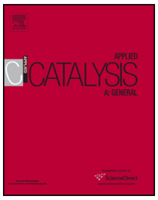
Applied Catalysis A: General 511 (2016) 78–86

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Catalyst structure and substituent effects on epoxidation of styrenics with immobilized Mn(tmtacn) complexes

Patricia Anne A. Ignacio-de Leon[1], Christian A. Contreras[2], Nicholas E. Thornburg, Anthony B. Thompson[3], Justin M. Notestein*

Department of Chemical and Biological Engineering, Northwestern University, 2145 Sheridan Road, Evanston, IL 60208, USA

ARTICLE INFO

Article history:
Received 14 August 2015
Received in revised form
30 November 2015
Accepted 1 December 2015
Available online 3 December 2015

Keywords:
Epoxidation
Hydrogen peroxide
Supported catalyst
Hammett relationships
Manganese

ABSTRACT

Monomeric and dimeric complexes of Mn 1,4,7-trimethyl-1,4,7-triazacyclononane (tmtacn) were immobilized under reaction conditions onto solid supports to create heterogeneous catalysts for epoxidation with H_2O_2. These solid supports consist of activated carbon or silica grafted or co-condensed with benzoic or C3/C4 acids that function both as tethering points and as required co-catalysts. Immobilized catalysts were as much as 50-fold faster than the analogous soluble system, and an immobilized, dimeric Mn(tmtacn) complex with a solid benzoic acid co-catalyst gave the highest yields to epoxide. A Hammett study on the catalytic epoxidation of a series of styrenes showed weak increases in yield for more electron-withdrawing *p*-substituents reactants for both immobilized complexes, which runs counter to previous observations with analogous homogeneous catalysts, and which appears to reflect a previously unappreciated tradeoff between the intrinsic epoxidation reactivity and strong catalyst inhibition by styrene oxides and glycols. Finally, these catalysts were tested with a variety of solid-co-catalysts, and were successfully utilized in the challenging epoxidation of divinylbenzene to industrially-useful divinylbenzene dioxide using a cascade of two catalyst charges.

1. Introduction

The selective oxidation of alkenes to epoxides or *cis*-diols remains an important research area for catalyst development and industrial use. Epoxides and vicinal diols are versatile and reactive chemical intermediates for commodity chemicals and fine/specialty chemicals alike. Dioxides (bisepoxides) such as divinylbenzene dioxide have particular application in epoxy resins, but their syntheses see very little research in the open literature. Alkene epoxidation/*cis*-dihydroxylation has been achieved using a wide variety of oxygen-transfer agents including H_2O_2, organic peroxides (e.g., *t*-BuOOH) [1], and organic peroxyacids (e.g., *m*-chloroperbenzoic acid) [2], and facilitated by small molecule inorganic and organocatalysts [3]. H_2O_2 is a preferred oxidant due to its low cost, high atom efficiency and environmentally benign co-product (water) [4–6]. Transition metal-containing epoxidation catalysts include salen [7–10] or porphyrin [11–13] complexes, and a class that takes inspiration from non-heme metalloenzymes and consists of Fe or Mn complexes of ligands including triazacyclononane (tacn) [14], tris(2-pyridylmethyl) amine (tpa) [15,16], bis(2-pyridylmethyl) ethylenediamine (bpmen) [17] and others [18–21].

Manganese 1,4,7,-trimethyl-1,4,7-triazacyclononane (tmtacn) complexes were first prepared and characterized in 1988 by Weighardt et al., [22]. and these and related triazacyclononane (tacn) complexes have been reported and reviewed [23,24] for olefin epoxidation and dihydroxylation [25–27], alcohol oxidation [28–31], sulfoxidation [32,33], and alkane oxidation [34–36] to alcohols, aldehydes and ketones via organic hydroperoxides [37]. Carboxylic acid co-catalysts are essential to achieve high catalyst productivity and selectivity [38–44], and the acids have been proposed to form adducts with the Mn complex [45,46].

