Kinetic Consequences of Open and Closed Supported Molecular Active Sites

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Introduction

A common trait of metalloenzymes is to enforce a coordinatively unsaturated and open active site within the catalyst resting state. Open sites have historically been recognized as the relevant active sites in synthetic heterogeneous catalysts as well (i.e. steamed Sn-β zeolite and TS-1 zeolite active site),1 where open refers to active sites that are able to covalently bind a reactant via release of a labile monodentate ligand on the Lewis acid metal center, whereas closed sites are unable to do this. In this paper, we demonstrate and discuss the design and synthesis of the first open and closed variants of a grafted Lewis acid site, using an organic-inorganic approach, which is based on grafted Al(III)-calix[4]arene active sites on the surface of partially dehydroxylated porous silica.

Materials and Methods

Al(III)-calixarene complexes and materials were synthesized based on procedures described previously for related systems. Catalysis was performed according to literature precedent.2,3,4

Results and Discussion

Catalysis using open catalyst 1 follows the previously observed and expected pseudo-zero-order rate dependence on ketone concentration. The turnover frequency for catalyst 1-SiO2(800) is virtually the same as that observed for homogeneous catalyst 2.2 No detectable leaching of the catalyst is observed via hot filtration test during catalysis (performed at reaction temperature – see supporting information for details). When comparing 1-SiO2(450) as catalyst at either dilute or saturation surface coverage of grafted Al(III)-calix[4]arene sites, there is no coverage dependence on the turnover frequency (see supplementary information). These data are consistent with the single-site nature of 1-SiO2(450) as catalyst, as observed for other grafted metallocalixarene-on-silica catalysts. In addition, the slightly lower rate for 1-SiO2(450) relative to 1-SiO2(800) suggests that a high degree of silica dehydroxylation may promote monodentate attachment of open precursors to the silica surface, since bidentate grafting is expected to synthesize MPV inactive sites within a closed configuration. The observations above rationalize the need for steaming, in order to open the coordination sphere surrounding heterogeneous Lewis acid active sites, when using Sn-β zeolite as catalyst for MPV reduction.

Significance

The first design and synthesis of open/closed grafted metal cations are synthesized and used to learn about catalysis for reactions involving hydride and oxo transfer. This also enables extensions to other metals, which will be discussed.

Figure 1. MPV catalysis: Open site 1-SiO2-450 in brown (■), Open site 1-SiO2-800 in red (●), and closed 3-SiO2-450 shown in black (▼), homogeneous catalysis with 2 in blue (○). Grafted aluminum isopropoxide on silica has a negligible catalytic activity, which is similar to that observed for 3-SiO2-450 for MPV reduction.

References