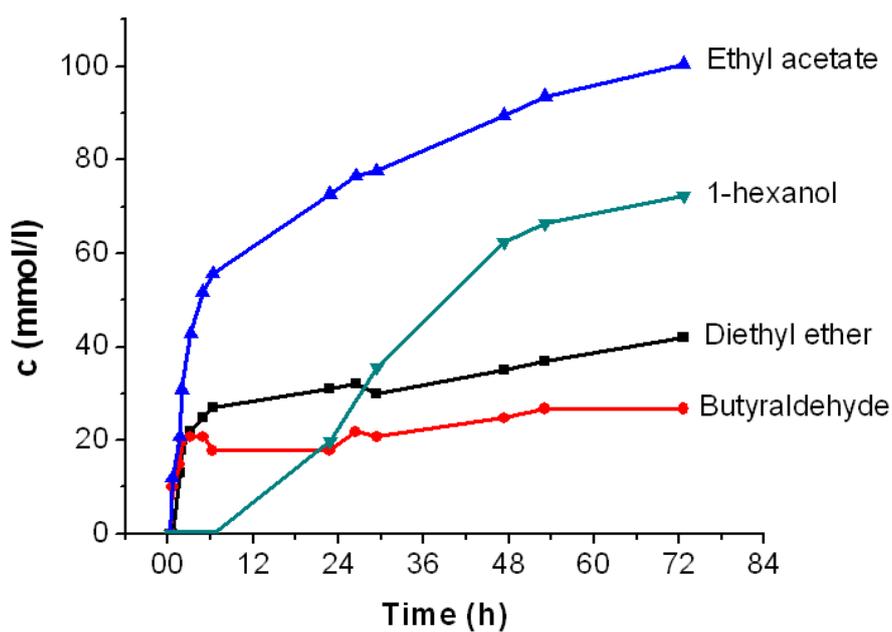
Figure 7. Acetaldehyde and 1,1-diethoxy ethane concentrations plotted as the function of time.
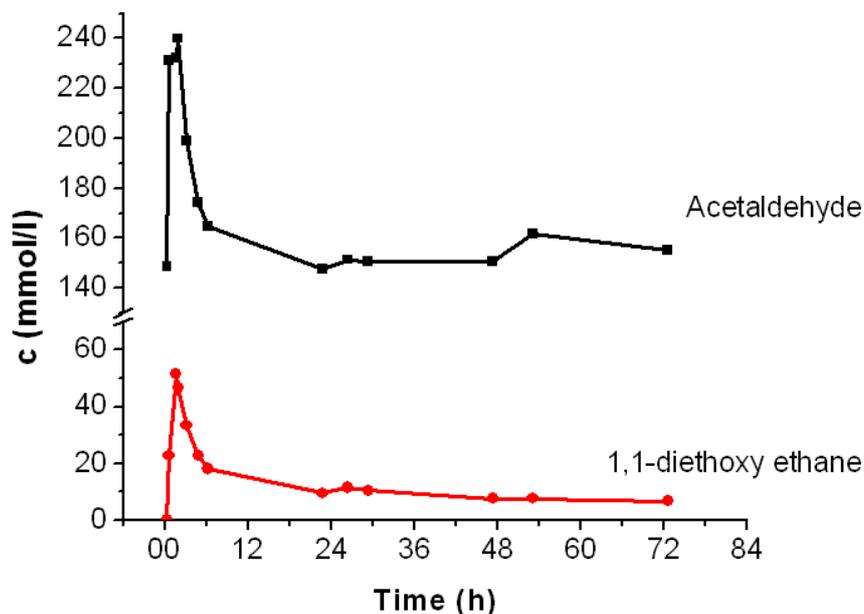

2.3.1. Gas-Phase Analysis after the Reaction

After heating the reactor to 250 °C, the pressure started gradually to increase from 76 bar to about 83 bar after which pressure remained virtually constant. The gas-phase analysis was conducted after the reactor was cooled down to room temperature (RT). At RT, the residual gas-phase was analyzed by a mass spectrometer (the gas-phase composition was similar in all carried experiments over the HTC-500). It was found that the gas composition was roughly 2/3 of hydrogen and 1/3 of methane. Only traces of carbon monoxide and carbon dioxide were found.

