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Bio-Olefins from Crude Industrial Waste Glycerol and Sugar Alcohols via Ru-Catalyzed Hydrodeoxygenation in Ionic Liquids

AUTHORS

Kwinten JANSSENS / KU LEUVEN, LEUVEN CHEM & TECH, CELESTIJNENLAAN 200F, LEUVEN
Aram BUGAEV / SOUTHERN FEDERAL UNIVERSITY, SMART MATERIALS RESEARCH CENTRE, ROSTON ON DON
Corresponding author : Dirk DE VOS / dirk.devos@kuleuven.be

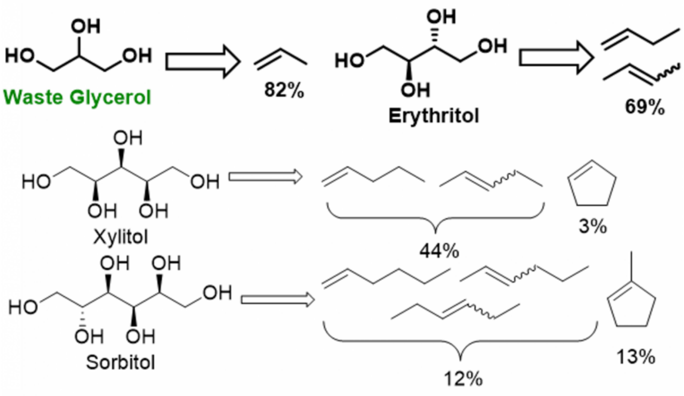
PURPOSE OF THE ABSTRACT

Due to the high oxygen functionality of biomass, the valorization of renewable substrates to valuable chemicals typically requires deoxygenation reactions, such as deoxydehydration (DODH) or simple dehydration. However, the conversion of biomass via dehydration with a higher oxygen content (C/O = 1), leads to a buildup of carbonyl compounds due to the enol-to-keto tautomerism. We hypothesized that if a fast dehydration is combined with exclusive hydrogenation of C=O bonds, even in the presence of C=C bonds, the overall sequence may result in the stepwise deoxygenation of the polyol to an olefin, as a kinetically stable end product. By using H2 as a reductant, this is essentially a hydrodeoxygenation (HDO), which would be formally similar to, but mechanistically different from the classical DODH reaction using atom inefficient reductants e.g. triphenylphosphine.[1] Therefore, it would be a greener, conceptually new complement to DODH. In this work we successfully converted crude biowaste glycerol directly into biopropene in high yield (82%) and olefin selectivity (94%) carefully avoiding overhydrogenation.[2] Next, a series of more complex, economically relevant sugar alcohols (erythritol, xylitol and sorbitol) were converted to their respective mono-olefins.[3] CO was discovered to be crucial to maintain high catalyst stability over multiple cycles, this was confirmed using X-ray Absorption Spectroscopy (XAS) at the European Synchrotron Radiation Facility (ESRF).

Intensive screening of different hydrogenation catalysts has led to the discovery of homogeneous Ru catalysts resulting in high olefins selectivities, rather than overhydrogenation to the less valuable alkane. It was hypothesized that this was a result of the formation of a stable Ru-Carbonyl-Halide complex, in multiple ways, e.g. through pretreatment with CO gas [2], in-situ decarbonylating of aldehyde intermediates [3] or via controlled thermal decomposition of formaldehyde [3]. All resulted in small partial pressures of CO which are essential to form the desired Ru-hydrogenation complex. The different steps in the formation of the active catalyst were characterized at ESRF to get in-depth insights in the Ru environment, confirming changes for both Ru-Halide and Ru-CO interactions. In order to tolerate common waste stream impurities (Water, MeOH, NaCl) found in crude glycerol from ex-biodiesel saponification, CO pretreatment again proved to be crucial in maintaining catalyst stability and selectivity over 8 cycles.[2] In addition, the catalyst applicability was extended to other biobased sugar alcohols: erythritol, xylitol and sorbitol. All were converted selectively to their respective mono-alkenes (>95% olefin selectivity).[3] To the best of our knowledge, this is the first report of the successful conversion of these higher polyols to mono-alkenes.

In conclusion, we discovered an innovative and green bifunctional catalytic system that selectively performs hydrodeoxygenation of crude industrial glycerol and sugar alcohols to their respective mono-alkenes over multiple cycles, being tolerant to the most impurities found in such waste streams. The catalytic system was extensively characterized using ex-situ XANES and EXAFS at ESRF, proving the crucial aspect of CO pretreatment for the formation of the very selective Ru-Carbonyl species.

FIGURES



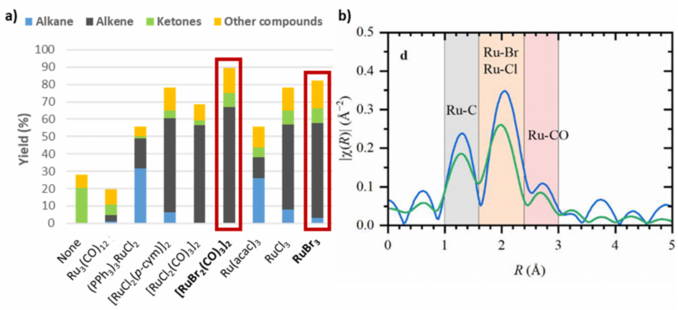


FIGURE 1

Scope of the investigated (waste) bio-polyols to their respective mono-olefins.

82% overall propene yield was obtained with 94% olefin selectivity. For higher sugar alcohols, no overhydrogenation to the alkane was observed under optimal conditions.

FIGURE 2

Hydrodeoxygenation of (waste) bio-polyols to olefins.

(a) Hydrogenation catalyst screening: 0.5mmol erythritol, 2 mol% Ru-cat, 200°C, 40 bar H2, 2h. (b) FT-phase-uncorrected EXAFS of [RuCl2(CO)3]2 in IL (green) and ex-situ Ru-catalyst in IL after reaction (blue).

KEYWORDS

Biomass valorization | Industrial waste glycerol | Sugar alcohols | Ionic liquids

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