NANOSTRUCTURED CATALYSTS: TAILORING VANADIUM +4 AND +5 SITES ON SILICATE BUILDING BLOCK SOLIDS

Ming-Yung Lee[1] and Craig E. Barnes[1]*
[1]*University of Tennessee, Knoxville, TN 37996-1600 (USA)*
*cebarnes@utk.edu

Introduction

The goal of preparing nanostructured materials is, in many ways synonymus with longstanding efforts by the catalysis community to prepare well defined, single site catalysts on the surfaces of support materials.[1] Traditional methods involving adsorption of catalyst precursors onto preexisting surfaces or sol-gel approaches to mixed metal oxides all are face well identified challenges in the context of preparing single site catalysts.

We are developing a different approach to the challenge of preparing well defined, single site catalysts which involves the combination of two different strategies: 1) the eventual metal based catalyst must be present and exert a controlling influence in defining its local environment as the catalyst-support matrix is formed. 2) The main structure directing element of the support should be a nanometer or larger sized "building block" to ensure site isolation in the final catalyst. Additionally, the "method of sequential additions" that we are developing utilizes nonaqueous covalent linking reactions that both create well defined catalyst ensembles in the matrix and knit these ensembles into the developing building block matrix. Controlling how and what ensembles are formed leads to single catalyst sites in the matrix.

In this presentation we will focus on recent work involving silicate matrices containing atomically dispersed vanadium +4 and +5 centers.[2] The silicate matrix is composed of the Si_8O_{20} cubic building block. Preliminary investigations of these materials as solid acid catalysts and in the context of selective oxidation reactions will be described.

Materials and Methods

The synthetic precursor to the cubic silicate building block, $Si_8O_{20}(SnMe_3)_8$ was prepared by the method of Feher.[3] Tetra and pentavalent vanadium precursors were VCl_4 and $VOCl_3$ respectively. The method of sequential additions refers to exposure of solutions of the building block with carefully measured doses of the metal chlorides above and silyl chlorides (e.g. $SiCl_4$, $HSiCl_3$, Me_2SiCl_2) to produce cross linked building block matrices linked by a random distribution of siloxane and V-O-Si bonds.

Results and Discussion

The catalysts that have been prepare consist of single atomic centers of vanadium 4+ and vanadyl (V=O) 5+ centers linked to a variable number of Si_8O_{20} building blocks. The number of V-O-Si links are varied via the sequential addition procedures described above. "Embedded" catalysts refer to vanadium centers connected to the maximum number of building blocks in the matrix. Vanadyl groups have a maximum connectivity of three and V(4+) centers have a max. connectivity of four. "Surface" catalysts refer to vanadium which is connected to the silicate matrix by only one V-O-Si link. Experimental evidence in support of catalysts described exclusively surface or embedded come from gravimetric studies, SSNMR V-51 NMR exeriments and vanadium K edge EXAFS studies.

Preliminary activity studies have focused on the competitive dehydration and oxidative dehydrogenation of 2-propanol to form propene and acetone, respectively. In contrast to recent reports of vanadia on silica catalysts[4], the primary product of the atomically dispersed vanadium catalysts prepared in this study was propene as illustrated in Figure 1.

Significance

The preparation of well defined, single site catalysts is still quite challenging. Here we describe a general procedure for the preparation of atomically dispersed, single site metal catalysts in silicate matrices and initial investigations relating the nanostructuring inherent in single site catalysts to their catalytic activity.

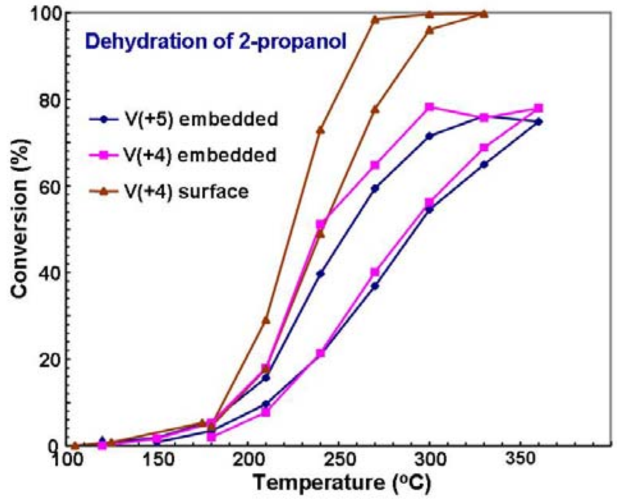

Figure 1. "Light-off" curves for the dehydration of 2-propanol with .three different vanadium-silicate building block catalysts.

References

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