SMALL PORE VPI-5: PORE BLOCKAGE DUE TO THERMALLY INDUCED STACKING DISORDERS

K. SØRBY [1], R. SZOSTAK [2]*, J.G. ULAN [3] and R. GRONSKY [3]

[1] *Dept. of Chemistry, U. of Oslo, P.O Box 1033 Blindern, 0315 Oslo 3, Norway*
[2] *Zeolite Research Program, Georgia Tech Research Institute, Georgia Institute of Technology, Atlanta, Georgia 30332, U.S.A.*
[3] *National Center for Electron Microscopy, Materials and Chemical Sciences Division, Lawrence Berkeley Laboratory, University of California, Berkeley, California 94720, U.S.A.*

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The transformation of VPI-5 to $AlPO_4$-8 generates stacking disorders with the crystal which severely restricts its function as a molecular sieve. Evidence of these stacking disorders is established with adsorption measurements and high resolution transmission electron microscopy (HRTEM). Even partial transformation (less than 10% conversion) results in an 80% loss in adsorption capacity. These stacking disorders originate from the symmetry of the VPI-5 structure.

1. Introduction

The realization in 1987 that an aluminophosphate referred to as VPI-5 [1] contains a pore diameter larger than 7 Å, renewed interest in ultra-large pore molecular sieves. The 18 member ring structure proposed for this material is based upon theoretical models first crafted by Barrer and Villiger [2] and further developed by Smith and Dytrych [3] and Maier [4]. VPI-5 possesses the largest known free pore dimensions of any molecular sieve, adsorbing hydrocarbons greater than 10 Å in diameter.

VPI-5 has been observed to undergo a polymorphic transformation to $AlPO_4$-8 [5] under mild thermal treatment (18 hours at 100 °C) [16]. The degree of conversion appears strongly dependent on the nature of the organic amine used in the crystallization. Addition of di-n-propyl amine results in crystalline material which completely converts to $AlPO_4$-8 when heated to 100 °C while addition of cationic amines results in crystalline material which does not as readily undergo

* Individual to whom correspondence should be addressed.

the transformation. Based on the X-ray powder diffraction pattern a structure for $AlPO_4$-8 has been proposed which contains elliptical 14-member ring pores [7].

The adsorption properties of the partially converted and wholly converted VPI-5 were investigated using a variety of adsorbates to gauge the extent of pore blockage which ensues upon transformation. VPI-5 and $AlPO_4$-8 were further characterized by high resolution transmission electron microscopy (HRTEM).

2. Experimental procedure

Samples of VPI-5 were prepared from recipes reported elsewhere [8,9]. Complete and partial conversion to $AlPO_4$-8 was accomplished by heating VPI-5 to 100 °C, either under ambient or vacuum conditions respectively. The X-ray powder diffraction data was collected on a Rigaku ® X-ray powder diffractometer with CuK_α radiation. All spectra were recorded at similar humidities. The adsorption data was acquired using a McBain-Bakr adsorption unit. Capacities were obtained after evacuation of the sample overnight, heating under vacuum to temperatures between 150 and 350 °C for 2–3 hours, cooling to ambient temperature, and introducing the adsorbate. After equilibrium was established displacement of the sample weight was recorded. Oxygen adsorption was acquired at −196 °C with oxygen pressures of 75 Torr. Cyclohexane, n-hexane and water adsorptions were obtained at ambient temperature (22–28 °C) with pressures of 50, 70 and 17.5 Torr respectively. X-ray powder diffraction patterns were recollected after adsorption experiments to determine if further conversion had occurred.

TEM specimens were prepared by crushing VPI-5 or $AlPO_4$-8 and dispersing on 400 mesh Cu grids. The HRTEM micrographs were obtained on a JEOL 200CX at 200 kV using low dose imaging techniques to avoid excessive electron irradiation damage. By correcting beam alignment, focus and astigmatism on an expendable area of the sample, then defocusing the beam and translating to a contiguous area of interest, a photographic exposure was made of the specimen at high spatial resolution. Electron diffraction data was obtained by Fourier analysis of the periodic structures recorded in the high resolution electron micrographs. Images were analyzed by both optical microdiffraction analysis [10] and digital analysis. Comparisons were made with simulated high resolution electron micrographs using CEMPAS [11] software.

