ANL/IPNS/CP--80966
Conf-940744--3

Inelastic Neutron Scattering and Molecular Dynamics Simulations of Water Adsorbed in the Molecular Sieves AlPO$_4$-11, AlPO$_4$-5, AlPO$_4$-8 and VPI-5

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To be published in :

The Proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, 17-22 July 1994

Edited by J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich

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Keywords : molecular sieves, inelastic neutron scattering, molecular dynamics simulation

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Inelastic neutron scattering and molecular dynamics simulations of water adsorbed in the molecular sieves $AlPO_4$-11, $AlPO_4$-5, $AlPO_4$-8, and VPI-5

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1. Introduction

The molecular sieves $AlPO_4$-11, $AlPO_4$-5 and VPI-5 form a series as they all contain one-dimensional pores which are formed from four- and six-ring building blocks. For $AlPO_4$-5, the pore is bounded by 6 four-ring and 6 six-ring units, resulting in a circular pore with a diameter of 7.3 Å. The replacement of the six four-ring units by fused four-ring units results in VPI-5, which has a circular pore with a diameter of 12.1 Å. Alternatively, removal of two of the four-ring units gives $AlPO_4$-11, which has an elliptical pore with a diameter of 6.3 x 3.9 Å These structures are shown in Figure 1.

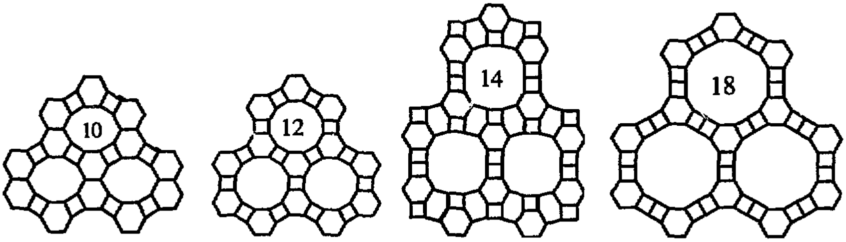

Figure 1. The structure of $AlPO_4$-11 (10-ring), $AlPO_4$-5 (12-ring), $AlPO_4$-8 (14-ring) and VPI-5 (18-ring) viewed down the pore opening

On the basis of this structural similarity, one would expect the properties of these compounds to be very similar, aside from pore size effects such as selective adsorption. However, the water adsorption isotherm for $AlPO_4$-5 is different from that for the other two compounds [1]. The adsorption of water by VPI-5 and $AlPO_4$-11 is characterised by a strong onset of adsorption at low p/p_0, while there is relatively little adsorption in $AlPO_4$-5 (20-25%) up to a p/p_0 of approximately 0.2. This behaviour could be explained by strong adsorption sites being present in $AlPO_4$-11 and VPI-5 but not in $AlPO_4$-5.

This is consistent with the reported structure of adsorbed water in VPI-5 [2], where two molecules are closely linked to the aluminium atom at the junction of the fused four-ring. A similar preference for a specific aluminium site is also found for $AlPO_4$-11 [3]. The structural evidence is in agreement with nmr measurements [4]. There is no structural evidence for specific association between adsorbed water and the framework atoms in $AlPO_4$-5, although nmr experiments [5] indicate that there are two types of water. Bound water that is presumably localised on the framework was distinguished from free water that diffuses freely in the channels on the nmr timescale. In this work the properties of adsorbed water in VPI-5 and $AlPO_4$-5 have been investigated using inelastic neutron scattering (INS), in conjunction with molecular dynamics simulations (MD) of $AlPO_4$-11, $AlPO_4$-5, $AlPO_4$-8 and VPI-5.

2. Experimental

The INS experiments were carried out on the QENS spectrometer at the Intense Pulsed Neutron Source located at Argonne National Laboratory. This spectrometer is capable of measuring spectra in the energy range 0-500 meV (0-4000 cm, 1 meV = 8.06 cm), with a particular emphasis on the lower end of this range 0-50 meV (0-400 cm^{-1}). The external vibrations of physisorbed molecules are usually found in the latter region.

