Cu-La/Beta – Bifunctional Zeolitic Catalyst for One-step Ethanol Conversion to Hexene- and Octene-rich Olefins

Background

- Large-scale ethanol production has been well established worldwide, and downstream ethanol to middle distillate technologies have offered a unique solution to produce renewable jet and diesel for decarbonizing the hard-to-electrify sectors. Prior efforts present challenges in the selective formation of longer chain C_{5+} olefins (e.g., hexenes, octenes), critical feedstocks for renewable jet, and diesel fuel production.

Approach

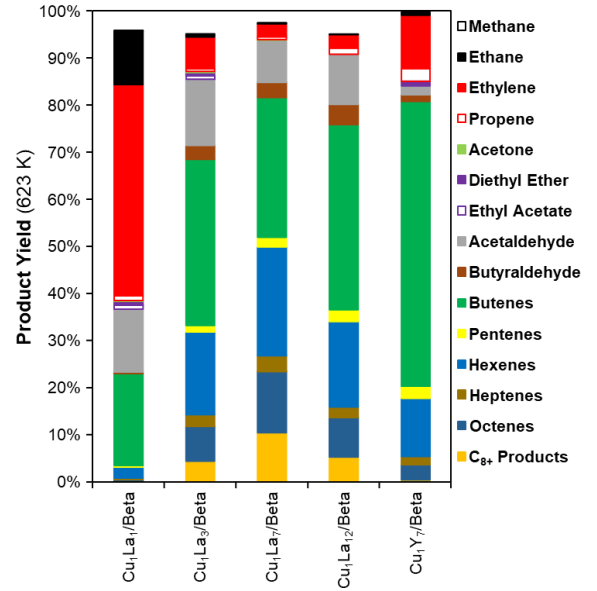
- We discovered that anchoring different rare-earth metals could tune the Lewis acidity of heteroatoms-substituted Beta zeolite for preferentially forming longer chain (C_{5+}) olefins. The as-synthesized Cu-La/Beta catalysts can facilitate multiple sequential C-C formation reactions to form long-chain intermediates while balancing the reactivities towards other critical reaction steps (i.e., hydrogenation and dehydration).

Results

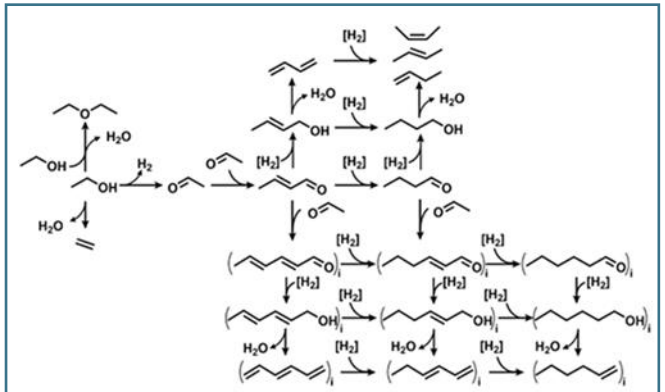
- A simple solid-state grinding synthesis procedure facilitates large-scale production of catalysts. We used highly dispersed rare-earth metal species (single atoms or nanoclusters) with loading up to 12 wt.%, with no formation of large nanoparticles.
- One-step ethanol conversion process achieved 98% conversion of ethanol, 87% selectivity into C_{4+} olefins, and <4% selectivity into C_1-C_3 hydrocarbons at 623°K, 1 atm. There was 43% C_{5+} olefins selectivity, mainly hexenes and octenes, which is superior to benchmarking Cu-Y/Beta catalyst only producing 20% C_{5+} products.
- Monometallic Cu/Beta or La/Beta samples are insufficient to catalyze the C_{4+} olefin formation.
- This work indicates a new reaction network for direct conversion of ethanol to long-chain olefins.

Significance

- Higher olefins for both chemical and fuel applications from ethanol can be renewably generated.
- This should inspire investigations of rare-earth-metal-based zeolites as a platform for applications driven by Lewis acid catalysis and further study of active sites and reaction mechanisms associated with ethanol to C_{4+} olefins over La-based and bimetallic catalysts.



Steady-state ethanol upgrading product yields obtained over Cu-La/Beta catalysts as a function of La loading with Cu_1-Y_7/Beta as reference.



Proposed reaction network for ethanol upgrading to butene, hexene, and octene isomers over Cu-La/Beta.

Cordon, MJ.et al. *ACS Sustainable Chem. Eng.* (2022) 10:5702-5707. doi.org/10.1021/acssuschemeng.1c07442