Novel Heterogeneous Catalysts for the Selective Oxidation of Phenolic Lignin Degradation Products Into Benzoquinones

Daniel L. Taylor, Lena Elenchin and *Craig E. Barnes**
[1]*University of Tennessee, Knoxville, TN 37996 (USA)*
*cebarnes@utk.edu

Introduction

As the earth's supply of fossil fuels diminishes, the value of alternative and environmentally sound routes to the production of fuels and fine chemical cannot be overstated. An abundant and cheap source of low molecular weight phenolic compounds can be extracted from the lignin component of biomass. The amorphous polymer lignin comprises of 15-30% of biomass by weight [1]. Exploring techniques to optimize biomass conversion as an alternative energy source presents a variety of challenges currently – one of which is to oxidize phenolic lignin degradation products into usable compounds.

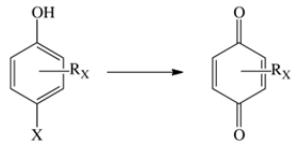

Figure 1. Selective oxidation of phenolic compounds to 1,4-benzoquinones. (R=CH_3, ^{t}Bu, OCH_3. X=H, CHO, CH_2OH)

Heterogeneous catalytic selective oxidation of organic compounds to platform or fine chemicals in industry is ever-expanding field. The transition from stoichiometric oxidation to less expensive and less hazardous catalytic oxidation processes has lead to investigations with aqueous selective oxidation catalysts [2]. Our research is predicated on a building block approach to the synthesis and design of targeted, single-site, heterogeneous catalysts wherein the environment of the active site and morphological features of the system can be controlled to optimize the reactivity and conversion of the desired substrate. Recent work has focused on the synthesis and application of silicate matrices with atomically dispersed titanium(IV) active metal sites (Fig. 2).

Titanium silicate catalysts have been documented for their successful role in the liquid-phase oxidation of various organic compounds. With respect to our titanium catalysts, we have observed high selectivity and conversion of alkyl substituted phenols into 1,4-benzoquinones with a family of atomically dispersed titanium catalysts in silica where the connectivity to the matrix is systematically varied.

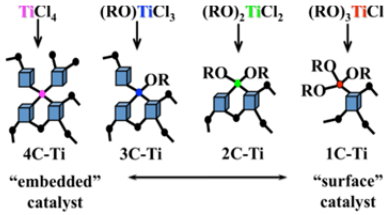

Figure 2 Structures of the 4-C, 3-C, 2-C, and 1-C Ti complexes.

Materials and Methods

All catalysts were synthesized following literature procedures and methods [3] by reacting the building block $Si_8O_{12}(OSnMe_3)_8$ with either $TiCl_4$, $TiCl_3O^iPr$, $TiCl_2(O^iPr)_2$, or $TiCl(O^iPr)_3$, depending on the desired connectivity as depicted in Fig 1. The cross linking of the building block with each titanium precursor followed the procedure of the literature methods described in preparing analogous vanadate species [4].

Catalytic reactions were conducted in 4mL glass vials with septum caps and carried out at various temperatures (35°C, 50°C, 70°) in 3mL of CH_3CN. 0.012mmol Ti (2-C catalyst contained 8.5 Ti wt%) reacted with 0.20mmol of different S-model substrates dissolved in acetonitrile. Excess aqueous hydrogen peroxide (35% w/w) was injected to initiate catalytic reaction. Aliquots were taken before H_2O_2 injection (t=0min) as well as throughout the reaction and analyzed via GC-MS and NMR.

Results and Discussion

Current selective oxidation reactions focus on S-model phenolic compounds obtained from lignin degradation. S-model phenols contain two methoxy substituents *ortho* to the –OH position on the aromatic ring, but vary in the *para* position as illustrated in Fig 1. Preliminary studies have indicated that S-models with no alkyl group *para* to the –OH group favor the 1,4-benzoquinone product the most, followed by CH_2OH *para* alkyl groups, while the CHO *para* aldehyde compounds are the least selectively converted substrates.

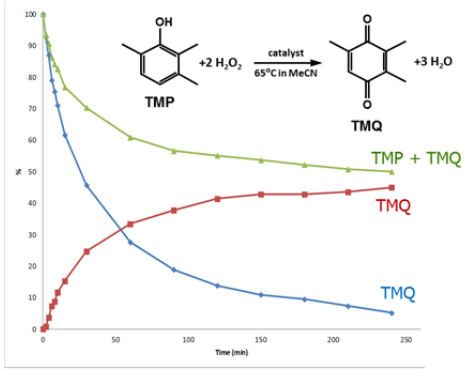

Figure 3 Kinetic data showing conversion (%) vs time for the reaction of trimethyl phenol (TMP) to 1,4 trimethyquinone (TMQ) for a 2nd-generation 4C-titanium in silica catalyst.

Significance

A new family of single-site titanium silicate catalysts selectively oxidize phenolic lignin degradation compounds into value added benzoquinones. The activity of specific catalysts depends on both the connectivity and imprinting of the matrix around the titanium site.

References

1. Weckhuysen, B., Jongerius, A., Bruijinincx, P., Zakzeski, J. *Chem. Rev.* 110, 3552 (2010).
2. Kholdeeva, O.A., Trukhan, N.N., *Russ. Chem. Rev.* 75, 5, (2006).
3. Clark, J.C., Barnes, C.E. *Chem Mater.* 19, 3212 (2007).
4. Lee, M., Jiao, J., Mayes, R., Hagaman., Barnes, C.E. *Catalysis Today*. 160, 153 (2011).