Conversion of Bioethanol to 1-Butanol – A Step Towards Sustainable Transportation Fuels

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Introduction

Ethanol is currently the biggest biofuel contributor in Europe and worldwide. This first generation bioethanol production uses edible food crops as raw material and causes increasing food prices by competing with human food production. In order to overcome this problem the second generation biofuel research focuses heavily on using woody biomass or agricultural waste as raw material for bioethanol. However, there are still many problems associated with the use of ethanol as fuel for combustion engines, *e.g.* its water solubility, corrosivity and the variation of its fuel properties compared to modern gasoline.

In order to overcome these disadvantage of ethanol as fuel one can carry catalytic valorization of bioethanol to higher alcohols *e.g.* 1-butanol. Compared to ethanol, 1-butanol has several advantages: *e.g.* it can be burned in existing gasoline engines without engine or car modifications, it has higher energy contents and air-fuel ratio than ethanol. In summary, the properties of 1-butanol resemble closely the properties of modern gasoline. Therefore, bioethanol derived 1-butanol is an ideal green replacement for a modern gasoline. Finally, one advantage of butanol is the fact that it can be distributed via the existing pipelines for gasoline. In the end, the consumer does not notice a difference when using 1-butanol as a fuel instead of modern gasoline. In this work we present our latest research in direct one pot catalytic conversion of ethanol to 1-butanol over heterogeneous catalysts.

Materials and Methods

Around 50 heterogeneous catalysts were synthesized, characterized and tested for direct one pot conversion of ethanol to 1-butanol. Combinations of Ni, Pd Pt, Au, Ag, Ru, Rh, Os, Ir on various supports including alumina, silica, activated carbon, carbon nanofibres, hydroxyapatite, micro and mesoporous materials were tested. The preliminary catalyst screening was carried out in micro reactors (V_L=1.5 ml) followed by detailed kinetic experiments in 300 ml Parr reactor set-up. The liquid-phase composition was analyze by CG and CG-MS whereas the gas-phase composition was analyzed by quadrupole MS. Reaction conditions were typically 250°C, 70 bar for batch wise conversion of ethanol to 1-butanol. Catalyst pretreatment and reduction effects were studies. Influence of different solvents and water removal was investigated. Several mechanistic studies were carried out using *e.g.* other alcohols (C1-C4), alcohol/acetaldehyde and ethanol/crotonaldehyde mixtures. All developed/tested catalysts were extensively characterized by H_2 chemisorption, N_2 physisorption, XRD, SEM, TEM techniques.

Results and Discussion

The results from extensive kinetic and mechanistic studies including detailed catalyst characterization will be presented. As expected, the product distribution varied a lot depending on the choice of the catalyst as a broad range of metals and support materials were tested. Catalyst reduction was found to have a negative effect on 1-butanol selectivity. Over reduced metal catalysts the selectivity towards diethyl ether increased. The acidic metal modified micro and mesoporous materials produced diethyl ether as main product with high selectivity. Over several metals (Ag, Ni, Pd, Ru) the highest selectivity towards 1-butanol was achieved using alumina as catalyst support. Water removal from the reaction mixture increased reactant conversion levels from 15% up to 30% under studied reaction conditions and reaction times. With the most promising catalyst a 30% ethanol conversion with 70% selectivity to 1-butanol could be reached. The kinetics of ethanol conversion to 1-butanol and other main products (acetaldehyde and diethyl ether) is illustrated in Fig. 1. The conversion of ethanol to 1-butanol exhibits a novel reaction mechanism. The experiments carried out with reactant mixtures do not support the tradition reaction path from ethanol-> acetaldehyde-> crotonaldehyde-> 1-butanol. The reaction seems to proceed by dimerization of two primary alcohols coupled with water removal.

Significance

The work presents the first liquid-phase one-pot conversion of ethanol to 1-butanol with high selectivity and good yield. The selectivity and yield are the highest ever reported for this model reaction. The work is of high industrial importance as it would allow simple catalytic conversion of bioethanol to more valuable and easy to use liquid fuels.

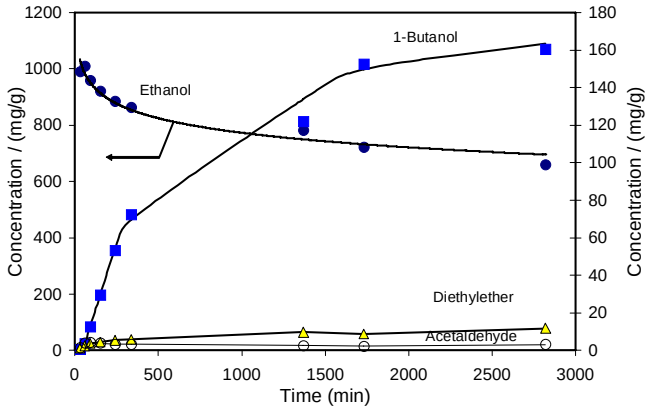

Figure 1. Valorization kinetics of ethanol to main products over a Ni catalyst in a bath reactor. Reaction conditions: 250°C, 70 bar.