

RESEÑA

STUDY OF THE STRUCTURAL, VIBRATIONAL AND SYMMETRY PROPERTIES OF ALUMINOPHOSPHATE $\text{AlPO}_4\text{-5}$

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The problem of the symmetry of the $\text{AlPO}_4\text{-5}$ unit cell has been the subject of a variety of studies since the synthesis of this material in 1982. The $\text{AlPO}_4\text{-5}$ possesses a one-dimensional 12 membered channel, which is surrounded by 4- and 6-rings. The 12-membered channel permits the adsorption of large molecules (e.g. hydrocarbons) and the use as catalysts. The substitution of aluminum and phosphorous by transition metal produces a new material, well known as metal-aluminophosphate or $\text{MeAlPO}_4\text{-5}$ ($\text{Me} = \text{Mg}, \text{Co}, \text{Fe}, \text{Mn}, \text{V}, \text{etc.}$), containing acidic as well as *redox* sites. Although the numerous experimental and theoretical studies about these materials a number of important questions does not have entirely established (for example, the amount, distribution and occupation sites of metals in the framework).

On the other hand, the diffusion mechanism of ethane in $\text{AlPO}_4\text{-5}$ has been the subject of several studies. According to previous Pulsed Field Gradient PFG-RMN experiments (time scale ≈ 100 ms) the diffusion of ethane in $\text{AlPO}_4\text{-5}$ occurs via a single-file diffusion regime. Different theoretical models have been employed for the description of this phenomenon. Particularly, some authors have been reported the existence of a concerted molecular motion of the ethane in $\text{AlPO}_4\text{-5}$. In contrast, Quasi-Elastic Neutron Scattering, QENS, experiments (time scale ≈ 1 ns) suggest the existence of a normal diffusion regime. The experimental discrepancies were explained by assuming that different $\text{AlPO}_4\text{-5}$ crystal structures have been used in the measurement. In the QENS experiments a non-defective $\text{AlPO}_4\text{-5}$ structure was assumed.

In this work a computational study of the structural changes produced in the $\text{AlPO}_4\text{-5}$ framework by different factors (temperature and crystalline defects of iron and vanadium) is presented. Also, it attempts to provide microscopic details of the static and dynamics properties of the adsorbed molecules in order to verify whether the conditions for the single-file regime can be achieved in a non-defective $\text{AlPO}_4\text{-5}$ crystal structure. For the description of interatomic interactions semi-classical techniques were used.

For the total energy minimization a combination of Buckingham potential (short-range interactions), electrostatic interactions (calculated by Ewald summation techniques) and three bodies' potential were employed. Polarizability of oxygen atoms was treated using the shell model developed by Dick and Overhauser. The Gibbs free energy calculations assume the quasi-harmonic approximation.

The total energy minimization at 0 K and the Gibbs free energy minimization at temperatures up to 600 K, indicate that the orthorhombic Pcc2 space group and the hexagonal P6 space group describe more adequately the calcined $\text{AlPO}_4\text{-5}$ unit cell. Besides, the very similar energy of the Pcc2 and P6 structures would suggest the phase transition of $\text{AlPO}_4\text{-5}$ unit cell with temperature. The calculated T-O-P bond angles at variable temperature for these structures are not linear in agreement with the experiment. The Al-O and P-O bond distances are practically temperature independent. In contrast, energy minimization of initially proposed space group, P6cc, reveals the existence of the imaginary eigenvalues. This fact means that the calculated energy corresponds to a saddle-point on the potential energy surface. The result supports that space group P6cc do not describe correctly the unit cell of the calcined $\text{AlPO}_4\text{-5}$.

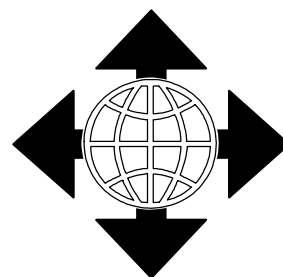
On the other hand the incorporation of the metals in the framework of the $\text{AlPO}_4\text{-5}$ was simulated using both energy minimization techniques and defect calculations. Energy and geometrical results show that iron is preferably incorporated as Fe^{3+} in the tetrahedral aluminum sites. The defect energy calculations support this suggestion. All possible configurations with one, two and three Fe^{3+} ions in tetrahedral positions were studied. According to the calculations T2-T5 tetrahedral sites are the most stable sites for the incorporation of the Fe^{3+} ion. Finally, incorporation of the Fe^{3+} ion produces a strong deformation of the $\text{AlPO}_4\text{-5}$ channels: the effective diameter of the 12-membered channel varies approximately 0.4–0.8 Å. Analysis of the configurations with two and three Fe^{3+} in aluminum tetrahedral sites suggests that the influence of interactions between iron defects and the symmetry constraints in the c direction of the $\text{AlPO}_4\text{-5}$ unit cell are two essential factors in the stability of the FAPO-5 structure. The combination of these factors leads to fact that configurations with the Fe^{3+} ions in the same side of $\text{AlPO}_4\text{-5}$ unit cell (or with the defects very near) have a low stability.

