

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

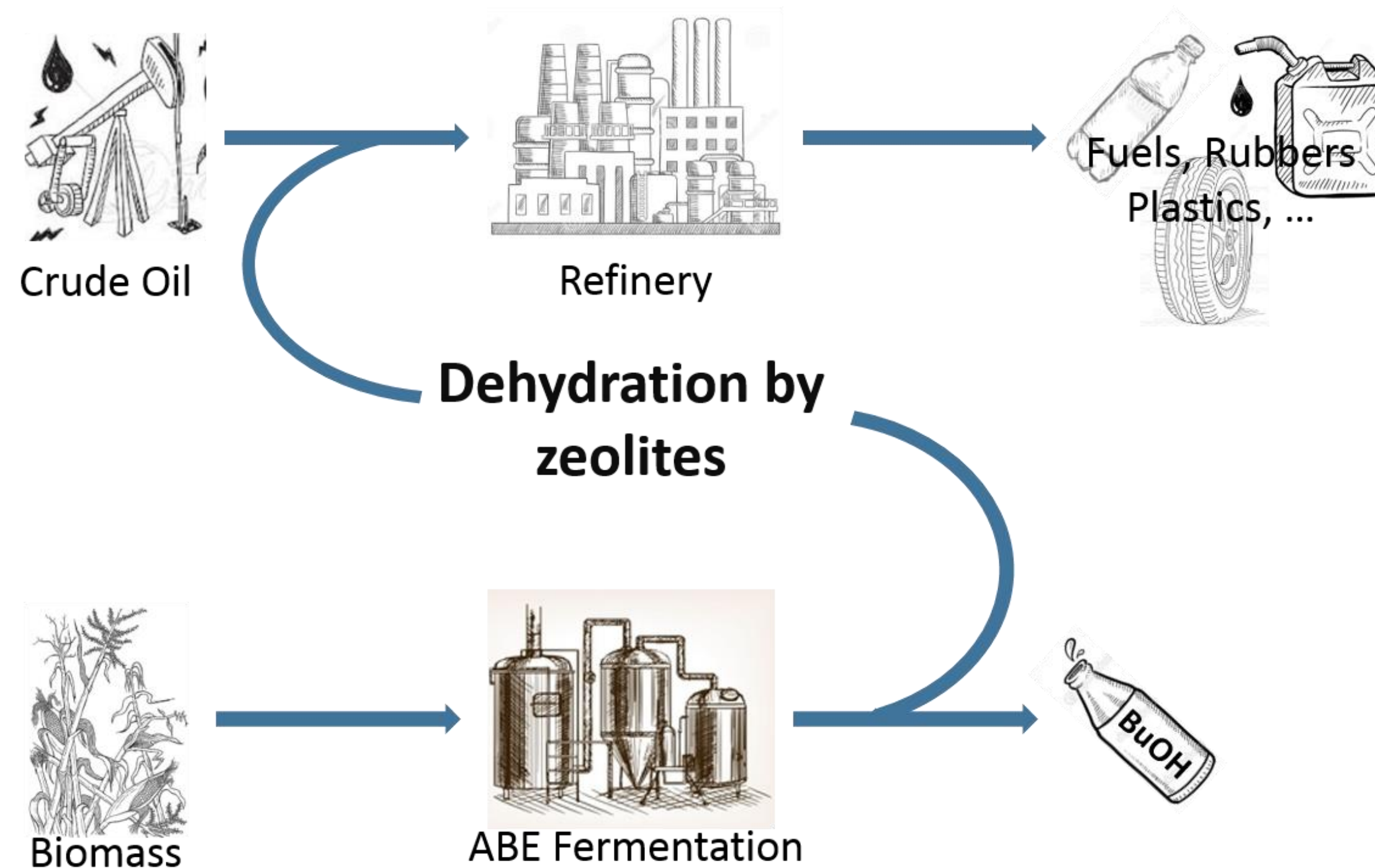
D. Gunst,<sup>1,2</sup> K. Alexopoulos,<sup>2</sup> M.F. Reyniers,<sup>2</sup> and A. Verberckmoes<sup>1,\*</sup>

<sup>1</sup> Industrial Catalysis and Adsorption Technology (INCAT), <sup>2</sup> Laboratory for Chemical Technology (LCT), Department of Materials, Textiles and Chemical Engineering (MaTCh), Ghent University

