Formation of Heavier Alcohols and C_8 Aromatics via Ethanol Upgrading Reactions on Hydroxyapatite

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Abstract: During ethanol upgrading reactions on hydroxyapatite catalysts, series of condensation reactions of C_2 alcohol to form heavier alcohols, known as the Guerbet reaction, compete with a set of alternating condensation of alcohol-derived aldehydes to form both ortho-/para-tolualdehydes (2-MB and 4-MB, respectively). In this study, the complete reaction network and the detailed reaction mechanisms of these competing reaction pathways have been investigated.

Keywords: Bioethanol, Butanol, Tolaldehyde, Hydroxyapatite

1. Introduction

Small oxygenates (e.g., acetone, butanol, and ethanol (ABE)) are readily produced from the fermentation of biomass (e.g., ethanol or ABE fermentations). Ethanol is unique, because it can be produced with high efficiencies and titers by robust organisms and is easily recovered from fermentation solutions by pervaporation or stripping. Although ethanol and other small oxygenates are useful fuel additives and chemicals, heavier products with greater value may be formed by catalytic upgrading (e.g., aldol condensation).[1] This process involves sequences of coupling reactions in order to form heavier products (e.g., $C_{\geq 8}$ alcohols); however, a myriad of self- and cross-coupling reactions typically give broad distributions of products and low yields for any given species.[2] Such mixtures may be useful as fuels, but it would be desirable to identify pathways and catalysts that convert ethanol into drop-in replacements for large market platform chemicals used to produce durable consumer products. Here in this study, we describe the detailed reaction mechanism of ethanol coupling reaction, Gurebet reaction, and another competing reaction pathway to form both both ortho-/para-tolualdehydes, which are potential precursors to form xylenes.

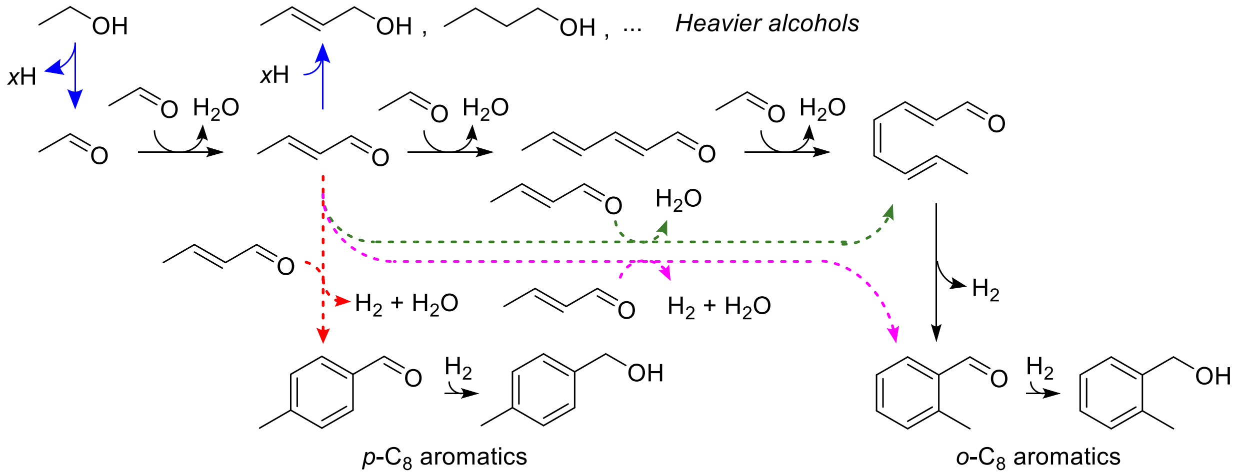
2. Experimental

The Ca-HAP catalyst with a Ca/P ratio of 1.67 was purchased from Acros Organics (Lot: A0333466). Aldehyde condensation and aromatization reactions were conducted using a packed-bed tubular glass reactor. The Ca-HAP catalysts were pre-treated in situ by heating at 773K for 2 h under He flow. Liquid phase reactants were introduced using a syringe pump. The total pressure of the system was maintained at 101 kPa by co-feeding H_2. The identity and concentrations of reactants and products were measured using a GC-FID equipped with a capillary column (DB-WAX). The molecular speciation was confirmed using a gas-chromatograph mass-spectrometer. Rates were measured at conversions of the limiting reactant which were less than 15% to identify primary reaction pathways and to ensure that depletion of reactants across the bed had a minimal influence on measured rates. Aldol condensation rates are calculated by dividing the conversion of the reactant aldehydes by the residence time. Selectivities are reported based on moles of carbon of the products (C-%).

3. Results and discussion

The drastic increase in the C–C bond formation rate by adding small amount of acetaldehyde (0.26 kPa C_2H_4O), together with the formation of 2-butenol and 1-butenal as the secondary intermediate products, suggested that the C–C bond formation proceeds via an aldol-type reaction between acetaldehydes derived from ethanol. Steady-state rate measurements, taken as a function of reactant concentrations (1–5 kPa C_2H_5OH, 0–0.5 kPa C_2H_4O), showed the first and negative order dependence on acetaldehyde and ethanol partial pressure, respectively. Isotopic method and *in situ* FTIR revealed the H-transfer reaction between alcohol and aldehydes (MPV-type reaction) and the formation of ethoxide species as surface intermediates, respectively. These detailed mechanistic information has been used to establish rate expressions for the conversion of C_2 species, and clarified the C–C bonds are formed via aldol condensation of aldehydes including kinetically relevant dehydrogenation step.[2] The continuous reaction produces C_4–C_{12} alcohols. The reaction network for ethanol upgrading were found to be described by a predictive model. It was demonstrated that a pseudo step-growth model can accurately describe the network of coupling reaction among alcohol-derived intermediates.[2] The model, however, suggests a broad product distribution, which results in low selectivity towards any specific product.

Under high acetaldehyde partial pressure (>0.25 kPa C_2H_4O), we have also identified alternative reaction pathways that selectively forms aromatic C_8 products, ortho-/para-tolualdehydes, that are useful as precursors for phthalic acid and phthalic anhydride.[3] The changes in product distribution along with the reactant conversion revealed that the unsaturated C_4–C_8 aldehydes are formed via the sequence of aldol condensation, which subsequently terminated by aromatization reaction of C_8 trienals. The selectivities for tolaldehydes exceed 30%, as a result of rapid cyclization reactions and steric protection that hinders further growth.[3] The exact positions at which C–C bonds form between C_4 co-reactants to create 4-MB products were investigated by using reactant mixtures containing combinations of 2-butenal, 2-butenol, and 3-methyl-2-butenal as model reactants. The analysis of the products suggests that 4-MB species form via 2-butenal self-addition by nucleophilic attack of the α-C to the carbonyl-C.[4] Scheme 1 describes the overall reaction pathways from C_2 reactants on hydroxyapatite.



Scheme 1. Overall reaction pathways to form heavier alcohols and ortho-/para-tolualdehydes.[3,4]

4. Conclusions

The complete reaction network and the detailed reaction mechanisms of ethanol upgrading reactions have been investigated. C–C bonds are formed via aldol condensation of aldehydes including kinetically relevant dehydrogenation step, and the formed aldehyde is hydrogenated to alcohol via a subsequent H-transfer reaction. Furthermore, when the C–C bond formation rates is sufficiently higher than for H-transfer rates, the sequential condensation reactions of acetaldehyde and 1-butenal gives 2,4,6-octatrienal and of highly reactive acyclic intermediate(s) for 2- and 4-MB products, respectively.

References

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