



Continuous liquid-phase valorization of bio-ethanol towards bio-butanol over metal modified alumina



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ABSTRACT

Commercial mixed-phase aluminum oxide was used as a heterogeneous catalyst support, providing slightly basic properties which are well-suited for the condensation of bio-ethanol to C₄ hydrocarbons, such as 1-butanol. Different metals (Cu, Ni and Co), at various metal loadings were deposited on the support. Consequently, the catalytic reactions were carried out in a continuous laboratory-scale fixed bed reactor operated at 240 °C and 70 bar. The catalysts were characterized by means of XRD, TEM, FT-IR, XPS and ICP-OES. Different metals were found to give entirely different product distributions. With the best catalysts, the selectivities towards 1-butanol close to 70% were reached, while the ethanol conversion typically varied between 10 and 30% – strongly depending on the metal applied. It was observed that low loading of copper and high loading of nickel were responsible for the formation of 1-butanol, whereas cobalt and high loading of copper resulted in the production of ethyl acetate. The reaction was found to be extremely sensitive to catalyst preparation conditions and procedures such as metal loading, calcination/reduction temperature and, thereby, to the formation of corresponding crystallite structure.

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1. Introduction

Bio-ethanol is one of the most widely discussed options for replacing traditional fossil fuels. It is well known that countries in the tropical zone, e.g. Brazil have implemented a high-level sugarcane-based ethanol production technology by applying farmland. In the Northern hemisphere, Nordic countries have remarkable forest resources which can be used for manufacturing of ethanol in pulp mills by taking advantage of the applicable polysaccharides in wood. Forest-based (lignocellulose) residual approach is well-known for its ability to serve as a non-edible source of sugars, not competing with human-related food production. Despite the high

interest in bio-ethanol, there are certain key issues that should be addressed.

Less than perfect physico-chemical properties of ethanol restrict its use as a fuel additive in conventional engines designed for fossil fuels, at least in higher portions (exceeding 10%) [1,2]. Some of the problematic features of ethanol are worth mentioning, such as its relatively low energy content (in comparison to e.g. gasoline), high water solubility and corrosive behavior. These arguments support the idea of developing a more suitable candidate for replacing ethanol. A plausible approach is based on the condensation of ethanol leading mainly to its four-carbon atom counterpart, 1-butanol. 1-Butanol resembles closely traditional gasoline in terms of its physico-chemical properties [1,2] and is, thus, suitable in much higher blending levels with gasoline [3].

Historically, two production processes for 1-butanol have dominated, a process either based on fossil raw materials (oxo- and aldol process) [4] or a bio-based method [5], such as the Acetone-Butanol-Ethanol (ABE)-fermentation. Today, there are numerous ongoing research efforts that deal with different bio-related pathways leading to the formation of 1-butanol [4–6]. 1-Butanol is not only valuable as a fuel component but it can also be utilized in the

Abbreviations: ABE, acetone butanol ethanol; GC-FID, gas chromatography-flame ionization detector; HPLC, high pressure liquid chromatography; GC, gas chromatography; TEM, transmission electron microscopy; XRD, X-ray diffraction; FT-IR, Fourier transform infrared spectroscopy; XPS, X-ray photoelectron spectroscopy; ICP-OES, inductively coupled plasma-mass spectrometer; UV-Vis, ultra violet–visible diffusion reflectance spectroscopy.

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manufacture of different esters, ethers, acetates and resins [5]. Additionally, other ethanol derivatives (e.g. ethyl acetate, 1,1-diethoxy ethane) have shown some potential as fuels for diesel engines [7–9].

From a viewpoint of modern chemical engineering, the straight one-pot continuous valorization of bio-ethanol to bio-butanol would be the most feasible route. There are a few scientific reports available presenting the desired reaction pathway [10–26]. The use of mixed alumina based oxides [10–16], γ -alumina [17], hydroxyapatite structures [18–21], magnesia [22,23], alkali cation zeolites [24], commercial cobalt powder [25] and sodium modified zirconia [26] have been demonstrated. Based on the structures of these materials, some conclusions can be drawn. For instance, low valence state metal cations form basic metal oxide structures seem to promote the reaction. Corresponding higher valence state oxides are known to have acidic characteristics. Also crystallite molecular structures seem to be a prerequisite. Additionally, the evaluation of the reaction mechanism has two different approaches. Some previous studies [17,22,24] suggest that ethanol condensation proceeds via a straight dehydration pathway, whereas a newer approach [10–16,18,21,23,26] supports the idea of aldol condensation. However, the temperature of the operating conditions may also have an impact on the reaction mechanism [20]. It is also important to evaluate the dominating by-product, ethyl acetate, that can be manufactured over similar kind of catalysts as can be used in the butanol synthesis [27–31] but also on e.g. silica catalyst [32]. We have found that especially cobalt supported on alumina indicates a tendency to form ethyl acetate.