During the course of the reaction, gaseous hydrogen ($P_{hydrogen}$ = 4 bar) that might promote hydrogenation of the intermediate products, was formed in the reactor. The chosen Ni/alumina catalyst is a known good catalyst for C=O and C=C bond hydrogenations. Moreover, it is also suggested that nickel might promote C–C-bond breaking of the ethanol molecule. Thus, this would lead to the emergence of hydrogen and methane [17]. Consequently, the previously proposed reaction sequence starting from dehydration of ethanol to acetaldehyde followed by aldol condensation and subsequent hydrogenation to 1-butanol sounds logical. However, in mechanistic studies when various amounts of acetaldehyde was present, the "promoting effect" could not be detected. Presence of acetaldehyde produced a lot of by-products (a total of 50–80 products) which could not be properly separated or identified.

The role of hydrogen was investigated in more detail by inserting known amounts of hydrogen in the reactor. Based on experiments at different initial hydrogen pressures, it could be concluded that the reaction rate decreased with increasing initial hydrogen pressure. Another point, which is related to the formation of gaseous hydrogen during the reaction, is that in the kinetic experiments the ethanol conversion *vs.* time curve and the hydrogen pressure vs. time curve follow an identical trend. It would be a plausible explanation that the *in-situ* formed hydrogen is inhibiting the ethanol dimerization reaction which proceeds well over an oxidized catalyst. The effect of initial hydrogen pressure to 1-butanol formation is presented in Figure 8 as a function of time.

Figure 8. The effect of different initial hydrogen pressures to the forming amounts of 1-butanol.
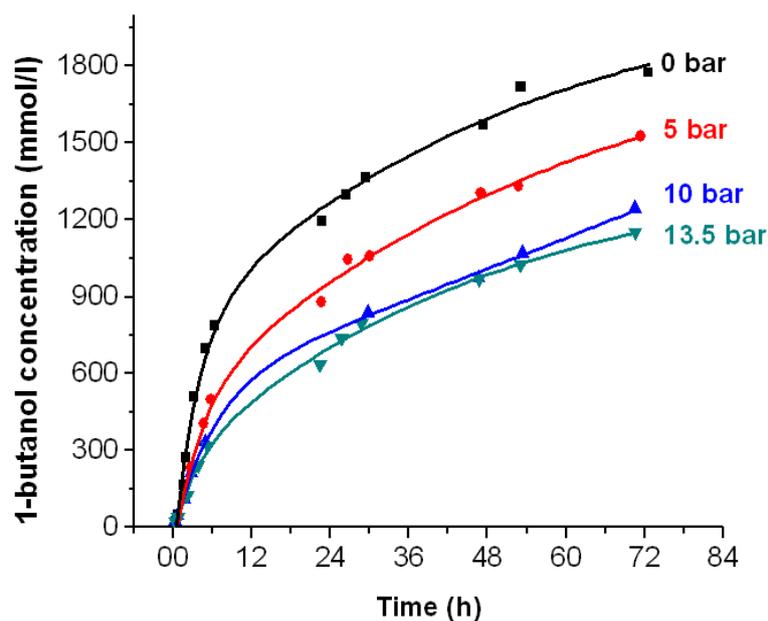
2.3.2. Catalyst Pretreatment

HTC-500 catalyst was reduced at 400 °C (maximum temperature for the reactor setup) under hydrogen for 3 h or used as received. The influence of added oxygen (3 bar) was also tested. The catalyst activity was independent on the pretreatments employed here. Selectivity towards diethyl ether was notably increased by a reductive pretreatment, simultaneously lowering the selectivity towards 1-butanol (Figure 9). The added oxygen had no detectable influence on the reaction. It seems that the Ni/alumina catalyst gives the highest selectivity when used without any reduction in the oxidized state.

