

## Acidity-reactivity relationships in catalytic esterification over ammonium sulfate-derived sulfated zirconia

### Abstract

New insight was gained into the acidity-reactivity relationships of sulfated zirconia (SZ) catalysts prepared via  $(\text{NH}_4)_2\text{SO}_4$  impregnation of  $\text{Zr}(\text{OH})_4$  for propanoic acid esterification with methanol. A family of systematically related SZs was characterized by bulk and surface analyses including XRD, XPS, TGA-MS,  $\text{N}_2$  porosimetry, temperature-programmed propylamine decomposition, and FTIR of adsorbed pyridine, as well as methylbutynol (MBOH) as a reactive probe molecule. Increasing surface sulfation induces a transition from amphoteric character for the parent zirconia and low S loadings < 1.7 wt%, evidenced by MBOH conversion to 3-hydroxy-3-methyl-2-butanone, methylbutyne and acetone, with higher S loadings resulting in strong Brønsted-Lewis acid pairs upon completion of the sulfate monolayer, which favored MBOH conversion to prenal. Catalytic activity for propanoic acid esterification directly correlated with acid strength determined from propylamine decomposition, coincident with the formation of Brønsted-Lewis acid pairs identified by MBOH reactive titration. Monodispersed bisulfate species are likely responsible for superacidity at intermediate sulfur loadings. [View Full-Text](#)