The as-prepared VPI-5 sample was equilibrated at a relative humidity (RH) of 15% in order to remove any water not located in the pores. The INS spectrum was then measured at 15K. The sample was subsequently outgassed at room temperature for 1 day to a pressure of approximately 10^{-5} τ and the INS measurement was repeated. After it was established that very little water remained in the sample (hydrogen is a strong scatterer and so the presence of water is readily observable), the equivalent of one water molecule per fused-four-ring aluminium was dosed onto the sample at room temperature.

The $AlPO_4$-5 sample was equilibrated at three different relative humidities, 15%, 35% and 79%. From the water adsorption isotherm [1], these represent samples containing approximately 0.03, 0.18 and 0.27 cm^3g^{-1} of liquid, which are equivalent to concentrations of 2.4, 14.6 and 22 molecules/unit cell (m/uc).

3. Simulations

The molecular dynamics simulations were based on the microcanonical ensemble with a static molecular sieve framework, and the adsorbed water was treated as a rigid molecule. The simulations were carried out at 300K for a

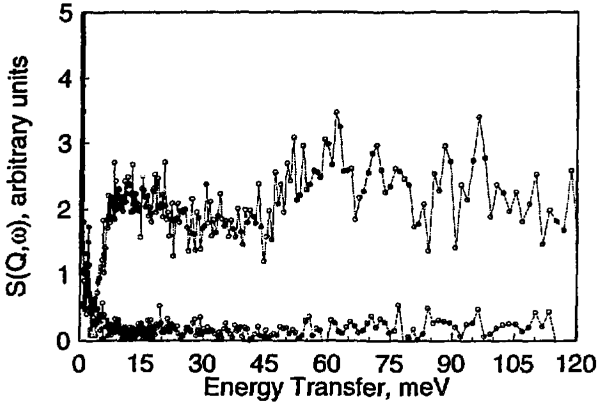

Figure 2. INS spectra of dry $AlPO_4$-5 and after equilibration at 79% RH (top).

The spectra measured for the fully loaded VPI-5 (equilibrated at 15% RH), the dried material, and the partially re-hydrated compound are shown in Figure 3. The scattering from the dried material is very weak compared with the other two, which indicates that the drying process was successful in removing most, if not all, the water. For the spectrum of the VPI-5 sample dosed with 3 m/uc, the general appearance of the spectrum is similar to the fully filled material but there are also peaks superimposed on the low frequency band.

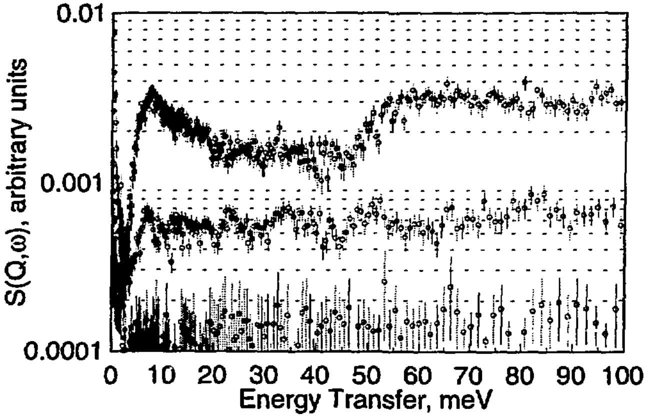

Figure 3. INS spectra of water in VPI-5. The bottom spectrum is for dry VPI-5, the middle for 3 m/uc and at the top is the sample equilibrated at 15% RH.

The data can be satisfactorily fitted with 5 Gaussians and a sloping background from 5-100 meV but skipping the range from 9 to 20 meV. There is extra intensity in the 9-20 meV window which is not included in the fit, but the quality of the data does not justify a detailed analysis of this region. The fit is shown in Figure 4.

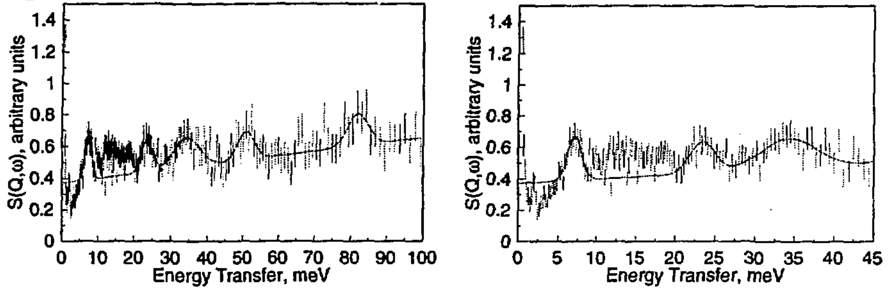

Figure 4. Fit of the INS data for VPI-5 using 5 Gaussians and a sloping background between 6 and 100 meV with an excluded region between 10 and 20 meV.