Immobilized versions of this catalyst have attracted interest due to ease of catalyst (or co-catalyst) separation [47–50]. Mn(IV) complexes have been covalently attached to insoluble polymers by *N*-alkylation of tacn [51], or immobilized as insoluble salts with polyoxometallates [52]. Our group has previously reported on immobilization of the dimer [Mn(tmtacn)-(μ-O)$_3$-Mn(tmtacn)] Mn_2 under reaction conditions onto the surface of carboxylic acid-

---

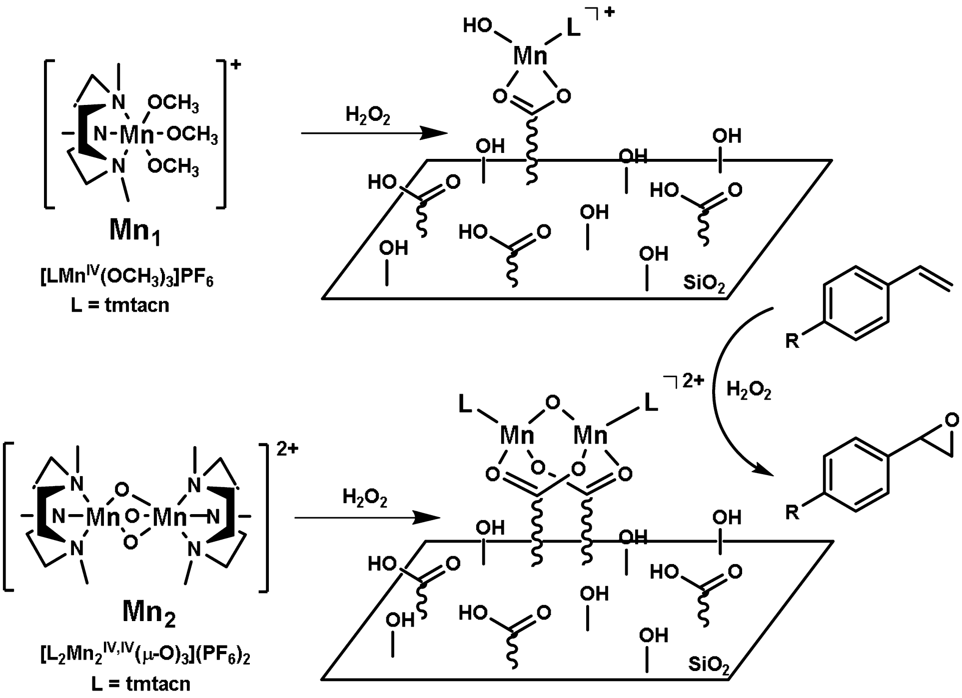
* Corresponding author at: 2145 Sheridan Rd., Technological Institute E136, Evanston, IL 60208, USA.
E-mail address: j-notestein@northwestern.edu (J.M. Notestein).

[1] Argonne National Laboratory, Energy Sciences Division, USA.

[2] GreatPoint Energy, USA.

[3] University of Minnesota, Department of Chemistry, USA.

http://dx.doi.org/10.1016/j.apcata.2015.12.002
0926-860X/



Scheme 1. The complexes **Mn**$_1$ and **Mn**$_2$ used in this study and a representation of the immobilized catalysts for the epoxidation of *p*-substituted styrenes[a].
[a]The structure of immobilized **Mn**$_2$ has been established earlier as a reduced Mn^{III,III} carboxylate-bridged dimer [14]; the Mn—O—Mn bond will open under reaction conditions. The structure of immobilized **Mn**$_1$ is proposed by analogy. Counteranions not shown. Supports include a silyl benzoate and a silyl propanoate grafted to SiO_2 and a butanoate species co-condensed into a SiO_2 framework.

modified solid supports (Scheme 1), and we have carried out epoxidation screening with diverse alkenes [53], and several solid supports [54]. Spectroscopic [14] and microkinetic modeling studies [55] are consistent with formation of dimeric Mn complexes with bridging carboxylates as the catalytic resting state, and a Mn hydroperoxo active intermediate, as has been argued by others [40].

