Bio-butanol dehydration via zeolites as a missing link between classic and bio refineries

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Introduction

To decrease oil dependency many alternatives are being researched. A promising method is the dehydration of bio-butanol to butenes with the use of zeolites.

Products formed by this catalytic reaction can directly be incorporated into existing classic refineries or can be used for oligo- and isomerization and polymer synthesis, ultimately resulting in a link between the bio- and classic refineries.

Scope & Setup

Experimental and theoretical evaluation of key parameters of the process of forming butenes via bio-butanol:

1. Si/Al ratio of the catalyst
2. Type of lattice
3. Butanol isomer

Each of these parameters are investigated in a broad range of site time and at same temperatures (503K or 513K) on a high throughput setup at a fixed pressure of 5 bar.

Si/Al Effect

tested on commercial H-ZSM-5 (513K)

- Increased activity with decrease Si/Al per site
- No selectivity shifts on formed products
- Decrease in acid strength with Si/Al

Difference is related to an identical shift of Free Gibbs values OR a difference in adsorption kinetics

Isomer Feedstocks

n-butanol vs. iso-butanol, the two prominent bio-butanol isomers (503K)

- Increased activity for iso-butanol vs. n-butanol
- No isobutene formation with n-butanol
- No ether formation with iso-butanol

Catalyst Comparison

tested on 3 commercial catalysts (513K)

MFI: 10 R, 3D
MOR: 8 (pocket) & 12 R, 2D
FAU: 12 R, 3D

Activity increase: MOR < FAU < MFI per site

- MOR improves the rate of double bound isomerization
- MOR represses formation to n-di-butylether
- FAU increases ether formation

Biggest effect on activity by lattice, slight possibility to tweak selectivity of butenes and ether by adjusting channel sizes and lattice topology.

Conclusion

- Out of the tested catalysts H-ZSM-5 has the highest activity and shows good selectivities towards butenes at high conversion which is suitable for industrial applications. A catalyst with low Si/Al ratio shows the best performance and leads to the use of less catalyst.
- Changing the feedstock from n-butanol toward iso-butanol increases overall activity of the catalyst and directly forms isobutene with high selectivity and no ‘unwanted’ ethers are formed.
- Modeling of the reaction network gives more understanding on the shifts occurring when changing the butanol isomer and can help to optimize the overall conditions.