

**Selectivity control during the one-pot conversion of aliphatic carboxylic acids to linear olefins through tandem hydrogenation/dehydration**J. Yeap<sup>1</sup>, B. Rozmysłowicz<sup>1</sup>, J. Luterbacher<sup>1\*</sup><sup>1</sup>Laboratory of Sustainable and Catalytic Processing (LPDC), Ecole polytechnique fédérale de Lausanne, CH-1015 Lausanne, Switzerland

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. The combination of the hydrogenation properties of earth-abundant Cu and the acid sites on silica-alumina allows hydrogenation and dehydration to occur simultaneously, a process that normally calls for different reaction conditions. At 483 K and 5 bar H<sub>2</sub> gauge pressure, we obtained 98.5% conversion of hexanoic acid, with a molar product distribution of 88.9% hexenes and 11.1% hexane. Remarkably, we observed a brusque selectivity switch to 99.9% hexane at 100% conversion. We hypothesize that the presence of a small amount of hexanoic acid on the surface of the catalyst prevents overhydrogenation of the hexenes. Current efforts are targeted at reaction kinetic studies as well as surface studies using FT-IR spectroscopy to ascertain the nature of this selectivity switch. Process runs using carboxylic acids produced from biomass fermentation will also be carried out to ensure process compatibility.