The fully loaded sample has two main bands of intensity, the first ranging from 10 to 50 meV, and a second from 50 to 120 meV. The latter is reminiscent of the high frequency band found for the $AlPO_4$-5 sample. There does not appear to be any structure in the low frequency band.

4. MD results

The Al-OH_2 single particle distribution function for fully filled VPI-5 at 50K and 300K are shown in Figure 5. At 300K, the peak is very broad, ranging from 1.5-2.5 Å, with roughly three peaks located at 1.6-1.7, 1.9-2.0 and 2.2-2.5 Å. At 50K, there are four distinct peaks at 1.63, 1.85, 2.05 and 2.1 Å.

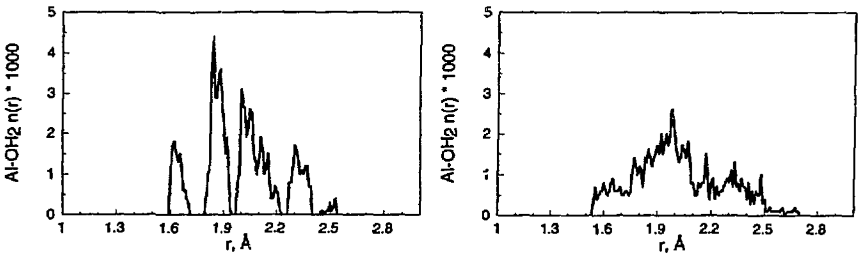

Figure 5. Al-OH_2 n(r) for water in VPI-5 at 50K (left) and 300K (right) for 42 m/uc.

In contrast to these results, Figure 6 shows that there are no water molecules within 3 Å of the framework aluminium for the case of $AlPO_4$-5. The result for $AlPO_4$-11 is similar and the function shows even less structure. Also shown is the same quantity for the case of $AlPO_4$-8, where there is a peak just below 2 Å.

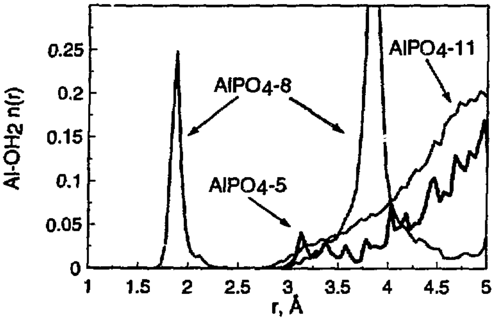

Figure 6. Al-OH_2 single particle distribution functions for $AlPO_4$-11, $AlPO_4$-5 and $AlPO_4$-8.

The Fourier transforms of the translational and rotational autocorrelation functions are shown in Figure 7 for $AlPO_4$-5 with a loading of 2 m/uc and 8 m/uc at a temperature of 50K. Figure 8 shows the same functions for VPI-5 and water loadings of 42 and 12 m/uc at 50K.

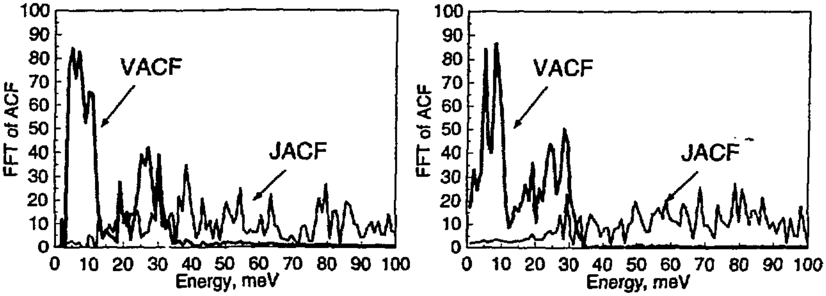

Figure 7. Fourier transform of the translational (VACF) and rotational (JACF) velocity autocorrelation functions of water adsorbed in $AlPO_4$-5. The plot on the left is for 2 m/uc and the other for a concentration of 8 m/uc.