3. Results and discussion

POLYMORPHIC TRANSFORMATION

The X-ray powder diffraction patterns for VPI-5, $AlPO_4$-8 (prepared from a 100 °C treatment of VPI-5 synthesized in the presence of di-n-propylamine [8]),

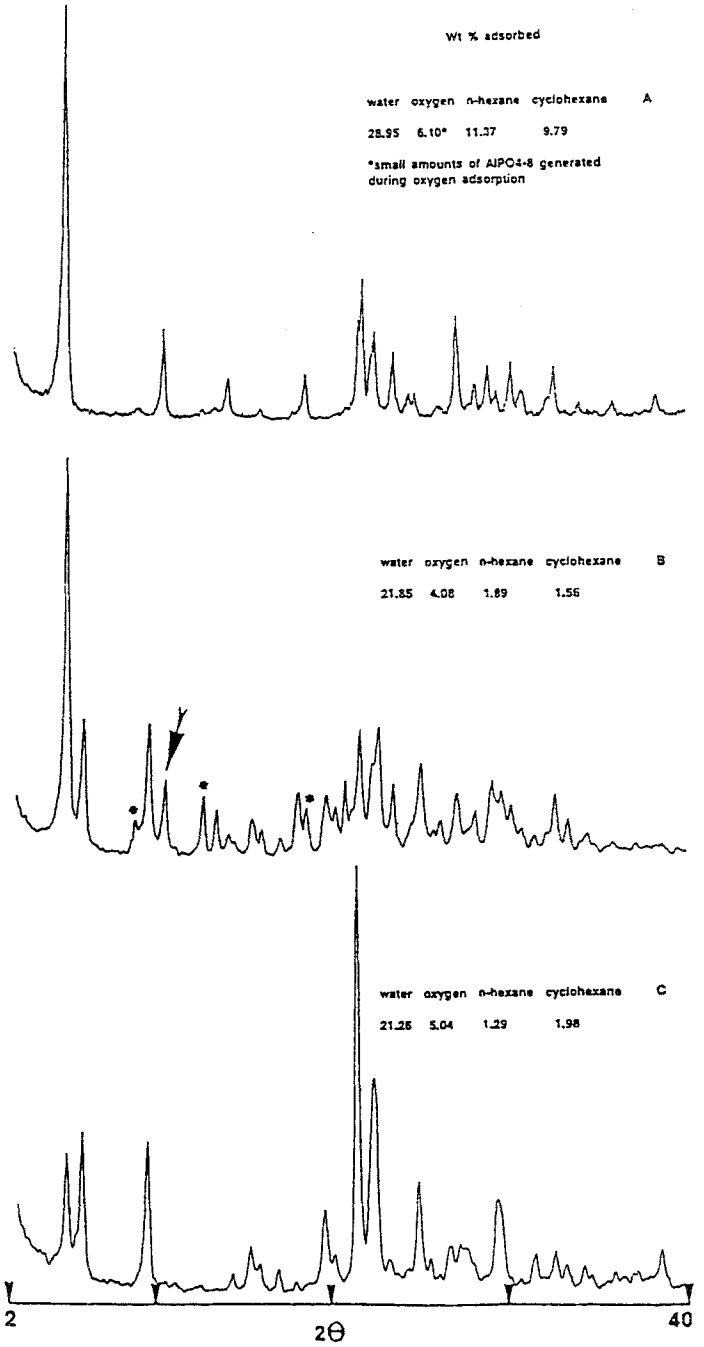

Fig. 1. A) VPI-5 as synthesized from di-n-propylamine containing system (similar capacities are observed for VPI-5 crystallized from TMA/triisopropanolamine containing gel, slightly lower adsorption capacities observed in the latter, ca. 10% due to H3 impurity); B) VPI-5/$AlPO_4$-8 formed from VPI-5 sample crystallized from TMA/triisopropanolamine containing gel, $AlPO_4$-8 phase appears upon heating to 100 °C under vacuum (* less than 10% H3 impurity identified in sample shown). The arrow indicates the intensity unique to VPI-5; C) $AlPO_4$-8 prepared from A heated in air to 100 °C.

and VPI-5/$AlPO_4$-8 (prepared from a 100 °C vacuum treatment of VPI-5 synthesized from TMA + /triisopropanolamine containing gels [9]) are shown in fig. 1. Selected adsorption properties of these materials are shown in the upper right hand corner of each diffraction pattern, Though both contain pores greater than the known 12-member rings of the zeolite molecular sieves [7,12], the solid state conversion of VPI-5 to $AlPO_4$-8 produces material with adsorption properties uncharacteristic of a very large pore structure. The maintenance of substantial water adsorption capacity indicates no destruction of the crystalline phase during this transformation. However, the drastic reduction in adsorption capacity of cyclohexane, n-hexane and even a small adsorbate such as oxygen (3.6 Å kinetic diameter) indicates significant blockage of the pores.