## 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**

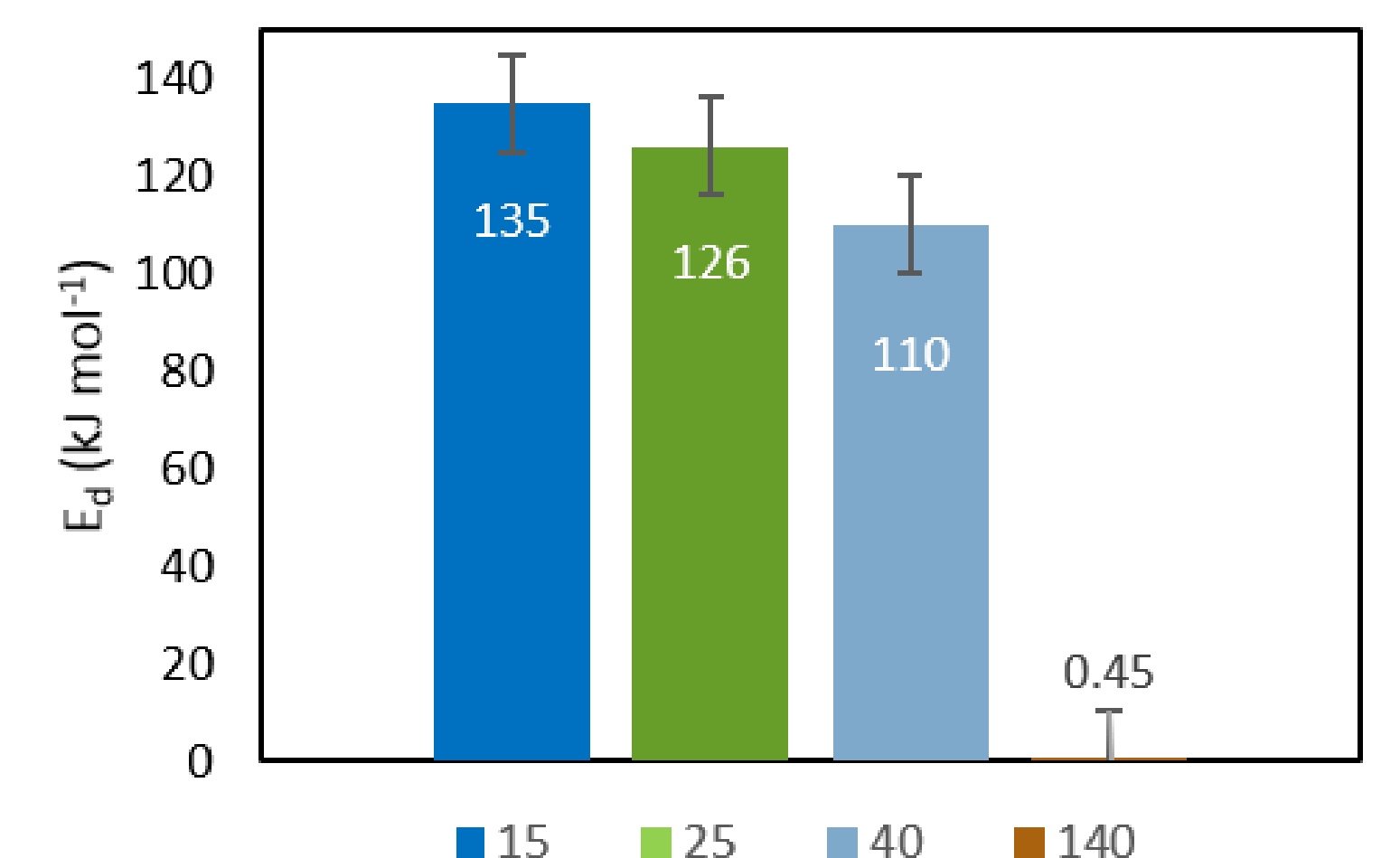
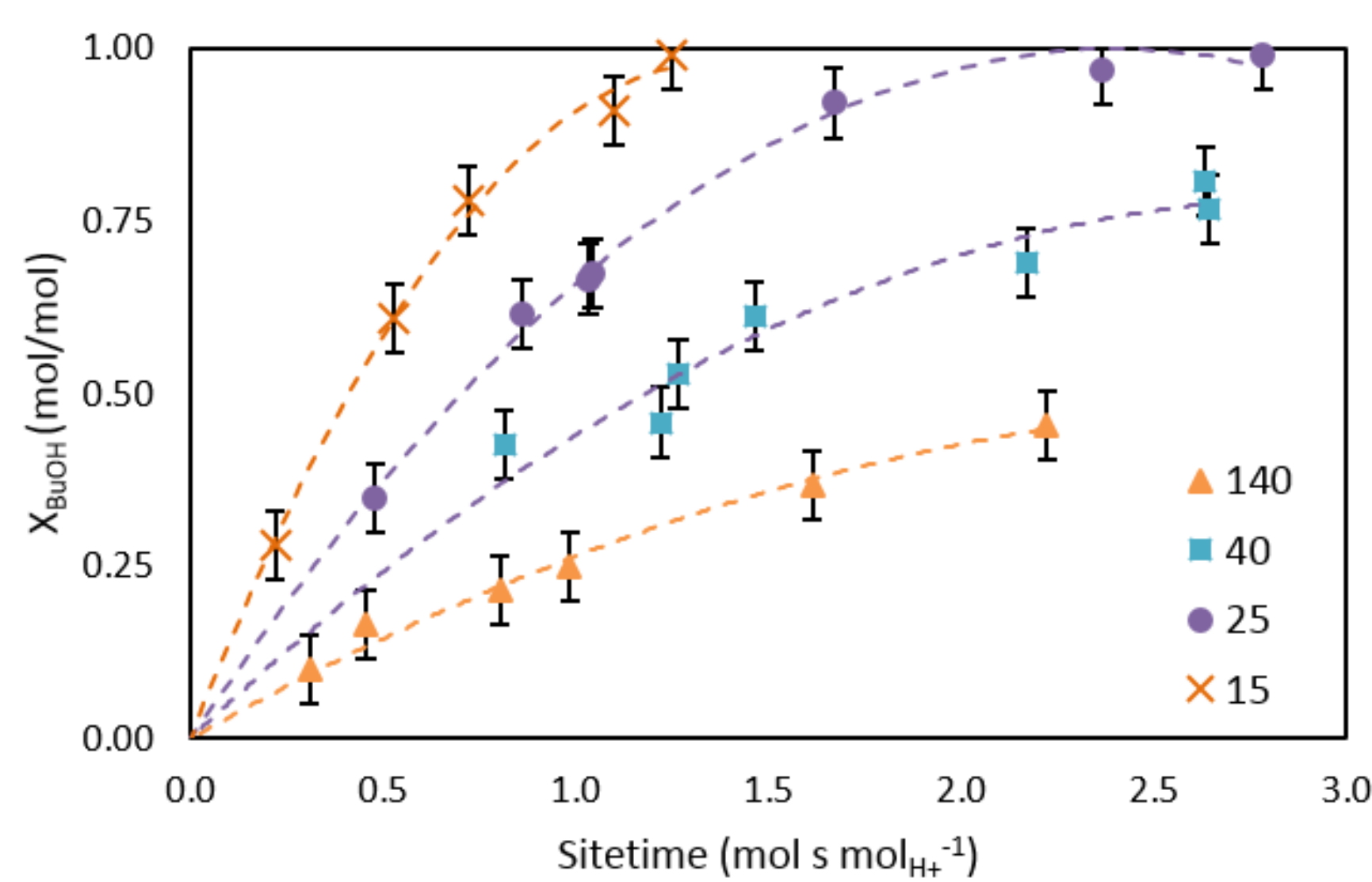
Each of these parameters are investigated in a broad **range of site time** and at **same temperatures** (503K or 513K) on a **high throughput setup** at a **fixed pressure** of 5 bar.

