The Adsorption of Water Vapour By VPI-5, A Large Pore Molecular Sieve

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The framework of VPI-5, the first molecular sieve having uniform pores larger than 1 nm diameter, is modified during removal of the zeolitic water; the interaction of VPI-5 with water vapour is examined.

Since Davis and his co-workers[1,2] reported the synthesis of the aluminophosphate molecular sieve VPI-5, it has attracted considerable attention.[3–5] VPI-5 is the first molecular sieve having uniform pores as large as 1.2 nm diameter and thus has great potential as a selective adsorbent or catalyst support. From X-ray diffraction (XRD) results,[6] hydrated VPI-5 has been assigned a framework made up of unidimensional channels circumscribed by rings of 18 tetrahedral atoms. In their early studies Davis *et al.*[7] used thermal gravimetric analysis (TGA) to show that the zeolitic water was removed in three stages and later refinements of the XRD pattern by Rudolf and Crowder[3] suggested that water molecules were arranged within the channels 'as a three-layer-thick onion skin,' although the exact locations of the water molecules are still in question. Recent work in our laboratories[5] has shown that the VPI-5 framework is modified during the removal of this zeolitic water, giving rise to some pore blockage. This modification of parts of the framework has been interpreted as a phase change to ALPO-8.[8] It was therefore decided to carry out a more detailed investigation of the interaction of water vapour with a sample of VPI-5 kindly supplied by Professor Davis.

The XRD pattern of hydrated VPI-5 agreed well with that published by Davis *et al.*,[6,7] confirming that the starting material was VPI-5. Also in agreement with Davis *et al.*,[7] TGA experiments have identified three different stages in the removal of zeolitic water from VPI-5. The temperature range and weight loss during each stage are given in Table 1.

To investigate further this relationship, water vapour isotherms were determined gravimetrically at 298 K using a quartz spring balance of the McBain–Bakr type. Fig. 1 shows the isotherm determined for a fresh sample of VPI-5 outgassed at 673 K for 16 h. Three distinct steps are observed at low relative pressure (p/p^0). The first occurs at very low p/p^0 and is likely to be associated with adsorption on a small number of strong specific surface or defect sites. Diffuse reflectance and transmission FTIR studies[9,10] suggest that these defect sites arise from broken Al–O–P sequences, resulting in surface P–OH groups. The second and third steps occur at p/p^0 = 0.013 and 0.060 respectively; between these steps there is a hysteresis loop. This loop is unusual as it occurs at a relative pressure too low for capillary condensation and is more probably associated with a phase transformation of the adsorbed water. It is also noteworthy that the weight gain in the third step of the isotherm (10.6%) agrees well with that removed during the first stage of the TGA experiments (10.5%). This is consistent in that the molecules least strongly adsorbed are removed first during heating. The three steps and the low-pressure hysteresis loop, along with the fact that the micopores are filled by p/p^0 = 0.2, suggests that the 18 T-atom channels readily accommodate a highly ordered hydrogen-bonded water network. At relative pressures above p/p^0 = 0.2; the isotherm shows an upswing due to adsorption on the external surfaces and between the aggregated crystals.

Successive water vapour isotherms were then measured on a single sample of VPI-5 which was outgassed at 298, 393 and 673 K. The results are given in Fig. 2 and are compared with the isotherm determined on the sample outgassed directly to 673 K. Each isotherm is of the same general shape but outgassing at 298 K resulted in a lower total uptake of water vapour than found for the sample outgassed directly to 673 K. By itself, this could be explained in terms of the incomplete removal of the zeolitic water on outgassing at 298 K, but only the water molecules associated with the strong specific sites or P–OH defect sites remained in the pores after outgassing at this temperature for 16 h. In fact, the weight loss was only 2% lower than after outgassing at 673 K. Furthermore, it can be seen that subsequent outgassing at temperatures sufficient to remove all the zeolitic water (393 and 673 K) results in further decreases in the total uptake.