Figure 9. Effect of catalyst pretreatment on diethyl ether formation over a Ni catalyst (HTC-500) in the bath reactor. Reaction conditions: 250 °C, 70 bar.
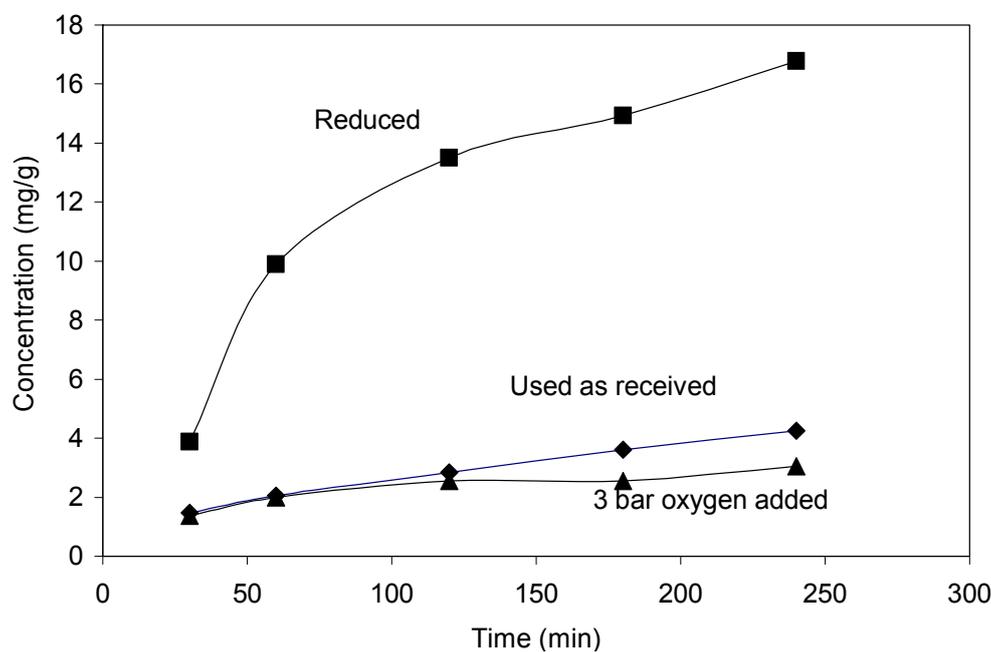
2.3.3. By-Product Formation

Formation of by-products, *i.e.*, acetaldehyde, diethyl ether, ethyl acetate and 1,1-diethoxyethane, can be explained by commonly known organic reactions [18] taking place under reaction conditions applied in the present work. Acetaldehyde is expected to emerge from the dehydrogenation of ethanol according to Scheme 2. At the same time, it also results in the formation of hydrogen that was experimentally observed as the major gaseous product. Diethyl ether is formed via a reaction of ethanol to ether and water (Scheme 3). In addition, ethyl acetate was formed over Au catalyst. In accordance to the Scheme 4, it is evident that the formation of an ester requires the formation of a carboxylic acid via oxidation of the alcohol. Au is a good oxidation catalyst which might explain the prominent ethyl acetate formation. Acetic acid was not detected in the GC analysis. However, it is possible that under our experimental conditions acetic acid immediately reacted to the corresponding ester. Finally, 1,1-diethoxyethane was formed via the acid catalyzed acetalisation of acetaldehyde and ethanol (Scheme 5). Most of these side reactions (excluding dehydrogenation of ethanol) formed water as a by-product. Still, also the target reaction forms 1-butanol and water. Therefore, it was of interest to study water removal during reaction. This will be discussed next.