HRTEM OF STACKING DISORDERS

In both the VPI-5 and $AlPO_4$-8 structures, 18- and 14-member rings formed in the *a-b* planes generate a unidimensional channel system running perpendicular to this plane. Extensive defect-free regions, indicative of open channels, were imaged in high resolution micrographs of VPI-5 which corroborates the adsorption capacity data. The micrograph of $AlPO_4$-8 shown in fig. 2 reveals a very

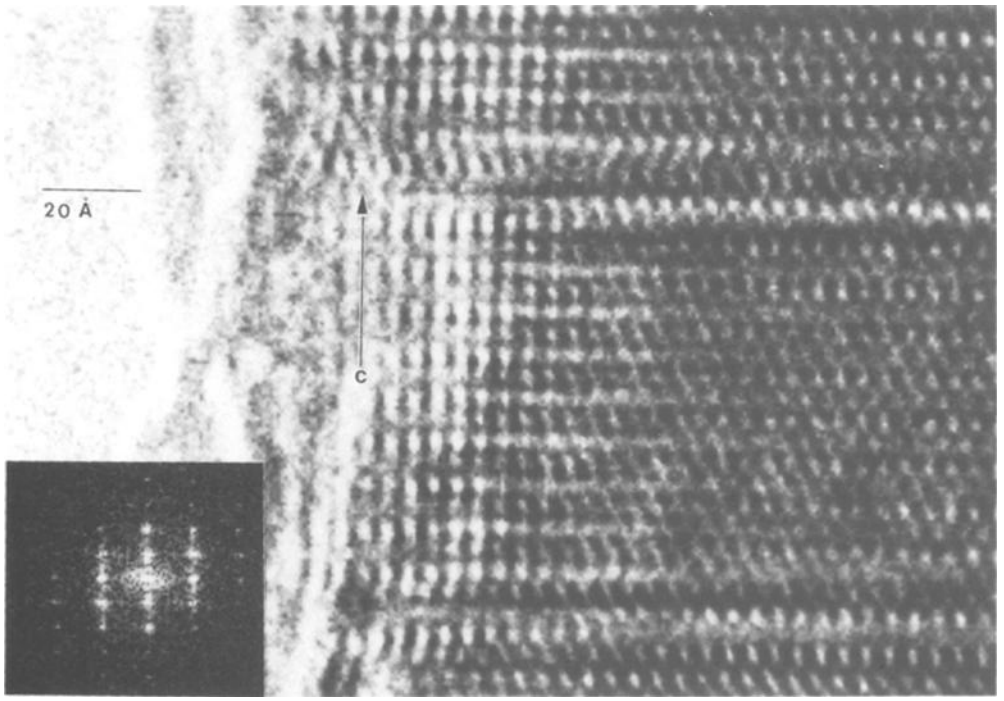

Fig. 2. HRTEM micrograph of $AlPO_4$-8 and corresponding diffraction pattern. Indexing of the diffraction pattern confirmed that the crystal is oriented perpendicular to the *c*-axis; the direction of this axis is indicated. Stacking disorders are observed perpendicular to the *c*-axis.

different state. $AlPO_4$-8 shows stacking disorders oriented perpendicular to the *c*-axis. Both defects induced by irradiation and by deformation during handling are ruled out as possible origins of the observed stacking disorders in $AlPO_4$-8 because under identical doses and handling VPI-5 showed extensive regions of perfect structure. Therefore, these stacking disorders were induced by the thermal treatment. Such stacking disorders would misalign the rings which define the channels and produce pore blockage. The significantly reduced adsorption capacities for all adsorbates larger than water supports the contention that pore obstruction due to the stacking disorders is occurring.

SYMMETRY RELATED STACKING DISORDERS

The presence of these stacking disorders can be understood when the high degree symmetry of VPI-5 is considered. Because of the hexagonal symmetry of the VPI-5 structure a polymorphic transformation to the $AlPO_4$-8 structure can begin in either of three degenerate directions in the *a-b* plane. The transformation is essentially a contraction of the crystal in one of these directions which results in a 20% reduction in volume, calculated from the difference between the volume of VPI-5 and $AlPO_4$-8, and a change to orthorhombic symmetry. Consequently,the directions are no longer degenerate. Regions of stacking disorders can arise where layers meet in which the transformation has originated from different directions.

4. Conclusions

A pronounced decrease in adsorption capacity is observed when VPI-5 undergoes a polymorphic transformation to $AlPO_4$-8. HRTEM images indicate the presence of stacking disorders perpendicular to the direction of the large channels. Even small impurities of $AlPO_4$-8 intergrown with the VPI-5 crystals produces significant pore closure.

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