16a Templated Organic-Inorganic Active Sites for Bifunctional Heterogeneous Catalysis

Alexander Katz, John D. Bass, and John Daniels

Base-catalyzed reactions undergoing an aldolate mechanism are an important class of chemical transformations. The catalytic activity for these reactions has been shown to dramatically increase for catalysts constisting of both weak acid and base sites; however, it has been difficult to systematically compare catalysts and determine the effects of framework, acid, and base site contributions to catalysis rates. We wished to study the effect of acid-base bifunctional catalysis and separate it from dielectric effects, within the context of a model base-catalyzed reaction. Our approach involved removing multiple competing effects in comparing rates from catalysts by using imprinting of bulk silica as a tool for synthesizing catalysts with differing acidity and dielectric environments surrounding the same catalytically active site. We recently discovered that site-isolated amines, which were synthesized by using a thermolytic imprinting methodology, were up to 120-fold more active for the Knoevenagel condensation of isophthalaldehyde and malononitrile compared with conventional amine-on-silica material. To investigate differences between active sites in imprinted and conventional catalysts, we used a variety of spectroscopic techniques to show that the amine site in imprinted is surrounded by an acidic outer-sphere environment comprising silanols, whereas anchored amines in conventional catalysts are surrounded by other amine sites and lack of an acidic environment. Here, we investigate the bifunctional nature of the catalytic sites in imprinted catalysts and unequivocally prove that it is the acid-base properties of the active sites that are responsible for their higher activity over conventional catalysts for the Knoevenagel condensation reaction. We apply these lessons for the synthesis of a new generation of hybrid organic-inorganic catalysts, which rely on further refined templated sites, for controlling activity and enantioselectivity in these chemical reactions. A systematic comparison of base catalysts demonstrates that a bifunctional catalytic mechanism significantly accelerates base-catalyzed reactions, which is not possible to achieve by tailoring the dielectric constant alone, and relies on organization between acid and base sites.