Scheme 2. Dehydrogenation of ethanol.
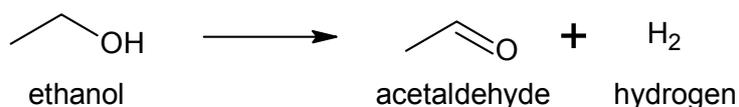
Scheme 3. Formation of diethyl ether from ethanol.
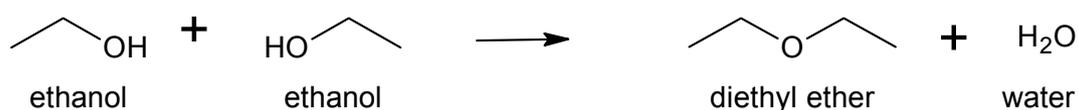
Scheme 4. Two step reaction sequence forming ethyl acetate from ethanol.
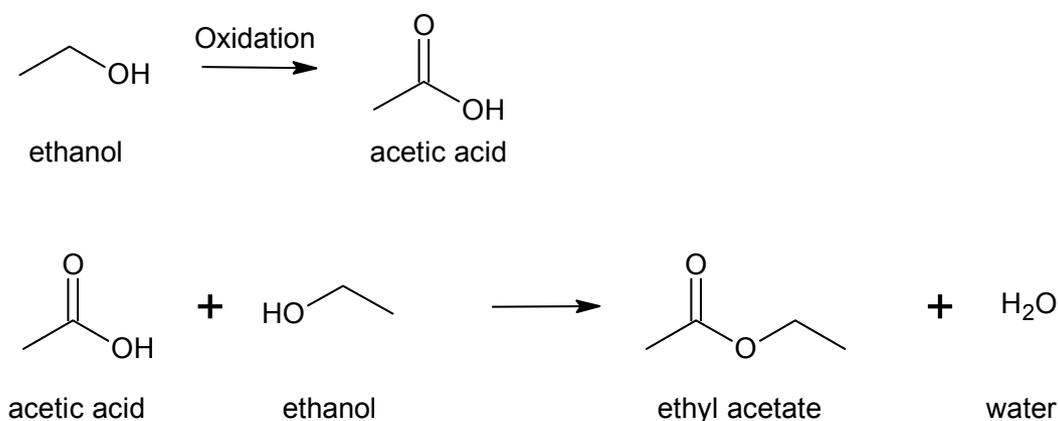
Scheme 5. Acetalisation of acetaldehyde and ethanol.

acetaldehyde ethanol 1,1-diethoxyethane water
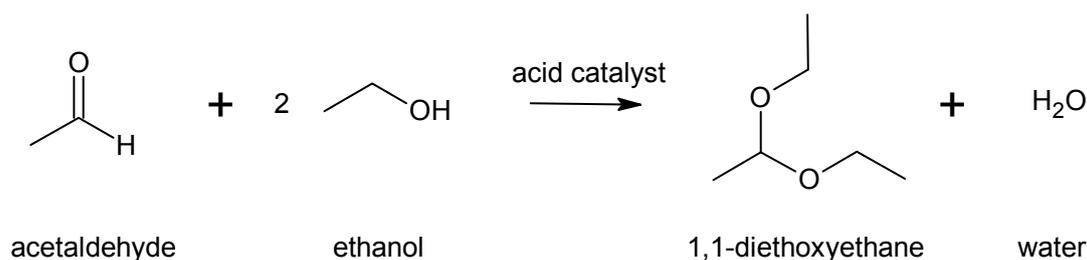
2.3.4. Water Removal from the Reaction Mixture

In a typical reaction sequence (Figure 6), we can clearly see that the ethanol conversion under studied conditions stabilized at a level around 20% (batch reactor experiments). In principle, the reactant conversion can be limited by catalyst deactivation or equilibrium limitations emerging, e.g., by the presence of formed water. A third aspect of water is the steam reforming of ethanol to hydrogen over nickel metal catalysts [19]. In the presence of water, ethanol and a Ni catalyst, hydrogen is formed. Therefore, the formation of hydrogen (via steam reforming reaction) might be a plausible explanation for the promoting role of water removal. The net reaction is dimerization of two ethanol molecules to 1-butanol and water (Scheme 1). Therefore, the removal of water was of interest. The reaction was carried out with pre-dried ethanol using 3 Å molecular sieves. The same molecular sieves were also added into the reactor to enable water removal during the reaction. The water removal procedure resulted in significant improvement of the ethanol conversion from 20% to 30%. This would indicate that the reactant conversion can be enhanced by water removal.