## Si/Al Effect

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

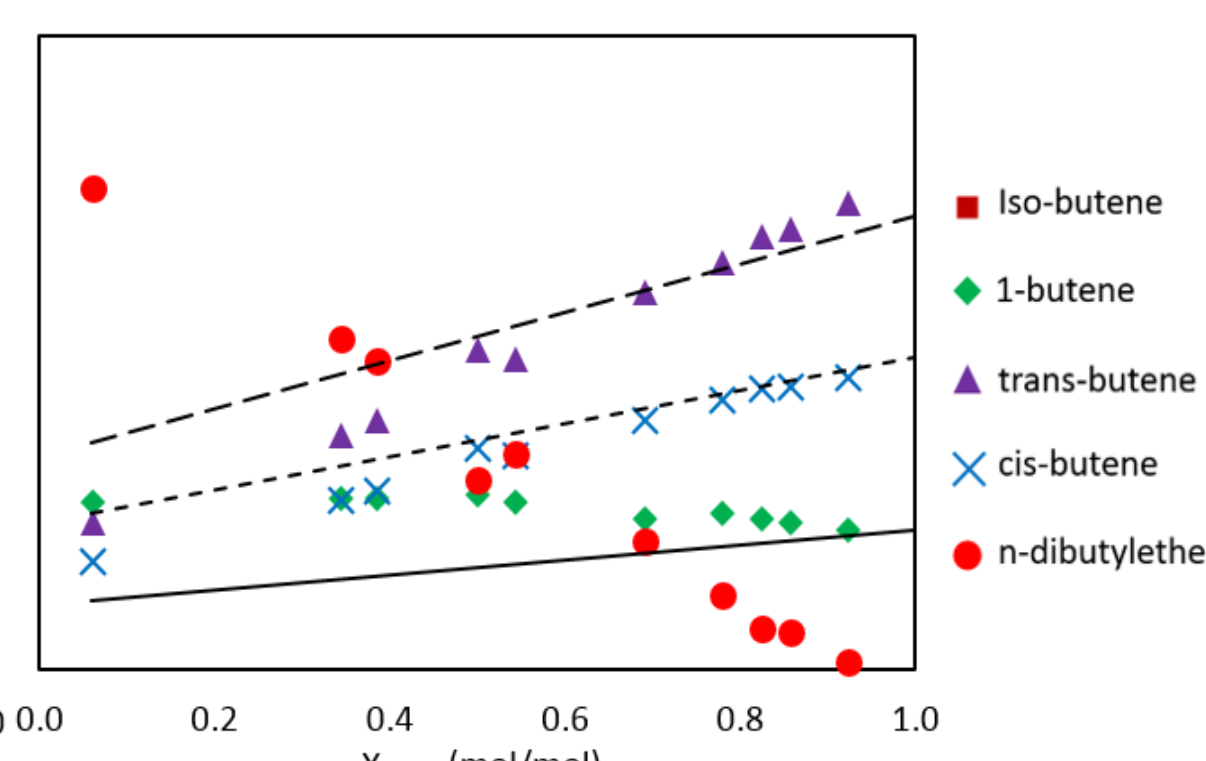
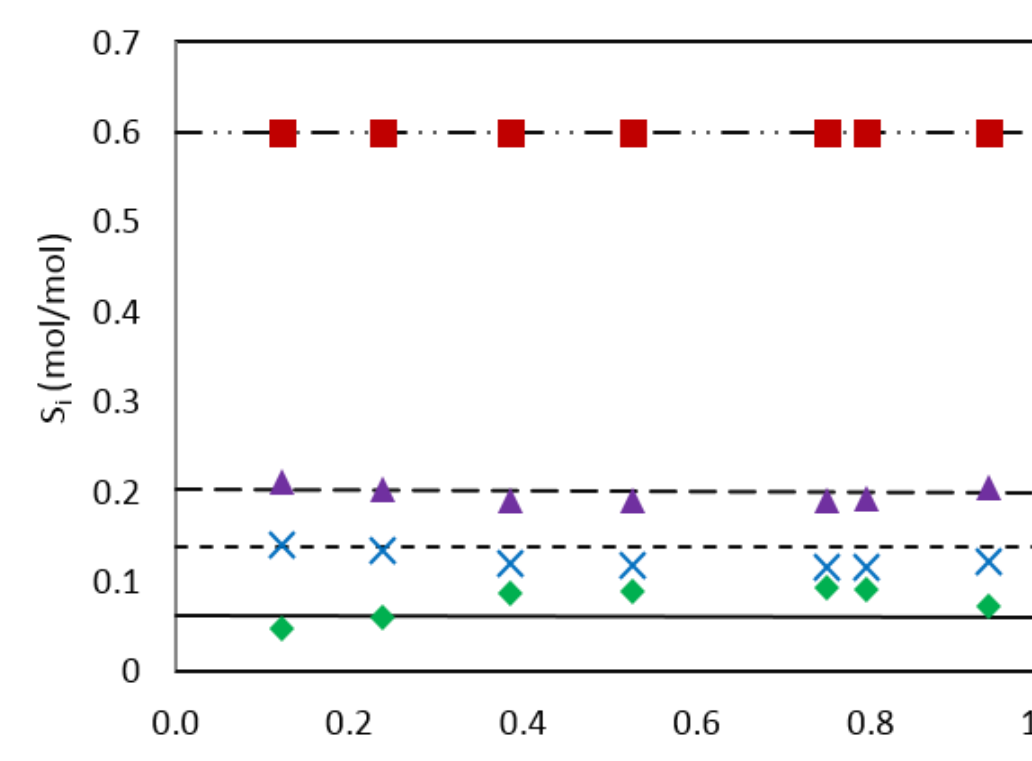
