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Diffraction Study of a Vanadium Phosphate Catalyst

Vanadium phosphates are uniquely superior as heterogeneous catalysts in the oxidation of *n*-butane (*1*) and *n*-butene (*2*) to maleic anhydride. Studies of crystal structures of the precursor material, $(VO)_2H_4P_2O_9$ (*3*), and the crystalline component, $(VO)_2P_2O_7$ (*4*), of the active catalyst have been carried out. However, conventional crystallographic techniques are unsuitable for the study of the working catalyst, which consists of a mixture of $(VO)_2P_2O_7$ and an amorphous phase.

The structure of the catalytically important compound, $(VO)_2P_2O_7$ (the pyrophosphate), is built of double chains of VO_6 octahedra which share opposite corners along the chains and edges across the chain. The compound from which it is derived by heating at ≃400°C, $(VO)_2H_4P_2O_9$, contains pairs of face-shared VO_6 octahedra. The structural relationship between these two compounds has been described in detail (*3*). On the other hand, studies of the structural nature of the working catalyst are not as straightforward.

A recent diffraction study (*5*) has suggested that the amorphous phase is related to the structure of β-$VOPO_4$. This interpretation is intuitively appealing since the structure of β-$VOPO_4$ contains only corner-shared VO_6 chains and has a formal oxidation state for vanadium of 5+, in keeping with the scheme of a redox cycle between V^{4+} and V^{5+} (*6*). However, this interpretation was based largely on limited data and the appearance of one feature in the radial distribution function (RDF) obtained from the scattering from the catalyst (*5*). This study was further complicated by the presence of an unidentified, crystalline, second phase in the working catalyst. The contribution by this second phase (which we believe to be either β^*- (*7*) or β'-phase (*8*)) to the RDF was not considered.

In order to test the conclusions of the previous study (*5*), samples of the working catalyst, which consists predominantly of the crystalline pyrophosphate, were prepared. More extensive X-ray diffraction data have been collected on this and the mostly amorphous material from which it is derived. By subtracting the contribution to the amorphous material of the crystalline component, the total scattering due to the amorphous material was derived. Comparisons with compounds of known topology (including β-$VOPO_4$) were then used to adjudicate between possible geometries and compositions for the amorphous material.

The catalyst precursor, $(VO)_2H_4P_2O_9$, was synthesized by refluxing a mixture of 85% phosphoric acid and vanadium pentoxide (reactant P/V atomic ratio = 1.2) in a solvent composed of isobutyl alcohol (10 parts) and benzyl alcohol (1 part). After refluxing, the precursor was recovered by vacuum filtration and dried. Elemental analysis indicated that the P/V atomic ratio was 1.01 and X-ray diffraction confirmed that the product was single phase $(VO)_2H_4P_2O_9$. Additional details of precursor synthesis have been reported previously (*9, 10*).

Conversion of the precursor to the working catalyst consisted of an air calcination followed by activation in the butane oxidation reaction atmosphere. Air calcination was accomplished by heating in 15% O_2/85% N_2, at 2°C/min, from room temperature to 400°C, and then holding at 400°C for 1 h. The catalyst activation was then carried out by lowering the temperature to 300°C, switching the atmosphere to 2%

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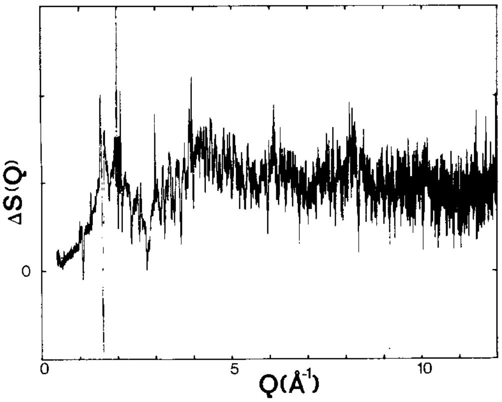

FIG. 1. The structure factor [$\Delta S(Q)$] for the amorphous component of the working vanadium phosphate catalyst. Note that the large variations in $\Delta S(Q)$ are due to the differences in the breadth of the Bragg reflections from the crystalline $(VO)_2P_2O_7$ in both the precursor and the catalyst from which it is derived (see text). This feature is not expected to affect the Fourier transform shown in Fig. 2; this will be dominated by contributions from the slowly varying function due to the amorphous material.

n-butane/15% O_2/balance N_2, heating at 2°C/min to 445°C, and holding at 445°C for about 60 h.

Detailed characterization was carried out on two samples. One was the product of the converted precursor after having only been calcined. X-ray diffraction showed that this material consisted of a large amount of amorphous component with some poorly crystalline $(VO)_2P_2O_7$. The second sample was the product of the converted precursor after having gone through the complete calcination and activation schedule described above. *In situ* high-temperature X-ray diffraction showed that the amorphous phase produced during calcination is gradually converted to vanadyl pyrophosphate during activation. The final activated product, or "working catalyst," displays an X-ray diffraction pattern which is in complete agreement with that expected for $(VO)_2P_2O_7$.

Data were collected at the X13A synchrotron beam line at the National Synchrotron Light Source, Brookhaven National Laboratory. A Ge(220) crystal was used to monochromate X-rays (λ = 0.6898 Å). Samples were in the form of pressed disks, enclosed in a chamber filled with helium, and mounted on a Huber four-axis spectrometer. An intrinsic Ge detector was used to detect the scattered photons. Corrections were made for air, Compton, and multiple scattering and both data sets were normalized to yield the total structure factors which were then subtracted to yield $\Delta S(Q)$, the difference structure factor (Fig. 1). This represents the residual scattering due to the amorphous phase. By taking the direct Fourier transform of this structure factor, a function is obtained (Fig. 2), which represents the radial distribution (RDF) or probability of finding electron density at a particular distance about each atom in the amorphous phase. Note that the smoothly varying function in Fig. 1 represents the scattering from the amorphous material.

