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Site Isolation in Vanadium Phosphorus Oxide Alkane Oxidation

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Abstract

Single crystal X-ray diffraction studies of vanadyl pyrophosphate indicate that at least two polytypical structures exist for this active and selective alkane oxidation catalyst. The crystal structures of these materials differ with respect to the symmetry and direction of columns of vanadyl groups within the unit cell. Single crystals of vanadyl pyrophosphate have been generated at extreme temperatures not often experienced by microcrystalline catalysts. The crystallography of the system suggests that other crystalline modifications or disordered phases might also exist. Zeroth-order models of crystal surface termination of vanadyl pyrophosphate have been constructed which conceptually illustrate the ability of vanadyl pyrophosphate to accommodate varying amounts of surface phosphorus parallel to (1,0,0), (0,1,0) and (0,2,4). Pyrophosphate termination of surfaces parallel to (1,0,0) likely results in the isolation of clusters of reactive centers and limits overoxidation of the alkane substrate.

1. INTRODUCTION

The vanadium phosphorus oxide (VPO) catalyst system performs the fourteen-electron oxidation of n-butane to maleic anhydride with exceptionally high selectivity [2]. The phase which is identified with optimal catalytic performance is vanadyl pyrophosphate, $(VO)_2P_2O_7$ [3]. However, the literature is anything but clear concerning the composition and structure of this phase. The solid-state chemistry of the VPO system is typified by the facile interconversion of numerous V^{4+} and V^{5+} phases, leading to considerable confusion in the interpretation of the experimental data. In an attempt to clarify the structural chemistry of these materials, our work has recently focused on a careful and exhaustive re-investigation of the crystal structure of vanadyl pyrophosphate. These crystallographic studies indicate that the differences observed in X-ray powder patterns of catalysts derived from differing syntheses [4] are consistent with the presence of polytypical structures of vanadyl pyrophosphate. Our attempt to understand the relationship between variable metal atom order and catalytic performance has led us to postulate "zeroth-order" models of crystal surface termination. Regardless of the dubious nature of such models, these studies raise some intriguing questions related to the evolution of both bulk and surface structure during catalyst preparation and burn-in.

2. DISCUSSION

The literature contains numerous citations concerning all aspects of the catalytic chemistry of the vanadium phosphorus oxides [5]. Clearly, controversy exists on several important structural issues, including: (i) the exact identity and structure of the active/selective phase, (ii) the role of V^{5+} species relevant to butane conversion to maleic anhydride, and (iii) the relationship between surface atomic P:V ratios and catalyst selectivity. The intent of this paper is to expound on the idea that the solid-state structure of vanadyl pyrophosphate may be highly variable, especially with respect to metal atom order and apparent phosphorus composition. We have isolated and determined the crystal structures for two polytypical forms of vanadyl pyrophosphate derived from near solidified melts of mature microcrystalline catalyst powders. While these studies clarify the poorly determined structure previously reported by Linde and Gorbunova [6], they also suggest that other forms of vanadyl pyrophosphate may exist. As for the role of V^{5+} in butane oxidation to maleic anhydride, Trifiro et al. [7] have established that selective VPO catalysts possess some limited and controlled number of V^{5+} sites and that the selectivity to maleic anhydride passes through a maximum for a well-defined value of degree of surface oxidation. Several authors believe that V^{5+} exists at the catalyst surface as β-$VOPO_4$ or a structurally related amorphous state [8]. However, in our experience, detectable quantities of $VOPO_4$ phases in commercial catalysts can be shown to be associated with performance loss. Possibly the most controversial issue relating to the composition of the catalyst concerns the presence of excess phosphorus associated with catalyst surfaces, and its role in stabilizing V^{4+} species and determining the selective properties of the catalyst. Garbassi et al. [9] have found a value of surface atomic P:V ratios in the range of 2.0-2.8, while that for bulk lies in the range of 1.0-1.4. Hodnett and Delmon [10] report that surface P:V ratios are approximately 1.0 for bulk stoichiometric P:V values of 1.0 or higher. Recent work by Okuhara et al. [11] supports the latter result, yielding surface atomic P:V ratios of 1.10 ± 0.04. As will be shown below, it is not difficult to conceive of structures based solely on vanadyl pyrophosphate which support both a controlled number of surface oxygen (and V^{5+}) sites and accommodation of varying amounts of non-stoichiometric surface phosphorus.