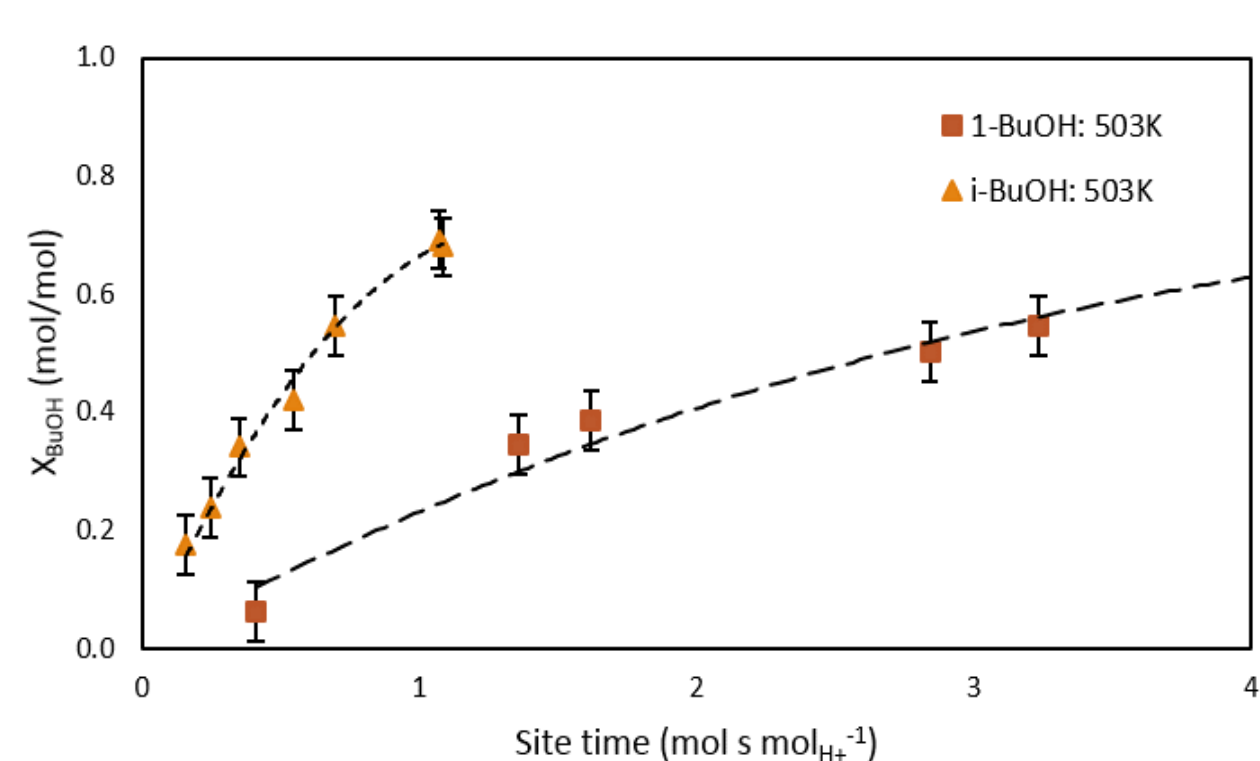
- Increased **activity** with decrease Si/Al **per site**
- **No selectivity shifts** on formed products
- Decrease in **acid strength** with Si/Al

