

LETTERS TO THE EDITOR

The Reversible Transition of the Molecular Sieve VPI-5 into ALPO_4^{-8} and the Structure of ALPO_4^{-8}

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In this letter we describe the reversibility of the recrystallization of the aluminophosphate molecular sieve VPI-5 to ALPO_4^{-8} , and the structure of ALPO_4^{-8} . VPI-5 is known to contain one-dimensional circular pores circumscribed by 18 tetrahedral atoms. Upon heating in the presence of moisture it is known to recrystallize to ALPO_4^{-8} . This transition now proves to be reversible. Although phase transitions of aluminophosphate molecular sieves have been described, this is the first report of such a transition being reversible. ALPO_4^{-8} is found to contain one-dimensional elliptical pores, with free diameters of 7.5 to 9.5 Å circumscribed by 14 tetrahedral atoms. This new pore system thus contains one of the largest openings described so far, second only to VPI-5. © 1990 Academic Press, Inc.

Zeolites have been known since their first description by Cronstedt in 1756 (1). The materials belong in a class described as molecular sieves, since their micropore systems allow them to act as sieves on a molecular scale. Many zeolite molecular sieves have been described, both natural and synthetic. Molecular sieving, however, is not limited to the aluminosilicate zeolites. In 1982, Union Carbide workers described a family of synthetic aluminophosphate molecular sieves (ALPO_4^{-n}) (2). Two years later the same workers described element-substituted materials based on aluminophosphate lattices (3). Recently, Davis *et al.* (4) announced the synthesis of a new structure type, called VPI-5, both in the aluminophosphate form and in the element-

substituted form. The material was described as containing one-dimensional pores, circumscribed by 18 tetrahedral atoms (4, 5). The structure was solved with X-ray powder diffraction by Crowder *et al.* (6), and independently with neutron diffraction by Richardson *et al.* (7).

In both natural and synthetic molecular sieves built from tetrahedral units, the largest pores known before the description of VPI-5 were circumscribed with 12 tetrahedral atoms. These include the natural zeolites faujasite, mordenite, gmelinite, and bogsite, the synthetic zeolites L and Y (a faujasite analog), and the aluminophosphate ALPO_4^{-5} . Since the report of the synthesis procedure for VPI-5 (8), many workers have attempted reproduction of the

experiments of Davis. A major problem proved to be the unwanted formation of an impurity phase, ALPO_4^{-8} , already described in the first Union Carbide patent (2). VPI-5 was found to transform to ALPO_4^{-8} upon heating to temperatures between 373 and 473 K in the presence of moisture. The transformation is sometimes complete, but usually only partial.

ALPO_4^{-8} can be synthesized directly with an organic structure directing agent also known to give VPI-5: tetrabutyl ammonium hydroxide. The material is described (2) as able to adsorb perfluorotributyl amine, $(\text{C}_4\text{F}_9)_3\text{N}$, to some extent. This molecule has a kinetic diameter of over 10 Å, suggesting extra-large pores could be present. Davis compared ALPO_4^{-8} and VPI-5 (9) and concludes that ALPO_4^{-8} is a distinct phase, not containing VPI-5. On the basis of his adsorption experiments he further suggests ALPO_4^{-8} does not contain extra-large pores. The latter suggestion will be shown to be incorrect.

We found the transition of VPI-5 to ALPO_4^{-8} to be reversible. When heating samples of VPI-5 containing small amounts of template in a high-temperature X-ray diffraction camera, samples containing over 50% ALPO_4^{-8} at increased temperature transformed back to essentially pure VPI-5 upon cooling (E. T. C. Vogt, J. van Oene, R. Visser, J. Aerts, and J. W. Richardson, Jr., in preparation). Factors promoting the initial transition of VPI-5 to ALPO_4^{-8} are impurity of the sample, the presence of moisture, and low heating rate. The reverse transition apparently is hindered by the presence of impurity phases. Only in samples with crystalline impurities will ALPO_4^{-8} remain visible at room temperature, although the amount present may be much lower than found at elevated temperatures.

VPI-5 samples showing no crystalline impurities can transform partially to ALPO_4^{-8} at about 350 K when the vacuum

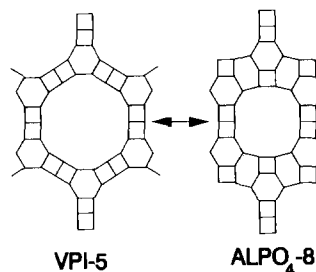


FIG. 1. Projection of the framework topology of VPI-5 and ALPO_4^{-8} . ALPO_4^{-8} : Orthorhombic, space group $Cmc2_1$, $a = 33.154$ Å, $b = 14.707$ Å; $c = 8.354$ Å.

applied for water removal or the heating rate is insufficient, but will completely transform back to VPI-5 upon cooling. Samples already calcined before the high-temperature XRD experiments also reversibly transform to ALPO_4^{-8} .

Thermal stability of a VPI-5 sample, as judged by the absence of ALPO_4^{-8} peaks in an XRD pattern recorded at room temperature after calcination, thus is no guarantee for the absence of ALPO_4^{-8} at higher temperatures.

Phase transitions occurring in aluminophosphate molecular sieves have been described before (e.g., the transitions of ALPO_4^{-21} to ALPO_4^{-25} (2, 10, 11), and ALPO_4^{-23} to ALPO_4^{-28} (2)), but reversibility of a transition between two aluminophosphate molecular sieves has not been previously reported.

The reversibility of the phase transition combined with data from transmission electron microscopy has led to a model for the structure of ALPO_4^{-8} , which was confirmed with XRD and neutron diffraction analysis. The Al–O–P linkages in four of the double four-rings in the VPI-5 are broken and recombine to form six-rings and single four-rings (see figure). ALPO_4^{-8} thus has a pore system circumscribed with 14 tetrahedral atoms. Strict alternation of Al and P in the tetrahedral sites is maintained, as is the alternation of up and down

bonds from tetrahedral sites. The detailed neutron diffraction study is forthcoming (12).

The difficulty in assessing the pore diameter and volume of ALPO_4^{-8} with adsorption techniques, in our opinion, is caused by blockage of the one-dimensional pores by the same impurity phases that also prevent recrystallization of the ALPO_4^{-8} to VPI-5.

ALPO_4^{-8} thus contains pores with an opening larger than any other zeolite or aluminophosphate-based molecular sieve with the exception of VPI-5.

Acknowledgments

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