2.1 Crystallography of Single Crystals of Vanadyl Pyrophosphate.

We have reported that carefully controlled recrystallization of mature commercial catalysts at temperatures in excess of 970°C results in the formation of large single crystals of vanadyl pyrophosphate [12]. Specimens harvested from these near solidified melts are variable in color, ranging from emerald-green to gray, and brown to red-brown. Emerald-green and red-brown crystals of vanadyl pyrophosphate crystallize in the non-centrosymmetric space group $Pca2_1$ [13]. All crystals studied exhibit some disorder of the vanadium atom sites. The disordered positions lie approximately 0.325Å above or below the distorted octahedral basal plane of the vanadium coordination sphere as illustrated in Figure 1. Emerald-green crystals of vanadyl pyrophosphate are composed of the structure earlier reported by Linde and Gorbunova. However, the structure exhibits vanadium atom disorder associated with only half of the metal atom sites. Addition of the disordered sites in cycles of least-squares refinement of the crystallographic model result in residual values in the range of R_1=0.035. Bonding interactions for all metal-oxygen and phosphorus-oxygen bonds fall within expected values including the vanadyl moieties, V=O, which average 1.604 (17) Å, and are all within two esd's of the average value. The disorder is a consequence of the coexistence within the crystal of both enantiomorphs of the Linde and Gorbunova structure.

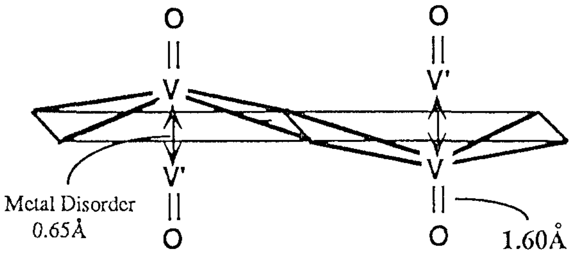


Figure 1. Vanadium site disorder across the pyramidally distorted octahedral basal plane.

Crystallographic models of the two enantiomorphs can be superimposed with respect to the pyrophosphate network, however, the resulting structure exhibits disorder for the vanadium atoms which lie in chains parallel to the c-axis and y=1/2, as illustrated in Figure 2. A similar interpretation of the disorder within the crystal structure of the red-brown material would indicate that it consists of a polytype of the Linde and Gorbunova structure in which the direction of the vanadyl columns parallel to the crystallographic c-axis at approximately y=0, are reversed in direction with respect to the a-axis. Superimposing the pyrophosphate network of this second

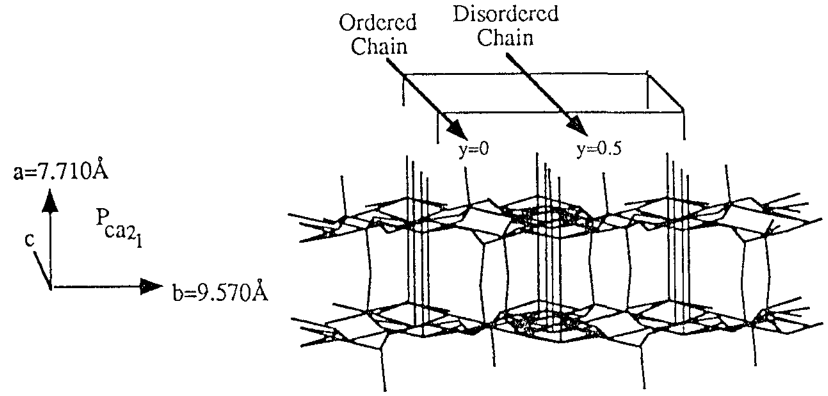


Figure 2. A model of the superimposed pyrophosphate networks of the Linde and Gorbunova structure of vanadyl pyrophosphate and its enantiomorph. Note that only half of the V-sites are disordered.

polytype with its enantiomorph yields a model in which all vanadium atom sites are disordered across the octahedral basal plane. This type of disorder, common in other transition metal crystal structures, is termed "linear displasive disorder" and is noted for producing diffraction streak effects similar to those reported by Bordes [14] in electron diffraction studies of microcrystalline catalysts.

The differences between the two proposed polytypical vanadyl pyrophosphates can be understood in terms of the symmetry of the eight columns of vanadyl groups that exist within the unit cell. These differences are schematically illustrated in Figure 3. The direction of the vanadyl columns represented for the first polytype correspond to the symmetry reported by Linde and Gorbunova. The direction of the vanadyl columns along the edge of the cell, parallel to the c-axis, have been reversed in the second polytype. The distance relationships between all vanadium, phosphorus and oxygen atoms within the idealized models of these two structures are identical, and as a result, we would expect the crystal energies of these species to be nearly identical. No phosphorus atom disorder is observed for either set of single crystals.