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



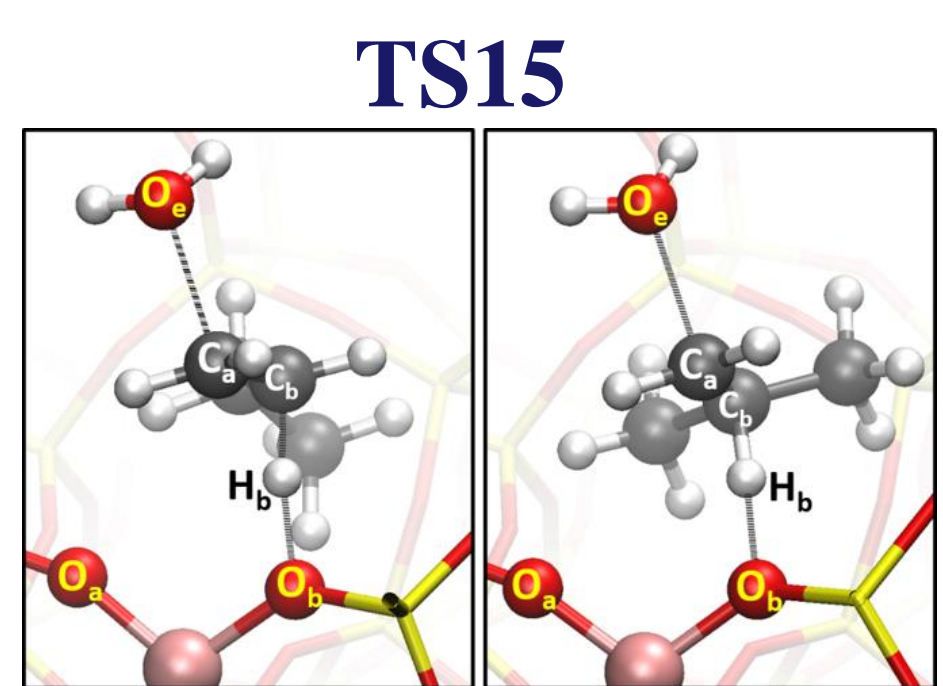
## Isomer Feedstocks

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



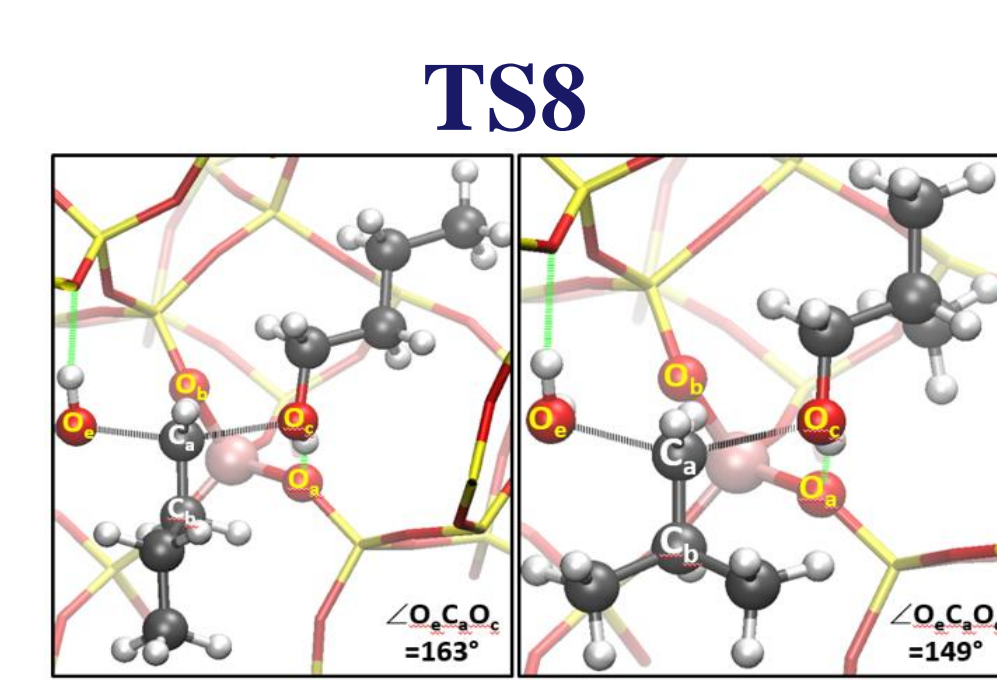
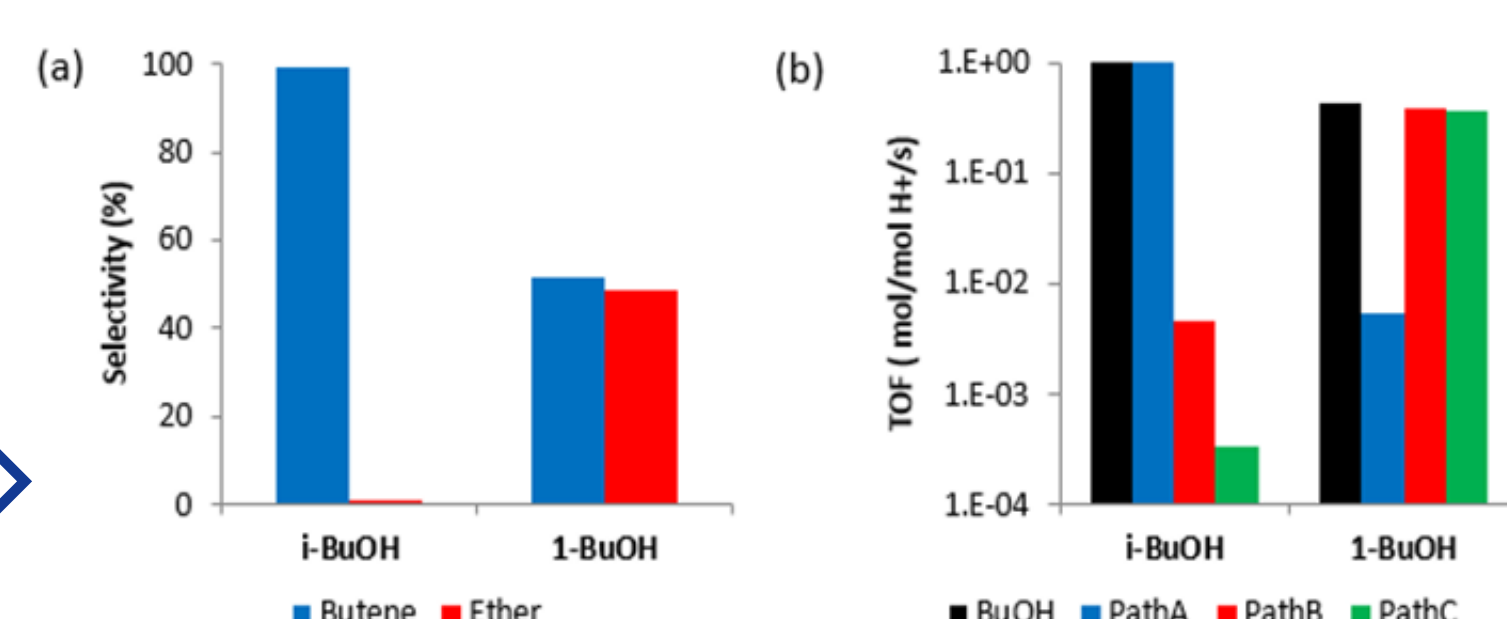
- **Increased activity** for iso-butanol vs. n-butanol
- **No isobutene** formation with n-butanol
- **No ether** formation with iso-butanol

