Surface-support interactions in Mn-based molecular oxidation catalysts

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Introduction

Supported oxide catalysts can exhibit complex relationships between reactivity and surface coverage (loading) due to the prevalence of structure-sensitive catalyst mechanisms. [1] In general, structures evolve from isolated cations at low surface coverage to crystallites at higher loadings. Methods exist for creating isolated sites via ligand-protected grafting [2] or the creation of crystallite domains via nanoparticle deposition. Intermediate oligomeric structures may also be formed, but the catalytic relevance and even existence of these bridged oligomeric oxides are not always obvious, in part because of limitations in site titration and spectroscopic handles specific to such structures. Oligomeric structures could also be expected to co-exist with isolated cations or small crystallites at intermediate loadings, but this will also be case-specific.

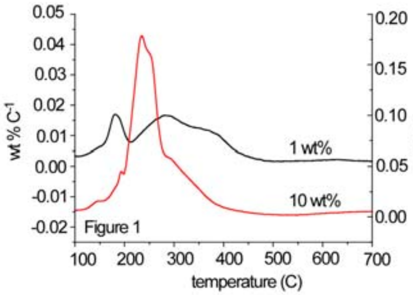
Rather than teasing out the existence of such structures from energetically diverse populations on surfaces, we will present preliminary results on our route to the deliberate construction of specific nuclearities (e.g. isolated species, dimers, or tetramers) of catalytic oxides on high surface-area supports. We will also present techniques that probe to role of mild support Brønsted acidity in determining not only the structure of supported catalyst domains, but also contribute co-catalytic or cooperative effects on the reactions. Multimeric Mn-oxo species are ubiquitous oxidation catalysts typified at the two extremes by salts impregnated within oxide frameworks [3] and enzyme photo-oxidation domains. [4] The utility of Mn oxide catalysts in a broad spectrum of reactions spanning combustion, selective oxidation, and selective catalytic reduction, has prompted us to focus on this metal.

Materials and Methods

All reactions were carried out using solid catalysts suspended in liquid phase batch reactors maintained at reaction temperature with an external cooling cycle. Periodic sampling and product analysis utilized a Shimadzu 2010 GC-FID with an organosiloxane capillary column calibrated against samples of known composition. Catalyst composition and structure were determined using a TA Instruments Q500 thermogravimetric analyzer (TGA) and a Shimadzu UV3600 UV-vis-NIR using a Harrick Scientific 'Praying Mantis' reaction chamber. NMR analysis of catalyst structure and confirmation of product composition was performed at the Northwestern analytical services laboratory. Reactants and catalyst precursors were obtained at the highest purity available commercially.

Results and Discussion

Mn oxide domains were controlled using two precursor classes – monomeric porphyrin or salen based systems that allow precise control over support-site interactions, and macrocyclic alkylamine complexes that allow construction of monomeric, dimeric, or tetrameric Mn oxide complexes with small changes to the ligand structure. Surface structures and reactivity are first probed using TGA to assess temperature-programmed reactions including decomposition of the precursor ligand and autoreduction at high temperature. As shown in Figure 1, reducibility is strongly dependant on surface density of the grafted molecular complex. Diffuse reflectance UV-visible-NIR is correlated with reactivity to assess structure-activity correlations. Figure 2 compares the unstructured catalysts produced by traditional impregnation and calcination methods and possessing a variety of surface structures, as shown by broad absorption curves and a high background intensity extending into the NIR, with that of a supported molecular complex displaying individual electronic transitions. The kinetics of epoxidation and hydroxylation using hydroperoxides will be presented and correlated to surface structures and synthesis method, as appropriate.



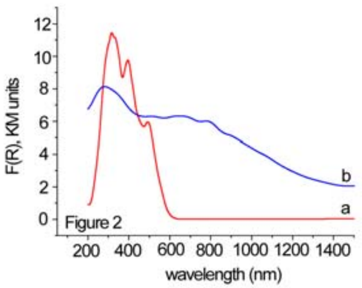


Figure 1. Using molecular precursors, the reducibility of supported manganese oxides changes dramatically with surface density, as shown here for 1 wt% and 10 wt% MnOx on an aluminosilicate. Reducibility is probed here using TGA in N_2. Note difference in scale.

Figure 2. Molecular precursors maintain precise structures at high loadings. Here, a dimeric precursor is loaded in SiO_2 at 10 wt% (a) to produce a well-structured, deep red catalyst and compared to a 'traditional' synthesis by impregnation and calcination (b) to produce a black, unstructured catalyst even though the loading and formal oxidation state are the same.

Significance

The ability to deliberately create a given dispersed metal oxide surface structure would be transformative to the field of heterogeneous catalysis. Borrowing principles from homogeneous catalysis, we will discuss preliminary work towards this goal for Mn oxide oxidation catalysts.

References

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