Citrate-mediated sol–gel synthesis of Al-substituted sulfated zirconia catalysts for α-pinene isomerization

Abstract

Solid acids are desirable heterogeneous catalysts for green chemistry, with zirconia and its sulfated analogues offering tunable Lewis/Brønsted character. A new route to sulfated ZrO_2, and Al-substituted ZrO_2 (SO_4/Al_xZrO_2), via carbonization and calcination of metal citrate gels and their subsequent sulfation by $(NH_4)_2SO_4$ is reported. Structural and acidic properties of these materials were characterized by XRD, Raman, XPS, TGA-MS, N_2 porosimetry, and propylamine and pyridine titration. Parent and sulfated materials all adopted the tetragonal zirconia phase, with Al-substitution (evidenced by contraction of the zirconia lattice parameter) at between 0.38–3.50 wt% increasing the surface area but decreasing acid strength, accompanied by an overall increase in total acid site loading and Lewis character. Low Al concentrations enhance α-pinene isomerization activity by up to 50% due to the increased acid site loading, however the Turnover Frequency (TOF) remained constant indicating a common active site. The TOF decreased for Al concentrations >3.5 wt% due to a further fall in acid strength, manifest as higher selectivity to polycyclic versus monocyclic products.