Insights via **ab-initio** calculations of dominant **reaction pathways**



**Lower activation barrier** (TS15) for path A due to **branching of chain**

**Validation reaction model** via **plug flow simulation**



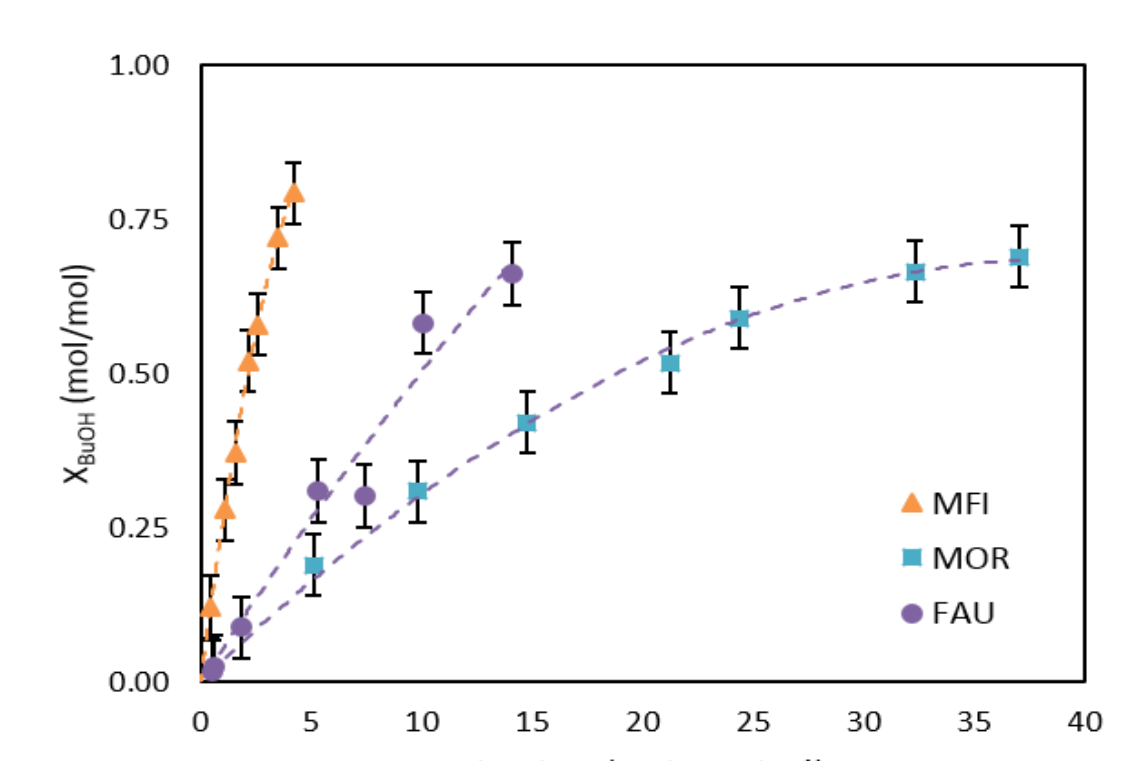
**Destabilization of TS8** (path B + C) due to **bound angle deformation**