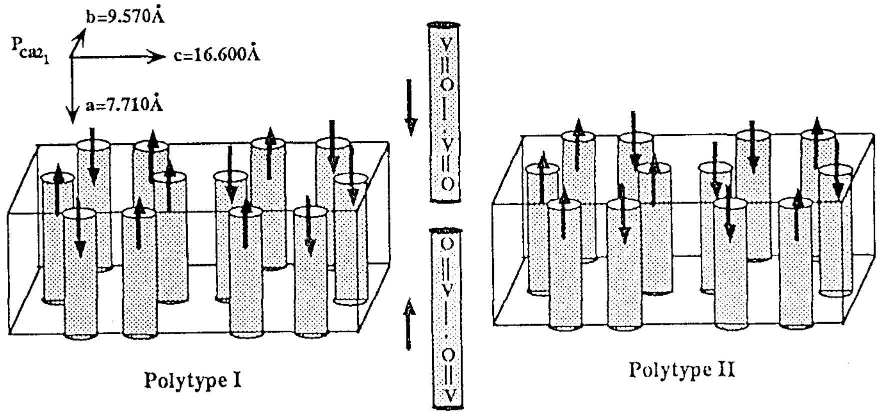


Figure 3. Schematic representation of the vanadyl column symmetry for two polytypical vanadyl pyrophosphate crystal structures.

While the structures of both polytypes would exhibit the same rigorous space group extinctions (P_{ca2_1}), the symmetry relationships between the vanadium and phosphorus atoms within the structure are not identical. This observation is also consistent with the differing Raman spectra exhibited by the two crystalline species [15]. It is clear that the topotaxy which transforms the intercalated orthophosphate precursors into the networked pyrophosphate structure [16] occurs with considerable reorganization of the long-range order of both the phosphate and vanadyl networks. Extreme broadening of several classes of reflections in X-ray powder diffraction patterns, apparent even in mature microcrystalline catalysts, supports the conclusion that crystalline order in the system is highly variable. We can conceive of numerous alternative symmetries for the structure of vanadyl pyrophosphate which retain identical bonding shell configurations, but would differ in second- and further-near neighbor environments. We would expect these structures to exhibit only nominal energetic differences associate with the coulombic interactions between differing metal-metal octahedral hole occupancy, and strain energy associated with the ability of each structure to pack efficiently (minimization of cell volume). The obvious question which we find ourselves asking relative to the structures of the single crystal materials and the microcrystalline catalysts, relates to kinetic vs. thermodynamic control in the evolution of the structure in the transformation from catalyst precursors to the vanadyl pyrophosphate phase. Is it possible that the acentric structures observed for the single crystals studied by Linde and Gorbunova, Middlemiss [17] and ourselves are simply a set of thermodynamically stable species, or do these materials form as a result of the synthesis procedures and only slowly, if at all, interconvert? The importance of this question can be realized when considering that the direction and symmetry of the vanadyl moieties within the structure have an effect on any proposed surface topology at the (1,0,0) surface of vanadyl pyrophosphate.

2.2 Zeroth-Order Models of Vanadyl Pyrophosphate Surface Termination

During the past decade there has been a remarkable increase in the detail of information available concerning the atomic geometry, bonding and electronic structure of surfaces. Much of this work, both theoretical and experimental, has concentrated on surface reconstruction of cleavage faces of tetrahedrally-coordinated compound semiconductors [18] and simple oxide materials [19]. The theoretical research, primarily based on the empirical Tight-Binding model [20], has been instrumental in guiding the interpretation of experimental data and has lead to mechanistic schemes which explain the reconstruction process in terms of surface bond rehybridization. Higher levels of theory will be necessary to properly describe the bulk and surface structures of octahedral metal-oxides and systems such as vanadyl pyrophosphate. However, the necessary prerequisite to theoretical studies involves the construction of "zeroth-order" models of the bulk and surface structures. Zeroth-order surface models are simply based on a rational termination of the crystal structure parallel to the desired surface, in a manner which preserves maximum bond valance for each atom under the constraint of generating a neutral surface. Needless to say, these models are a matter of conjecture, but they often help rationalize less than obvious features of the surface chemistry.