2.3.5. Thermodynamic Calculations

In order to distinguish if the obtained maximum ethanol conversions levels (20–30%) are due to catalyst deactivation by the *in situ* formed hydrogen or due to equilibrium limitations, the equilibrium composition for the main reaction was calculated. Based on the calculations under our reaction conditions at 250 °C and 70 bar, the theoretical maximum conversion of ethanol to 1-butanol was found to be 98.5%. Therefore, we suggest that the reason for the attained 30% ethanol conversion is catalyst deactivation under reactions conditions (due to *in situ* formed hydrogen) rather than equilibrium limitations.

2.3.6. Other Alcohols as Reactants

The performance of the catalytic system was evaluated in mini-bomb screening reactors using methanol, ethanol, 1-propanol and 1-butanol as reactants over the HTC-500 catalyst. Interestingly, under studied conditions (250 °C), only ethanol seems to produce *n*-alcohol dimerisation products. The inactivity of methanol might be due to the difficult methanol dehydration (water removal) when compared to longer chain alcohols. The mechanism accounting for the dimerisation of ethanol to 1-butanol should be able to explain the specificity of the reaction to ethanol but not, e.g., 1-propanol and 1-butanol as reactants. One such mechanistic proposal was proposed by Suchida *et al.* [14] where the Guerbet alcohols formed predominantly from ethanol yield linear alcohol products (1-butanol)

whereas reactions involving longer alcohols (C_3, C_4, ...) result in the formation of branched Guerbet alcohols.

2.3.7. The Effect of Sub- *vs.* Super-Critical Conditions

For the next step, we studied whether super-critical conditions could be advantageous in the investigated reaction. The tests were performed by means of the above mentioned mini-reactors at the temperatures below and over 240 °C which is approximately the triple point of ethanol. The test method was exactly the same as previously mentioned while the only difference was the temperature. However, the results indicated, that at least in our case, we could not find any beneficial effects related to super-critical conditions. The product distribution was the similar under sub- and super-critical conditions. Furthermore, several authors' calculations indicate [20–22] that ethanol hydrogen bonding properties change significantly under super-critical conditions.

3. Experimental Section

3.1. Catalyst Screening

Catalyst screening was carried out in small, 2 mL isobaric mini-reactors equipped with magnetic stirring (Figure 10). The reactors were made of stainless steel and could be used for the reaction carried out at pressures up to 100 bar and temperature up to 250 °C (maximum for the Teflon coated stirrer magnet). The catalyst testing procedure was as follows: the reactor was loaded with the catalyst (10 or 50 mg) 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). While opening the reactors, it was noted that in many cases notable gas formation had taken place during the experiment (sealed reactors). The gas-phase composition could not be analyzed in the catalyst screening mode; however, it could be done during the kinetic experiments carried out in the standard high pressure Parr autoclave.

Figure 10. Reactors used for catalyst screening ($V_{reactor} = 2$ mL).

3.2. Kinetic Experiments

Proper kinetic experiments were carried out in a 300 mL high pressure Parr autoclave equipped with a mechanical Rushton turbine type of a stirrer. The reactor was loaded with the catalyst (typically 3.3 g) and flushed with inert gas (He). In some experiments, catalyst reduction under flowing hydrogen, at 400 °C for 3 h, was carried out. The catalyst-to-reactant molar ratio was identical as in the case of catalyst screening experiments in small mini-autoclaves. The ethanol reactant (100 mL) was degassed for 10 min with inert gas before injection to the reactor. The reactor was heated rapidly to 250 °C and the reaction was monitored by taking small liquid samples (0.5 mL). The gas-phase composition was analyzed at the end of the reaction after cooling the reactor back to room temperature (RT). Gas chromatographic analysis (Agilent, DB-Petro 100 m column) was calibrated with commercial standards. The initial compound identification was based in GC-MS identification of the peaks using the same column. The semi-quantitative gas phase analysis was based on a quadrupole mass spectrometer (Balzers). The stirring rate applied throughout the the matrix of catalytic experiments was 1500 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 low, the danger of external mass transfer limitations can be regarded as negligible.

