# Functionalized metal oxide nanocrystals as a highly acidic heterogeneous catalyst

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Nowadays industry faces additional pressure to be cleaner and greener, which requires implementation of new greener processes and catalysts. Many industrial processes often use homogeneous catalysts due to their high activity, allowing for all of the molecules or metal ions to be potential active sites. However, these are in the same phase as the reaction and difficult to separate. Mineral acids are heavily used in acid catalysed industrial processes in agriculture, food processing, manufacturing of medical drugs, fuels and many others. However, they are connected with corrosion and environmental pollution. Heterogeneous catalysts are high surface area solids that offer easy separation and a high purity product, easy catalyst removal and recyclability, tailored active sites and selectivity towards desired products.

Current commercial solid acid catalysts suffer from relatively small numbers of active acid sites and low acidity. The most attractive of them, polymeric resin Amberlyst 15, offers relatively high numbers of Bronsted acid sites by mass, and good physical and chemical stability, but it degrades at higher temperatures or during regeneration processes. Another group of solid acid catalysts are metal oxide nanoparticles, offering high stability and reusability in both aqueous and organic media but possessing lesser number of active sites. Functionalization with acidic species on their surfaces creates Lewis or Bronsted acid sites with a synergistic effect between the metal core and the functional group, while also stabilizing reactive high energy surface sites.

We study $TiO_2$ and $ZrO_2$ nanocrystals and their functionalized analogues by introducing higher numbers of Bronsted and Lewis acid sites in the esterification of Levulinic acid into ethyl levulinate. A strong electronic withdrawing effect imposed by sulphates results in high Lewis acidity of the neighboring exposed Ti atom while two additional Bronsted acid sites are created, one on the neighbouring oxygen atom and another with proton on the sulphate group. Type, quantity and strength of acid sites are examined with $^{31}P$ NMR technique using TMP as a highly selective probe, and correlated with surface properties of nanocrystals.

The understanding of surface structure of very small nanoparticles with a large number of stable active sites plays an important role in the development of more commercially attractive heterogeneous catalysts.