We would like to advance several simple concepts with respect to models of surface termination for VPO phases. (i) Surface vanadium centers are expected to be minimally five-coordinate. The sixth-coordination site could be unoccupied for the case where the vanadyl oxygen is inward directed, or coordinated by a weakly interacting adduct. Alternatively, the sixth coordination site could be occupied by an outwardly directed surface vanadyl oxygen. (ii) Since the amount of phosphorus associated with the surfaces of VPO phases is clearly a matter of interest, our models will maximize the use of phosphorus by fulling the coordination spheres of all metal atoms with shared pyrophosphate oxygen. We think this is a physically reasonable assumption since the active/selective phase is synthesized in an excess of phosphate. The effect generated in this manner

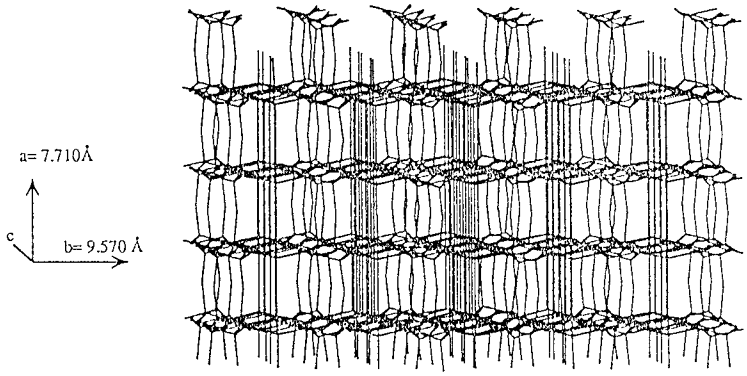
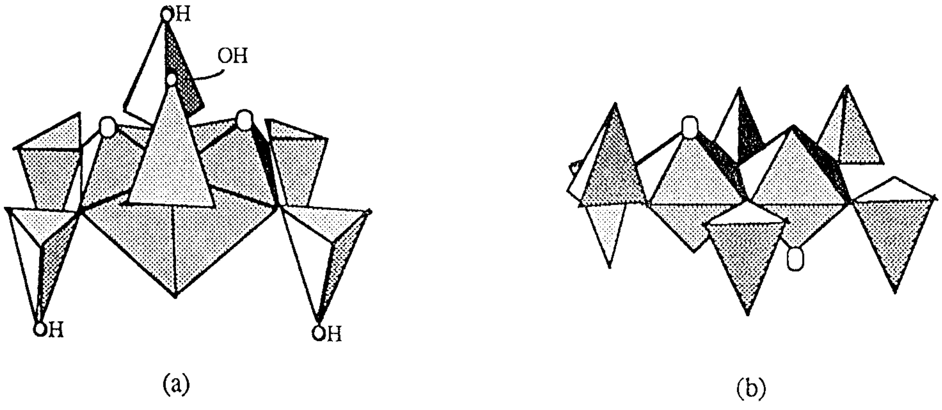


Figure 5. Illustration of two possible cases of surface termination parallel to the (1,0,0) surface of vanadyl pyrophosphate: phosphorus-rich pyrophosphate termination (top of figure), and stoichiometric orthophosphate termination (bottom of figure).

surround each dimeric pair of vanadyl centers of the layered $VOHPO_4 \cdot 1/2\ H_2O$ structure. Of the six hydroxyl moieties associated with the phosphate groups, four are oriented above the basal plane, and two below (or vise versa) as illustrated in Figure 6a. For the pyrophosphate phase, three pyrophosphate groups bridge layers in either direction but do so with a maximum of 2-fold symmetry as shown in Figure 6b. This non-centrosymmetric structure, as reported by ourselves and previous authors, cannot be constructed with fewer than four independent phosphorus atoms regardless of the symmetry of the vanadium occupancy (i.e., the assignment of the space group symmetry is maximally that of P_{ca2_1}). As we have previously described [12], terminating the idealized (1,0,0) surface of $(VO)_2P_2O_7$ with pendent pyrophosphate groups sterically isolates vanadium centers in cavities or clefts. The degree of isolation of these centers, and the symmetry in the cavity, is influenced significantly by the orientation of the vanadyl columns within the structure, a factor which we have noted to be different for each of the poly-



(a)

(b)

Figure 6. Idealized polyhedral structures for (a) $VOHPO_4 \cdot 1/2\ H_2O$, and (b) $(VO)_2P_2O_7$.

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