For the vanadium-aluminophosphate (VAPO-5) study two cases were studied: the substitution of Al^{3+} by V^{3+} and the substitution P^{5+} by V^{5+} . The introduction of V^{3+} ion in aluminum sites leads to a great structural disorder while the incorporation of V^{5+} ion in phosphorous sites leads to comparatively smaller deformations of the aluminophosphate framework. Also, a new band (near 830 cm^{-1}) in the simulated vibrational spectrum (in agreement with experimental measurement) is a strong evidence of the incorporation of vanadium as V^{5+} in tetrahedral phosphorous sites. Therefore, energy, geometrical and vibrational results suggest that vanadium is preferably incorporated as V^{5+} in the tetrahedral phosphorous sites. The $\text{V}^{5+}\text{-O}$ bond distances are approximately 1.60 Å and the T-O-Al and O-T-O bond angles are not significantly influenced by the vanadium incorporation (T = Tetrahedral phosphorous position). Very similar energies were obtained for the six independent phosphorous sites of the asymmetric unit cell, which suggest that the V^{5+} ion could occupy any of these sites with the same probability. Similarly to the Fe^{3+} study, all possible configurations with one, two and three

V^{5+} ions in the tetrahedral phosphorous positions were studied. The unit cell volume and the a and c unit cell parameters critically depend on the amount of incorporated V^{5+} ion, in agreement with experimental results. However, in this case a correlation between the structural stability and V^{5+} ions distribution was not observed. The incorporation of the V^{5+} in tetrahedral phosphorous sites could explain the *redox* behavior of VAPO-5.

In respect to the ethane diffusion, a harmonic potential molecular dynamics (MD) model to describe the structural and vibrational properties of the $AlPO_4-5$ framework was proposed. The potential parameters were determined using an empirical method. The comparison with the experiment (IR spectrum, atomic coordinates, bond distances and angles) shows the quality of the model proposed to describe the main properties of aluminophosphates. Additionally, the model was employed in the study of the interaction framework-guest molecule (ethane), being confirmed the importance of considering the vibrations of crystal in diffusive processes, when the dimensions of the molecule that spreads are of the order of the dimensions of the channel. Also, the diffusion regime of ethane in $AlPO_4-5$ was studied. In simulations both, static and dynamics conditions, were used. The MD calculations suggest the a normal diffusion regime in a defect-free $AlPO_4-5$ structure according to the QENS experiments. Besides, the simulations did not provide evidence for concerted ethane cluster diffusion for the molecules in the aluminophosphate. The diffusion coefficients simulated are very close to those experimentally determined using QENS techniques.

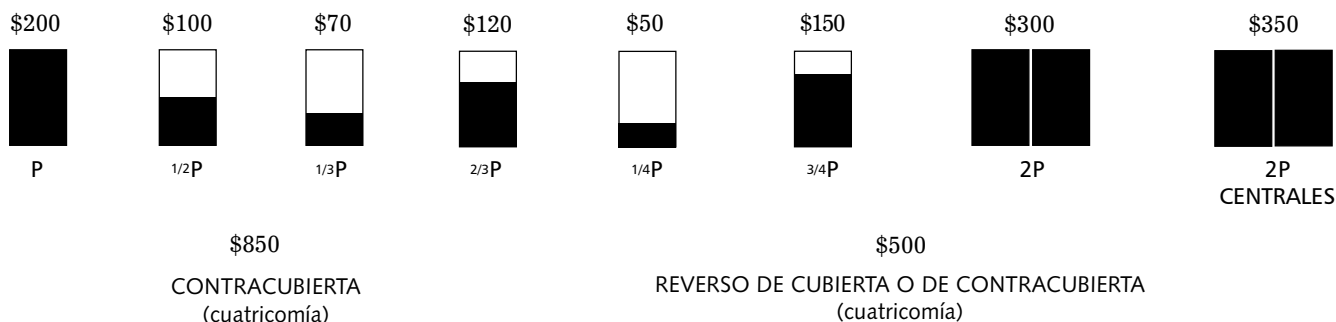
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