

# Room Temperature Methoxylation in Zeolites: Insight into a Key Step of the Methanol-to-Hydrocarbons Process

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## -Supporting Information-

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## 1. Sample preparation

The zeolites ZSM-5 and HY used were commercial catalysts obtained from Zeolyst International, both with Si/Al = 30. The zeolite Y samples were received in the catalytic proton form, already steam dealuminated to this composition. The ZSM-5 samples were received originally in the NH<sub>4</sub> form. These were activated into the catalytic H-ZSM-5 form by heating to 798 K for 4 hours, with a heating rate from room temperature of 5 K/min. The zeolites were then dehydrated at 120°C under flowing helium. After cooling to room temperature, methanol was then loaded by bubbling He as a carrier gas through the liquid to a loading equating to 4 molecules per unit cell. The samples (4.5 grams in total) were transferred inside a glovebox under argon to thin walled aluminium containers of annular geometry. The same samples were used for both the inelastic neutron scattering and the quasielastic neutron scattering experiments.

## 2. Inelastic neutron scattering experiments

Inelastic neutron scattering (INS) was used in order to probe the species that formed in both the zeolites at room temperature. The INS technique is especially sensitive to the vibrational modes involving hydrogen due to its uniquely high incoherent scattering cross section. It is an ideal vibrational spectroscopy method for these systems, as it allows access to vibrations in the low energy region without limitations due to selection rules or low transmittance of the framework, which inhibit optical spectroscopy.

The experiments were carried out using high-flux INS spectrometer MAPS<sup>1-2</sup> at the ISIS Pulsed Neutron and Muon Source, (STFC Rutherford Appleton Laboratory, Oxfordshire, UK). The samples were prepared as in section 1. The cans were placed in a top-loading closed cycle refrigerator cryostat so that all measurements could be taken at 10 K. Measurements were taken in a range of 500 – 4000 cm<sup>-1</sup> with an incident neutron energy of 650 meV and then in a range of 400 – 1600 cm<sup>-1</sup> with an incident neutron energy of 250 meV to give a higher resolution measurement of the lower energy vibrational modes. The spectra obtained are depicted in figure 1 of the main article, showing high energy (a, b) and low energy (c, d) data for methanol in zeolite Y (top) and ZSM-5 (bottom).

## 3. Quasielastic neutron scattering experiments

The quasielastic neutron scattering (QENS) method, as with INS, is useful for studying hydrocarbons due to the large incoherent scattering cross section of hydrogen, so only the dynamics of the hydrogenous compound are measured. The diffusivity is related to the broadening of the QENS peak as a function of neutron momentum transfer vector  $Q$ . This broadening due to quasielastic signal is fitted to a Lorentzian function and the  $Q$  dependence of the half-width at half-maximum describes the motions observed: for example, in the case of Fickian diffusion the data can be described by a  $DQ^2$  law where  $D$  is the diffusion coefficient. A detailed explanation of the QENS method and its application in studying hydrocarbon diffusion in microporous systems has been given previously.<sup>3</sup>

All measurements were performed using the time-of-flight backscattering neutron spectrometer OSIRIS<sup>4</sup> at the ISIS Pulsed Neutron and Muon Source. The cells were placed in a top-loading closed cycle refrigerator cryostat so that a resolution measurement could be taken at base temperature of 6 K.

QENS measurements were then taken at 298 K in a  $Q$  range of  $0.2 - 1.5 \text{ \AA}^{-1}$ . Graphite (002) analyser crystals were used to give an energy resolution of  $24.5 \text{ \mu eV}$  with energy transfers measured in a window of  $\pm 0.55 \text{ meV}$ . The measurement was taken of an empty zeolite sample and then the signal was subtracted from the signal of the loaded zeolite so that only the signal derived from the methanol was measured.

All QENS spectra were fitted using the neutron analysis software DAVE.<sup>5</sup> The dynamic structure factors ( $S(Q, \omega)$ ) measured at 298 K over a sample of  $Q$  values are depicted in Figures S1 and S2 for H-ZSM-5 and zeolite HY respectively. The red dotted line represents a delta function convoluted with the resolution spectra taken at 5 K.

