Outer-Sphere Effects in Heterogeneous Catalysis

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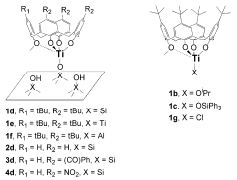
Introduction

A promising approach for elucidating heterogeneous chemical reactivity is to synthesize well-defined molecular complexes that are subsequently covalently anchored within controlled inner- and outer-sphere environments surrounding the active site. We apply this approach for understanding selective oxidation catalysis using grafted calixarene-Ti complexes on silica, which are single-site heterogeneous catalysts for the epoxidation of alkenes using organic hydroperoxides.[1,2] Here, we synthesize novel calixarene ligands containing electron-withdrawing substituents, which together with previously described complexes, form a series of geometrically identical Ti-phenolate complexes preorganized for similar covalent grafting onto oxide surfaces. We further investigate the role of outer-sphere Brönsted acidity on epoxidation catalysis by synthesizing TiO_2- and Al_2O_3-grafted versions of the catalyst, and compare epoxidation rates over these materials to that of SiO_2-supported **1d** and a homogeneous model compound consisting of similar coordination around the Ti center, achieved by replacing a silanol on the silica surface with triphenylsilanol in the synthesis recipe. These incremental modifications to the inner and outer sphere enable us to assemble a comprehensive picture of the role of the support as an active outer-sphere ligand in Ti epoxidation catalysts, and to unequivocally answer which bonds are being made and broken during peroxide binding and other kinetically relevant steps.

Materials and Methods

The catalysts below were synthesized in particular to address the kinetic significance of calixarene-Ti and silica-Ti connectivity for epoxidation catalysis.



Results and Discussion

A previously developed correlation for all Ti-SiO_2 materials is given by the dashed line.[2] This correlation fails to account for the low reactivity of homogeneous catalyst **1c** and Al_2O_3-supported **1f** which possess no or too strong of a Brönsted acidity, respectively. The data in Figure 1 demonstrate that effects other than electronic effects at the metal center and coordinative saturation are responsible for the low catalytic activity when grafting calixarenes on alumina (as well as anatase using a solid-state NMR spectroscopic comparison), and in the case of the homogeneous model catalyst 1c, which entirely lacks a protic outer-shere. Kinetic data on different calixarene upper rim compositions reveals a very weak dependence on olefin epoxidation reactivity on the upper rim, strongly suggesting that calixarene-Ti connectivity remains intact in all kinetically relevant steps. When the above data is taken together, the effect of outer-sphere environment can be rationalized. Stronger Brönsted acids' ability to hydrogen bond to metal-bound peroxo entities weakens the O-O bond, activating it for oxygen transfer reactions, but too much outer-sphere Brönsted acidity disfavors peroxide binding. Silica as catalyst support for olefin epoxidation represents a compromise between these two competing effects.

Significance

Grafted calixarenes are used as persistent surface organometallic ligands to study the effect of environment on Ti(IV) Lewis acid-catalyzed heterogeneous epoxidation catalysis. Results lead to a unified model in which there is an active role for support defect sites within the epoxidation mechanism for activating bound hydroperoxide.

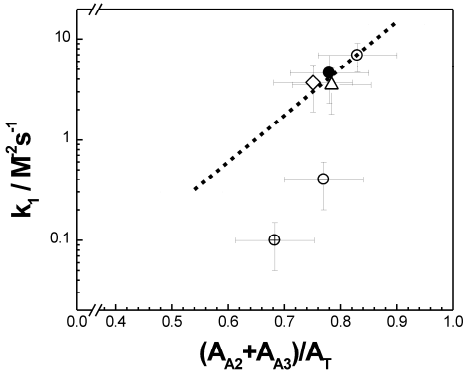


Figure 1. The epoxidation rate constant (pretreated at 393 K, epoxidation of cyclohexene with TBHP) is plotted against XANES pre-edge component peaks relative area $(AA_2+AA_3)/A_T$ for materials **1c** (O-with dash in middle), **1d** (O), and **1f** (⊕). The dashed line marks a correlation developed previously that spans all tested 4- and 5-coordinate Ti-SiO_2 materials.[2]

References

1. J.M. Notestein,. E. Iglesia, A. Katz, *J. Am. Chem. Soc.*, 126 (2004), 16478.
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