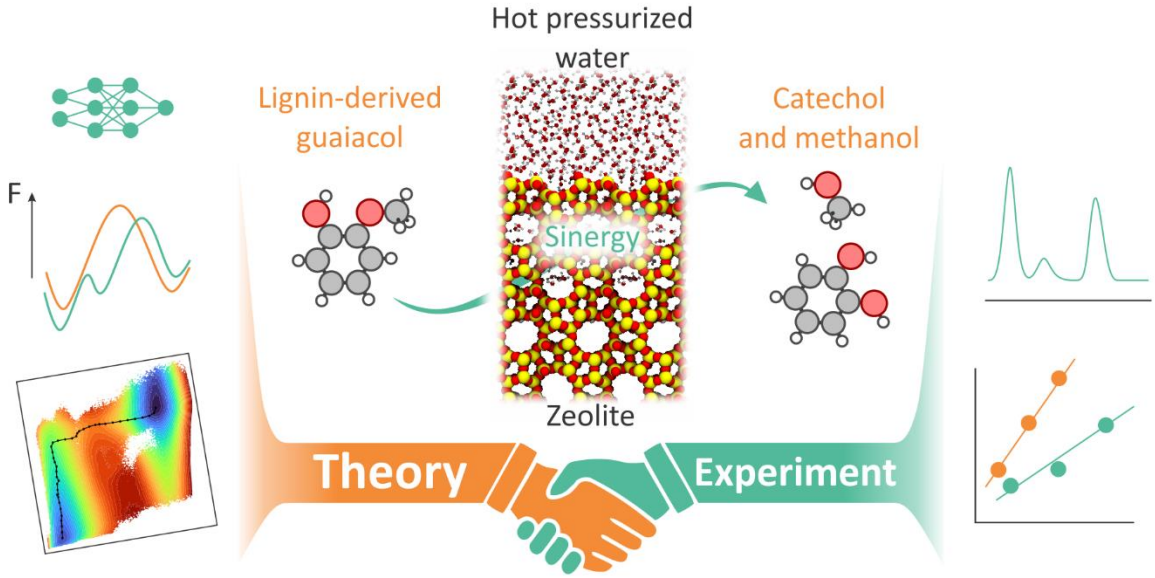
Towards a realistic modeling of complex zeolite-catalyzed reactions: the case of guaiacol demethylation

Massimo Bocus,[1,*] Elias Van den Broeck,[1] Matthias Bal,[2] Xian Wu,[3] Jeroen Bomon,[2] Louis Vanduyfhuys,[1] Bert Maes,[2] Bert Sels,[3] Veronique Van Speybroeck[1]

[1] *Center for Molecular Modeling, Ghent University, Technologiepark 46, 9052 Zwijnaarde, Belgium*
[2] *Organic Synthesis Division, Department of Chemistry, University of Antwerp, Groeneborgerlaan 171, 2020 Anwerpen, Belgium*
[3] *Center for Sustainable Catalysis and Engineering, KU Leuven, Celestijnenlaan 200F, 3001 Heverlee, Belgium*
** Email : massimo.bocus@ugent.be*

The conversion of renewable biomass to commodity chemicals is expected to play a pivotal role in the chemical industry of the future [1]. To understand and efficiently develop a new generation of catalysts able to process the complex organic feedstock, molecular modeling can provide an effective tool to complement and guide the experiment. However, the typical reaction conditions – high temperatures, pressures and solvent environment – require a methodological leap forward to provide reliable results [2]. Here, we present a full computational investigation of the Brønsted acid-catalyzed O-demethylation of guaiacol to catechol in hot pressurized water, as this reaction plays a key role in the conversion of lignocellulosic biomass to commodity chemicals [3]. We compare the reaction mechanism in homogenous phase and in the Beta zeolite using enhanced sampling ab initio molecular dynamics. The confinement effects in the zeolite pores are shown to affect the activity and behavior of the hydronium ions, thereby reducing the computed reaction barriers. We find that a concerted, O-activated S_N2 mechanism is preferred, without the formation of a stable intermediate oxonium ion. The computational results are extensively supported by the experiments, through detailed kinetic analysis of the reaction in the two catalytic systems.



A combined theoretical and experimental approach is used to fully elucidate the mechanistic features of the homo- and heterogeneous Brønsted acid-catalyzed O-demethylation of guaiacol in hot pressurized water.

[1] Schutyser, W. et al. *Chem. Soc. Rev.* **2018**, 47, 852-908.
[2] Van Speybroeck, V. et al. *Chem. Soc. Rev.* **2015**, 44, 7044-7111.
[3] Bomon, J. et al. *Angew. Chem. Int. Ed.* **2020**, 132, 3087-3092.