3.3. Catalysts

A total of 13 catalysts were studied in the present work. Both in-house prepared and commercial catalyst were used. For commercial catalysts, the available characterization data can be found in Table 2, whereas in the case of in-house prepared ones the catalyst preparation is described below and the characterization results are reported in Table 2.

3.4. Analytical Procedure

The liquid-phase analysis was carried out with an Agilent Technologies, 6890 N gas chromatograph (GC) equipped with a DB-Petro (122-10A6, 100 m, i.d. 0.250 mm) column. The products were identified by means of an Agilent gas chromatograph coupled to a mass spectrometer (GC-MS) equipped with the same column. Calibration of the GC was carried out with commercial standards using octane (Fluka > 99%) as internal standard. The calibration was carried out using the following commercially available chemicals: ethanol (Altia 99.5%, Aa), butyraldehyde (Lancaster, 99%), diethyl ether (Merck, max 0.0075% H_2O), ethyl acetate (Fluka, >99.5%), 1-butanol (Acros Organics, 99%), 1,1-diethoxy ethane (Fluka, ≥95%), 1-hexanol (Fluka, ≥99%), 1-octanol (Riedel-de Haën, ≥99.5%)

The qualitative gas-phase analysis was carried out with a quadrupole MS. After cooling down the reactor contents to room temperature (RT), the remaining gas phase was analyzed with MS.

3.5. Catalyst Characterization

Thirteen (13) different catalysts were tested in the screening phase. The catalysts were characterized with TEM, XRD, physisorption and chemisorption. To identify crystal phase and size of the catalyst (and in some cases of the support) X-ray diffraction analyses were carried out using Cu Kα radiation (Siemens D5000 diffractometer equipped with a graphite monochromator to suppress fluorescent and

Cu Kβ radiation). The average crystallite size of catalyst particles was estimated using Scherrer's equation from the halfwidths of the most intensive reflections. Transmission electron microscopy (LEO 912 OMEGA, energy-filtered TEM, 120 kV) has been used to study microstructure and particle size of catalyst samples. Histograms of particle size distribution were obtained by counting typically 100 particles on the micrographs.

3.6. Thermodynamic Calculations

The equilibrium composition for the main reaction, *i.e.*, 2 ethanol = 1-butanol + water was calculated in order to check if the conversion would be equilibrium limited. The calculations were performed with the software PRO/II (PRO/II 8.3 invensys Systems, Inc.) using the Gibbs reactor module. At 250 °C and 70 bar the conversion of ethanol to 1-butanol was found to be 98.5%.

4. Conclusions

Several heterogeneous alumina supported metal catalysts were screened in the direct liquid phase one-pot conversion of ethanol to 1-butanol. For the most promising catalyst (20.7% Ni/Al$_2$O$_3$, HTC-500), a 25% ethanol conversion with 80% selectivity to 1-butanol could be reached. Based on the results achieved, the investigated metals can be ranked in terms of the selectivity towards 1-butanol as follows: Ni > Pt > Au~Rh > Ru >> Ag. Additionally, the results achieved indicate that the most plausible reaction pathway follows the Guerbet route. The reaction was specific to dimerisation of ethanol. Linear *n*-alcohols could not be produced from methanol, 1-propanol, or 1-butanol as the reactants. This reaction has a great potential in overcoming disadvantages of bioethanol and serving as yet another step toward wider portfolio of sustainable transportation fuels. We will attempt to optimize the catalyst characteristics in the quest towards the optimal 1-butanol selectivity. Also, on-going experiments with a new continuous operating fixed bed reactor designed at operating in the liquid phase conditions will be utilized.

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