The amounts adsorbed in steps one and three remain constant for all isotherms and the loss in total uptake is due to a decrease in step two. Hence, the most strongly and most weakly bound water molecules are largely unaffected by the changes to the framework.

These results are in agreement with earlier studies[5] and clearly demonstrate that the VPI-5 framework is irreversibly altered not only during the removal of the original zeolitic water but also during subsequent hydration and dehydration cycles. XRD of the samples[9] following the water isotherm measurements revealed the presence of significant amounts of

Table 1 Thermal gravimetric analysis of VPI-5

Stage	T/K	Weight loss (%)
1	298–348	10.5
2	348–368	9.3
3	368–396	3.2
Total		23.0

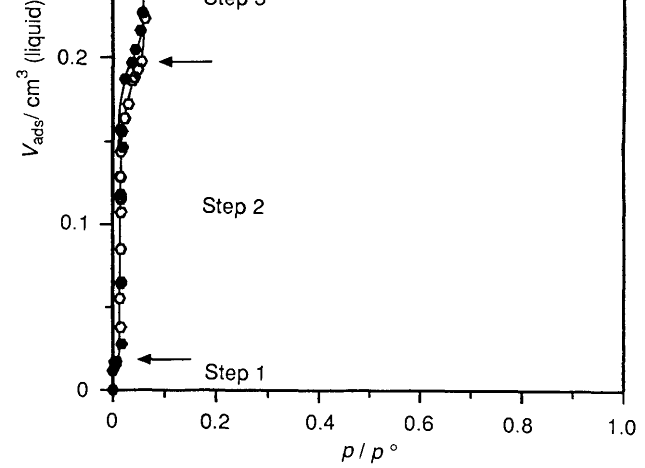

Fig. 1 Water vapour adsorption (open symbols) and desorption (closed symbols) isotherm determined at 298 K using a fresh sample of VPI-5 outgassed at 673 K for 16 h

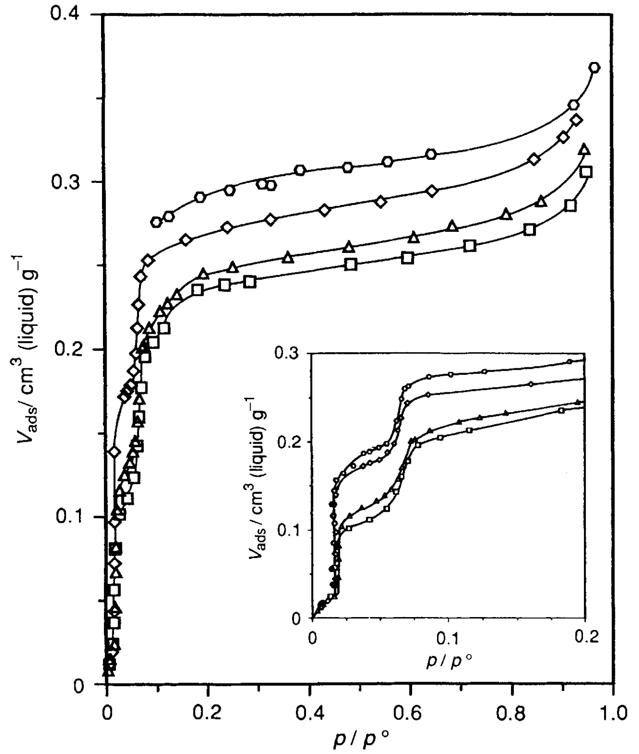

Fig. 2 Water vapour isotherms determined using a sample of VPI-5 successively outgassed at 298 (◇), 393 (△) and 673 K (□). Data from Fig. 1 (○) are given for comparison. Inset are the low relative pressure regions

ALPO-8. It is also evident that the treatment used to remove the zeolitic water affects the extent of the framework modification. Rapid removal of the zeolitic water by outgassing at 673 K reduces the degree of framework modification compared to the slower removal of the water by outgassing at 298 K.

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