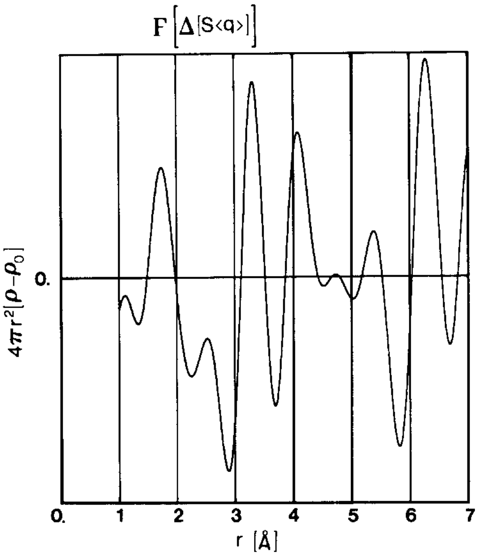

FIG. 2. Radial distribution function (RDF) for the amorphous component of the vanadium phosphate catalyst. The peaks in the RDF have the following assignments (see Fig. 3 as well as Ref. (*4*)): $r \approx 1.8$ Å, V–O and P–O; $r \approx 2.5$ Å, V–O; $r \approx 3.2$ Å, V–P; $r \approx 4.1$ Å, V–V and V–O. This last distance is a second shell distance and may be of little consequence in the amorphous material.

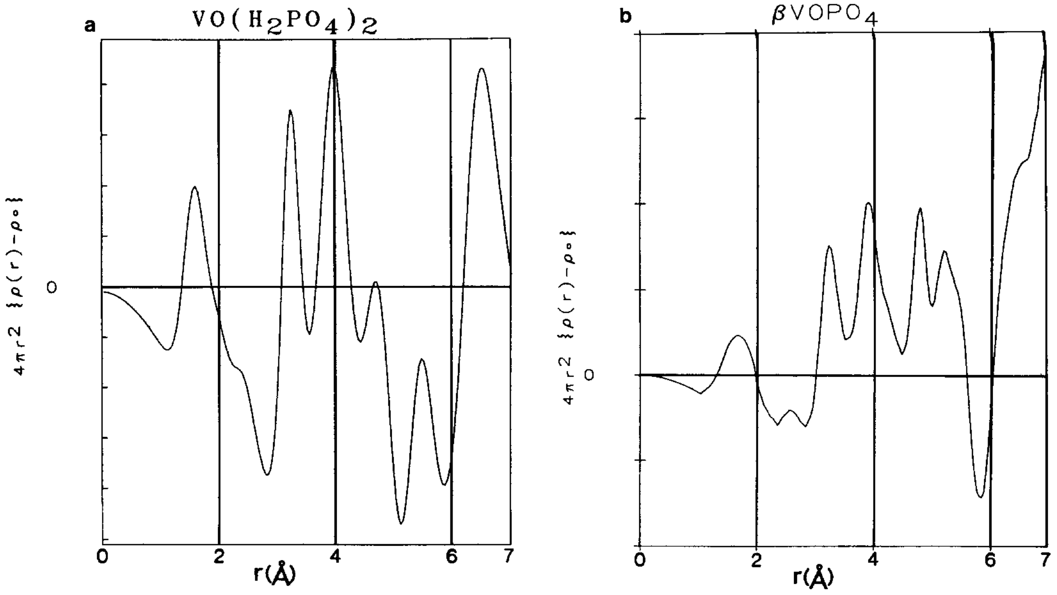

FIG. 3. Calculated RDFs for (a) $VO(H_2PO_4)_2$ and (b) β-$VOPO_4$. The peaks have been assigned according to the values given in Fig. 2.

The higher frequency signal results from the incomplete subtraction of the crystalline $(VO)_2P_2O_7$ from the calcined, amorphous material. This is due to the difference in breadth of the Bragg peaks for $(VO)_2P_2O_7$ in the working catalyst and in the predominantly amorphous material.

By choosing vanadium phosphates of known crystal structure, radial distribution functions were calculated, using the program RADMOR (*11*), for comparison with that shown in Fig. 2. Those structures containing chains of corner-shared VO_6 octahedra yielded RDFs which best matched that for the amorphous component of the working catalyst. Both $VO(H_2PO_4)_2$ (*12*) and β-$VOPO_4$ provided the basis for structural topologies which lead to acceptable fits to the RDF for the amorphous material (Fig. 3). This is not to say that the chemistry of the amorphous phase is best described by either $VO(H_2PO_4)_2$ or β-$VOPO_4$.

What can be stated with confidence is that the features in the RDF (Fig. 2) were best modeled by crystalline models containing corner-shared VO_6 octahedra. This follows the trend from face to edge and corner sharing, as the precursor, $(VO)_2H_4P_2O_9$, is decomposed to $(VO)_2P_2O_7$ and an amorphous phase. It should not be surprising that no one crystalline model was entirely satisfactory. The use of a model compound with full three-dimensional long-range order to model an amorphous material is unrealistic. Precise structural and compositional characterization of the amorphous component of the working catalyst is not possible from diffraction-based studies alone. The proposed core of V^{4+} surrounded by an amorphous material containing V^{5+} (*5*, *6*) is not supported by this diffraction study.

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