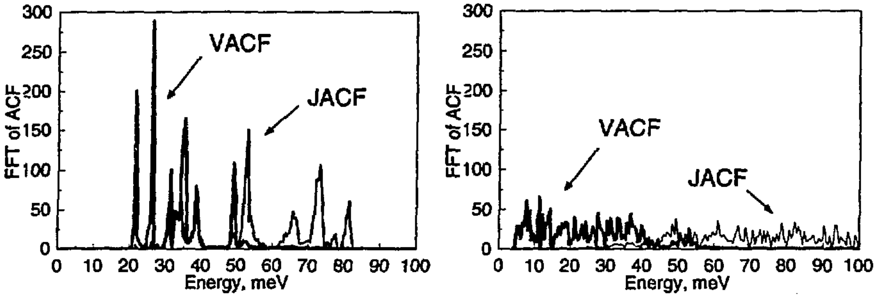

Figure 8. Fourier transform of translational (VACF) and rotational (JACF) velocity autocorrelation functions of water in VPI-5. The left and right plots are for 12 m/uc and 42 m/uc respectively.

5. Discussion

From the work of McCusker *et al* [2], a basic structural requirement for the simulations is that there should be a close contact between two water molecules and every Al(1) atom in the framework, for the fully filled VPI-5 material at 300K. The framework-water potentials were tuned to give the shorter Al-OH_2 contact for this aluminium atom, which is located at the junction of the fused four-rings. The diffraction experiments gave two positions for the water molecule located at the Al(1) atom, with Al-O distances of 1.94 and 2.06 Å and a $<u2>^{1/2}$ of 0.16 Å. The agreement between experiment and simulation is reasonable, particularly as the main peak in the n(r) occurs at about 1.9-2.0 Å. As can be seen from the sharpness of the peaks in the 50K n(r), a low temperature experiment would be worthwhile due to the greater localisation of the water molecules.

The importance of the fused four-ring unit for adsorbed water localisation is confirmed by the similar short distance Al-OH_2 contact found in $AlPO_4$-8. Again, a low temperature experiment on partially hydrated $AlPO_4$-8 would provide a strong test of the simulation model.

The lack of a such a clear cut hydration site interaction in $AlPO_4$-5 is confirmed by the Al-OH_2 n(r), where there are no close contacts. This is also the case for $AlPO_4$-11, although there is experimental evidence that the water might possibly prefer to be near a phosphorus atom. This is contrary to the behaviour observed in VPI-5 where there is a distinct preference for the aluminium site. However, it should be noted that the simulations were based on the structure determined for MnAPO-11, and they should be repeated using the co-ordinates reported by Khouzami *et al* [3].

The agreement between the predicted and measured INS spectra for VPI-5 is good. The MD does not reproduce the peak at about 10 meV, and it also appears to have an extra peak in the 20-28 meV range. The missing 10 meV peak is attributed to the motion of the framework atoms which is not included in the calculation. In addition, it is likely that the static framework makes the predicted water modes much sharper than would be the case for a dynamic lattice. The disappearance of the sharp modes for the case of 42 m/uc is in good agreement with experiment, and this suggests that perhaps the 12 m/uc INS sample was not adequately equilibrated after rehydration. An inhomogenous distribution of the adsorbed water would result in undercoordination of the Al(1) sites in some regions and higher water loadings in other regions. This could explain the excessive background observed in the INS experiment.

The MD results for $AlPO_4$-5 are equally satisfactory mainly because there are essentially two low frequency peaks present, both due to the translational motion of the water molecule. The MD results for 2 m/uc and 8 m/uc are very similar which is consistent with a the proposed lack of specific adsorption sites in this compound.

6. Conclusion

MD simulation results show that there is a specific adsorption site located at the fused four-ring aluminium atom found in VPI-5 and $AlPO_4$-8. There is no such specific adsorption site in $AlPO_4$-5 or $AlPO_4$-11.

The MD simulations are in good agreement with INS experiments on VPI-5 at high and low loadings of water. There is also good agreement between theory and experiment for $AlPO_4$-5.

Acknowledgements

Work supported by US Department of Energy, BES-Materials Sciences, under contract W-31-109-ENG-38. This work has benefited from a grant of computer time on the Energy Research supercomputers at the National Energy Research Computer Center.

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