Selectivity control during the single-step conversion of aliphatic carboxylic acids to linear olefins

Jher Hau Yeap*,[†], Florent Héroguel[†], Robert L. Shahab[†,‡], Bartosz Rozmysłowicz[†], Michael H. Studer[‡] and Jeremy S. Luterbacher[†]

[†]Laboratory of Sustainable and Catalytic Processing, Institute of Chemical Sciences and Engineering, École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland.

[‡]Laboratory of Biofuels and Biochemicals, School of Agricultural, Forest and Food Sciences, Bern University of Applied Sciences (BFH), CH-3052 Zollikofen, Switzerland.
*jherhau.yeap@epfl.ch

Olefins are important building blocks for the synthesis of higher value chemicals in the petrochemical industry and they are typically produced from fossil fuels. As an alternative to fossil fuel-based chemicals, biomass-derived carboxylic acids could serve as a viable replacement feed for olefin production. However, the production of olefins from carboxylic acids in one step remains a challenge due to the stability of carboxylic acids and the tendency of olefins to over-hydrogenate during hydrogenation, leading to alkanes.

In the present study, we have studied the one-pot catalytic conversion of linear aliphatic carboxylic acids to linear olefins via tandem hydrogenation/dehydration reactions. Hexanoic acid was converted to a mixture of hexenes over Cu nanoparticles supported on commercial silica-alumina (Siral 70) in a continuous flow reactor. At 210 °C and 5 bar H_2 pressure, we obtained 96.7% conversion of hexanoic acid, with a molar product distribution of 92.0% hexenes and 7.3% hexane. Remarkably, we observed a brusque selectivity switch to 99.8% hexane at 100% conversion.

A product intermediates study shows that when switching from a feed of pure hexene to a mixture of hexene and hexanoic acid, overhydrogenation of hexene can be suppressed. In addition, hexene temperature-programmed desorption (TPD) and FT-IR spectroscopy reveals that adsorption of hexanoic acid prevents hexene from accessing the catalyst surface, thus avoiding overhydrogenation. Reactions using butanoic acid as feed also exhibit similar phenomena. We have also performed reactions utilizing butanoic acid derived from biomass fermentation, albeit with significant catalyst deactivation.

We propose that the presence of a small amount of carboxylic acid on the surface of the catalyst prevents overhydrogenation of the olefins. In light of these results, current efforts are targeted at applying this concept to explain similar phenomena in other reactions, particularly in biomass conversion. The presence of numerous carboxyl groups in native/pre-treated biomass might explain the difference in catalyst performance/selectivity when processing model feed versus real biomass. Furthermore, the addition of carboxylic acids to the reaction medium during biomass upgrading could afford more control over the selectivity of the reaction.