Influence of hydroxyapatite composition on the catalytic conversion of bio ethanol

The production of chemicals from renewable raw materials such as bio-ethanol (obtained by recycling vegetable biomass) is a major societal concern. In particular, the production of platform molecules such as n-butanol (also directly used as a solvent and gasoline fuel additive) or butadiene (monomer of synthetic rubbers and polymers) from bio-ethanol is an important route toward a more sustainable chemical industry.[1,2] The complex ethanol reaction network leads to the formation of crotonaldehyde that is a common intermediate for the formation of n–butanol or butadiene by competitive routes associated with total hydrogenation or selective hydrogenation followed by dehydration step, respectively. Surprisingly, the catalysts reported to be highly selective in n-butanol (hydroxyapatite)[1] or butadiene (magnesium silicate)[2] do not exhibit any obvious (metallic) hydrogenation function and it is often assumed that a suitable acid-base balance would be a key point to govern the selectivity of the reaction. The aim of this study is to investigate how tuning the acid-base properties of the catalyst and metal doping may favor one reaction pathway over the other.

Hydroxyapatite is bio-compatible calcium phosphate material known as the main mineral component of bones and teeth. It is also widely used as a metal sorbent and as a heterogeneous catalyst for acid-base and bifunctional reactions.[1,3] Its composition can deviate from the Ca10(PO4)6(OH)2 ideal formula resulting in tunable acid-base properties. In addition, its framework flexibility enables various substitutions, likely to modulate the nature and the strength of the acidic sites and/or to confer redox properties to the system.[3]

In this project, phosphate groups and calcium cations will be substituted by silicate groups and Zn2+, Ni2+, Cu2+ cations, respectively. Direct one pot co-precipitation synthesis using an automated reactor will be carried out to tune the substitution rate and the textural properties of the catalysts. The catalysts structure and composition will be characterized by complementary techniques (XRD, Raman, ssNMR, XRF) and their influence on the n-butanol and butadiene selectivity will be evaluated. Structure-reactivity relationships will be discussed in line with the acid-base properties and with the hydrogenating / dehydrogenating ability of the related surfaces.

We are looking for a motivated PhD candidate with a background in material chemistry and/or catalysis.

[1] Ben Osman et al., ChemCatChem 2019, 11, 1765