Structural Studies of M1 Selective Oxidation Catalyst via Aberration-corrected Scannning Transmission Electron Microscopy

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Abstract – The M1 selective oxidation catalyst is a complex metal oxide framework structure with an orthorhombic unit cell and 11 cation sites in the framework and two types of channels into which additional species can intercalate. It has the potential to allow for the production of acrylonitrile (ACN) from propane feedstock rather than the currently used propene. The propane process will be more carbon and energy efficient, resulting in significant cost savings. Variations in synthetic conditions are known to produce dramatic differences in catalyst performance [1-3]. Aberration-corrected HAADF STEM has been used to measure the extent of substitution at the various cation sites in a number of specimens, as well as to evaluate the crystalline imperfections such as voids and intergrowths. Variations in yield from various catalyst preparations correlate with variations in occupancies within the metal framework and the intercalated sites, and also with the extent of long range order in the crystallites.

Selective oxidation catalysts are used extensively to produce either intermediate chemicals or final products incorporated into consumer goods. Acrylic acid and acrylonitrile are two products in high demand that are currently produced from propene over multicomponent bismuth molybdate catalysts [5-6]. A multiphase MoVNbTeO catalyst is the most promising candidate for the substitution of propane for propene [5]. Extensive research has been undertaken to improve both the activity and selectivity of this complex system, however there are still a number of basic questions that remain unresolved. A series of specimens with varying structural and chemical substitution have been examined with aberration-corrected STEM in order to try to understand the role that chemical substitution and long range order play in the reported ACN yields. High angle annular dark field (HAADF) STEM images follow a Z^2 dependence (Z being atomic number) which allows for the estimation of V occupancy based upon the relative contrast. Figure 1 shows some of the variations in cation site contrast among different samples. The reported ACN yields and V content in the proposed active site [4] derived from the HAADF STEM images correlate very well. In addition to directing the substitution of V in the framework in different ways, synthesis conditions also have a large role in the extent of good long range crystalline order as shown in Fig. 2. Specimens exhibiting high yields always possess good long range order.
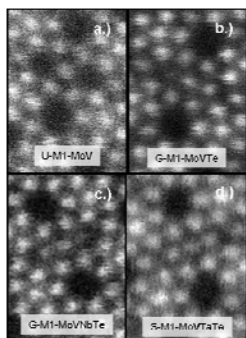

Figure 1: HAADF STEM images of the proposed active site in the M1 catalyst for a number of specimens.
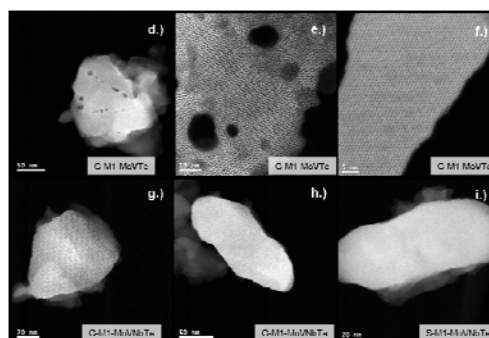

Figure 2: HAADF STEM images of two different specimens showing the effect composition and synthesis conditions have on long range order

References

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