Utilization of Mn(tacn) catalysts has overwhelmingly focused on the dimeric complexes, even though a mononuclear active species [56]. has been proposed to be produced from the dimer. Likewise, unusual reactivity of an immobilized Mn(tacn) was proposed to be due to stabilization of a monomeric structure [47]. However, there are relatively few reports on the direct utilization of monomers or systematic studies of the effect of alkene and catalyst structure, especially for solid-supported systems. Ilyashenko et al. recently compared Mn_1 and Mn_2 as homogeneous catalysts and suggested unique catalytic active species for each, as evidenced by a marked difference in reactivity patterns towards various alkenes [57]. In this new contribution, monomeric and dimeric Mn precursor complexes Mn_1 and Mn_2 are immobilized on several different solid co-catalysts and studied in the epoxidation of a family of *p*-substituted styrenes with varying electron density (Scheme 1). In addition to mechanistic insight, these results are valuable for optimizing reaction conditions over this important class of catalysts, which we demonstrate for the challenging reaction of divinylbenzene (DVB) epoxidation, as relevant to the synthesis of epoxy resins.

2. Experimental

2.1. General considerations

N_2 sorption experiments were performed with a Micromeritics ASAP 2010. Diffuse reflectance, fourier transform-infrared spectroscopy (DRIFTS) was performed with a Nexus 870 spectrometer (Thermo Nicolet). ^{13}C NMR (CP-MAS) spectra for solid samples were collected with a Varian 400 MHz VNMRS. Elemental analyses were carried out by Galbraith Laboratories. Electrospray ionization mass spectrometry (ESI-MS) was carried out in the positive ion mode using a Bruker AmaZon SL Ion Trap. Scanning electron microscopy (SEM) used a Hitachi S4800-II cFEG SEM.

2.2. Catalyst synthesis

1,4,7-Trimethyl-1,4,7-triazacyclononane (tmtacn) was synthesized in several steps of tosylation, cyclization, and reductive amination following literature procedures to give a viscous, light yellow oil whose ^1H NMR spectra agreed with literature (overall 18% yield) [58]. $[Mn(tmtacn)(OMe)_3](PF_6)$ (Mn_1) was synthesized according to published methods and collected as dark brown needles (10% yield) [26]. Mass spectrum (ESI$^+$): *m*/*z* 319.17 ($[M-PF_6]^+$). Elemental analysis (calc. $MnC_{12}H_{30}N_3O_3PF_6$): C 31.1% (31.0), N 8.9% (9.0), H 6.6% (6.5), Mn 14% (11.8). $[Mn_2(tmtacn)_2(\mu\text{-}O)_3](PF_6)_2$ (**Mn**$_2$) was synthesized via modification of a known procedure and collected as red crystals (59% yield) [22]. Mass spectrum (ESI$^+$): *m*/*z* 645.17 ($[M-PF_6]^+$). Elemental analysis (calc. $Mn_2C_{18}H_{44}N_6O_4P_2F_{12}$): C 26.9% (26.7), N 10.3% (10.4), Mn 13.0% (13.6).

2.3. Co-catalyst synthesis

Silica-based solid co-catalysts were prepared by grafting or co-condensation. Prior to surface modification, a commercially available mesoporous SiO_2 (Selecto brand, 32–63 μm particle size) was pre-treated by heating to 150 °C under dynamic vacuum for 12 h. Grafted co-catalysts were prepared as previously reported at nominal loadings of 0.25, 0.5 or 1 mmol/g from grafting of 2-(carbomethoxy) ethyltrimethoxysilane or ethyl 4-(triethoxysilyl) benzoate to dehydrated SiO_2 in pyridine. After reflux and washing, the free acids were generated by refluxing in 1 M HCl and washing to yield propanoic acid- and benzoic acid-modified silica (PA-SiO_2 and BA-SiO_2), respectively [54]. Sol–gel materials were