**Model explains** the experimental **trends** for both feeds.

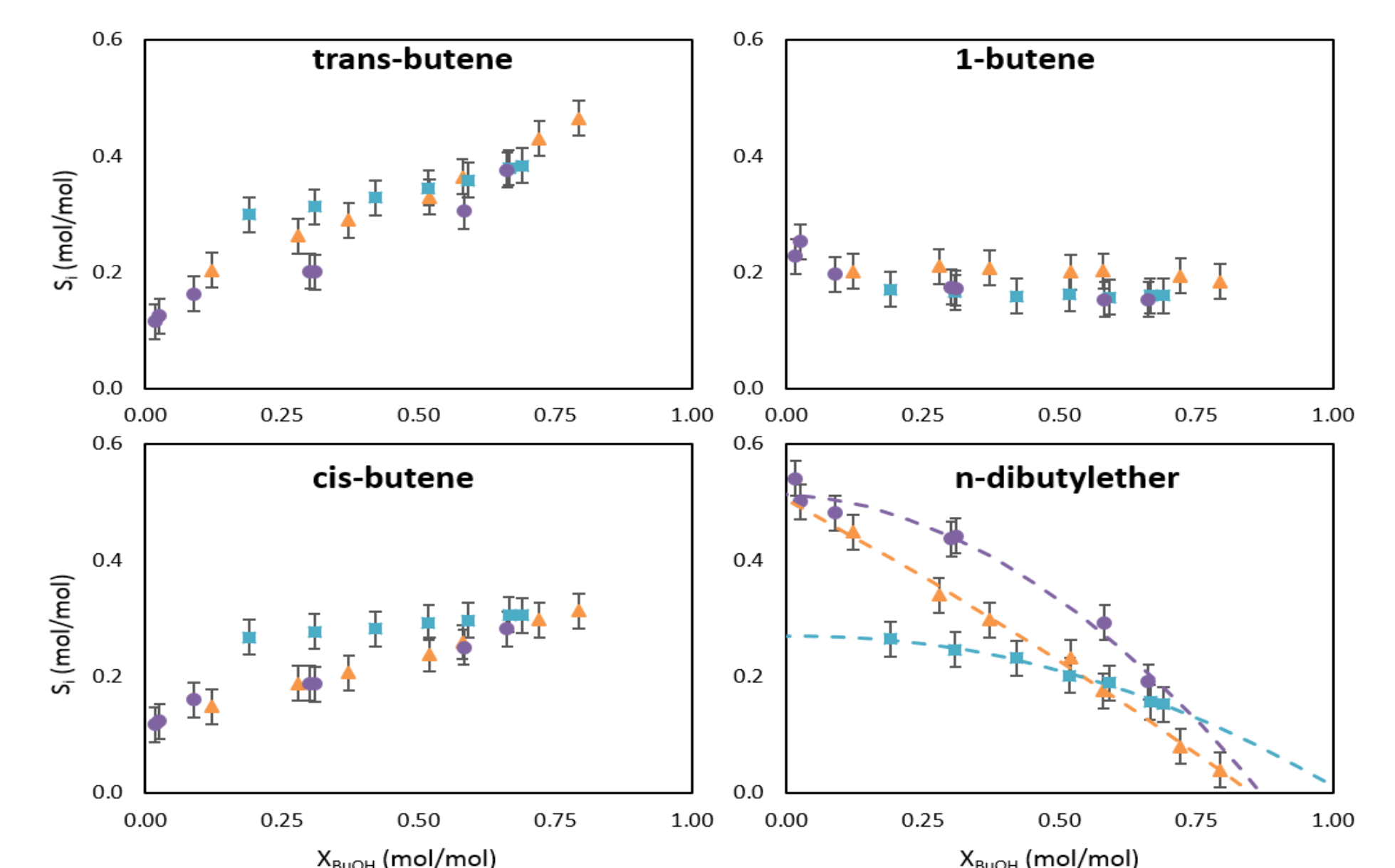
## Catalyst Comparison

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 bond **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**.