In our previous publication [33] covering qualitative screening of alumina supported catalysts, more evidence was obtained which supports the condensation type reaction mechanism and, at the same time, the significance of by-products essential for the reaction were identified. Hereby we demonstrate a continuous liquid phase one-pot synthesis strategy based on an extensive alumina based catalyst optimization. A more profound view on the engineering aspects of bio-based ethanol valorization is available [34,35].

2. Materials and methods

2.1. Catalyst preparation

All alumina supported metal catalysts were prepared with the deposition-precipitation method based on the hydrolysis of urea, aiming at producing small and uniform metal cluster size distributions. In a typical procedure, a commercial mixed phase (α , β , γ , θ) alumina support (Euro Support, A 201) was crushed and sieved to 150–250 mesh fraction. The iso-electric point of the support is known to be approximately $\text{pH} = 8.4$, which indicates a slightly basic behavior. Thereafter, weighted amounts of metal nitrate (NiNO_3 , CoNO_3 , CuNO_3), urea and alumina were mixed in deionized water under magnetic stirring. The solution was heated to 82 °C overnight under continuous stirring. The solution was cooled, filtered and washed with water to remove remaining ammonia as a result of urea decomposition. Additionally, the catalysts were let to air-dry overnight followed by a higher temperature drying in an oven (100 °C) overnight. The final active form of the catalyst was achieved upon calcination under synthetic air (in case of Cu) or by reduction with pure hydrogen (in case of Ni, Co). The only parameters in the synthesis were the nature of the metal, the amount of it and the calcination or reduction temperature. The prepared catalysts were denoted according to the nominal metal loading excluding commercial HTC-500 catalyst as follows: HTC-500, Ni-19, Co-16, Cu-1.8 and Cu-4.5 (Tables 1 and 2).

Table 1

Preparation parameters of the investigated catalysts.

Catalyst	Preparation method	Optimized calcination or reduction temperature and atmosphere	Metal precursor
HTC-500	Used as received	No treatment	Unknown
Ni-19	Deposition precipitation with urea	Reduction at 500 °C pure hydrogen	NiNO_3
Co-16	Deposition precipitation with urea	Reduction at 500 °C pure hydrogen	CoNO_3
Cu-1.8	Deposition precipitation with urea	Calcination at 400 °C synthetic air	CuNO_3
Cu-4.5	Deposition precipitation with urea	Calcination at 400 °C synthetic air	CuNO_3

2.2. Evaluation of catalytic properties of synthesized catalysts for valorization of bio-ethanol to bio-butanol

The performance testing of different alumina supported metal catalysts was carried out in a laboratory-scale continuous stainless steel fixed bed reactor operated in liquid-phase (Fig. 1). In a typical experiment, 2 g of metal/alumina catalyst was placed in the reactor followed by heating to 240 °C and setting the reactor pressure to 70 bar (Ar). The reactor (length = 21 cm, diameter = 1.6 cm) was operated to upward flow and the packing of the reactor is depicted in Fig. 2. Thereafter, the HPLC-pump was turned on and the flow rate was adjusted to 0.1 ml/min. This facilitated the contact of the reactant (Etax Aa, 99.5% ethanol) with the catalyst bed and the product flow was cooled thereafter for sampling (room temperature). The sampling was carried out by a special valve capable of draining 1 ml sample. The treatment of the sample is described below. All catalysts were compared at the same steady-state temperature, pressure, flow rate, size fraction and mass. The LHSV (Liquid Hourly Space Velocity) value was 4.3(1/h) and ethanol specific velocity 8.3×10^{-6} (m/s).

2.3. Reaction product analysis

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) in gas chromatography (GC)-vial. The pre-treated 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.

2.4. Catalyst characterization

2.4.1. Structural analysis

Energy-filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB₆ filament, 120 kV) was used to assess particle size and reveal the microstructure of the samples. The crystal phases of the support and catalyst particles are evaluated by X-ray powder diffraction (Bruker D8 Discover, Cu K α). From the broadening of the peaks in the patterns, Scherrer's equation was applied to estimate

Table 2

Measurement of the metal contents of catalysts using ICP-OES.

Catalyst	Nominal loadings (wt-%)	Measured (wt-%)	Rsd (%) ^a
Ni/Al ₂ O ₃ (Ni-19)	20	19	0.51
Co/Al ₂ O ₃ (Co-16)	20	16	2.16
Cu/Al ₂ O ₃ (Cu-1.8)	2	1.8	1.23
Cu/Al ₂ O ₃ (Cu-4.5)	5	4.5	0.53

^a Rsd (relative standard deviation) within three (3) replicates.

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