In H-ZSM-5 the broadening of the QENS peak as a function of  $Q$  is minimal. This lack of broadening, persistence of the elastic line and close fit to the elastic resolution spectra even at the higher  $Q$ -values (in the rotational region) suggest immobility of methanol, certainly on a translational scale. A Lorentzian component to the overall fit was only present at higher  $Q$  values. This was a very small component and was independent of  $Q$ . This is indicative of rotational motion; however it is important to note that due to such a small quasielastic component, the elastic incoherent structure factor (EISF) could not be fitted to models developed previously to describe rotational motions of methanol trapped in H-ZSM-5 (including one developed for a methoxy group).<sup>6-7</sup> However, this problem is probably due to the difference in dynamical time scales sampled by the spectrometer between the present and previous studies.

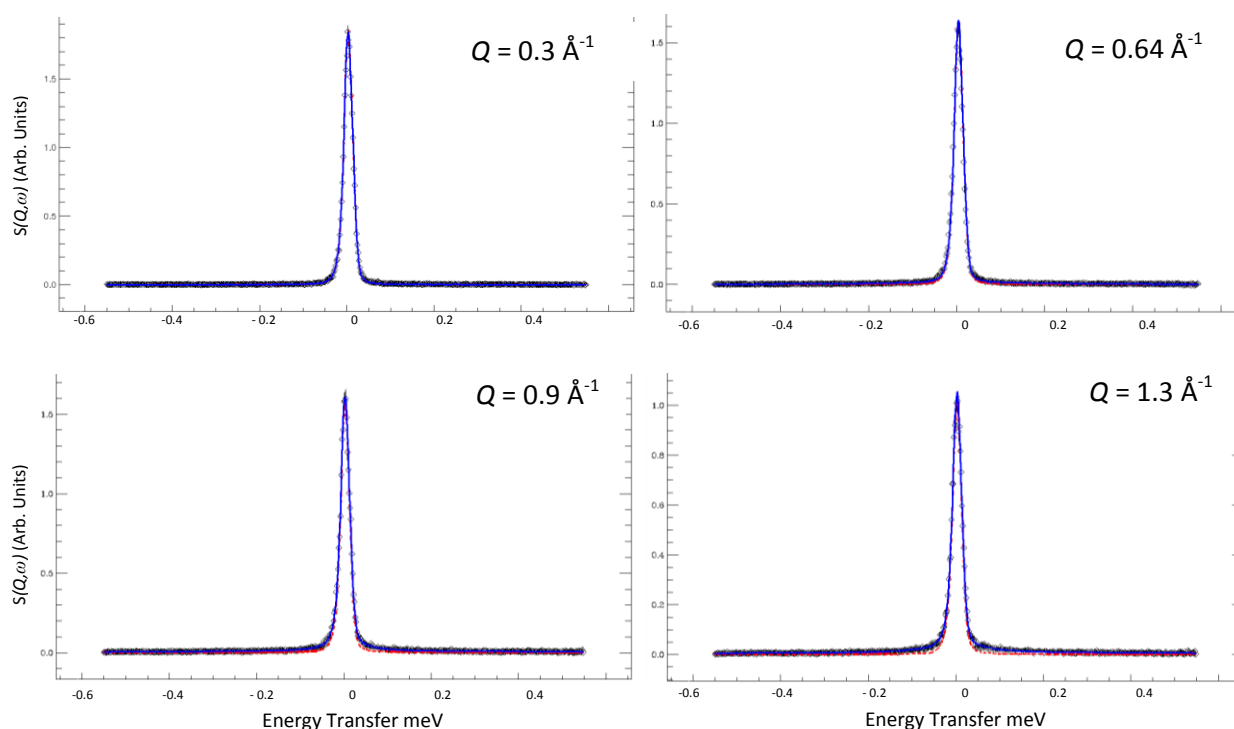


Figure S1. QENS spectra of methanol at 300 K in H-ZSM-5 with the total peak fit (blue line). The red dotted line represents a delta function convoluted with the resolution function (measured at 5 K).

In contrast the QENS spectra of methanol in zeolite Y are shown in figure 2. Significant broadening from the resolution spectra is observed compared to H-ZSM-5 due to a large quasielastic signal, suggesting relatively high mobility on a translational timescale. Initial fitting suggests that the data can be fitted to two Lorentzian components, one with a  $Q$ -dependence relating to jump diffusion, and

the other relating to Fickian diffusion in a confined volume. Detailed analysis of the diffusion behaviour of methanol in HY will be deferred to a subsequent publication.

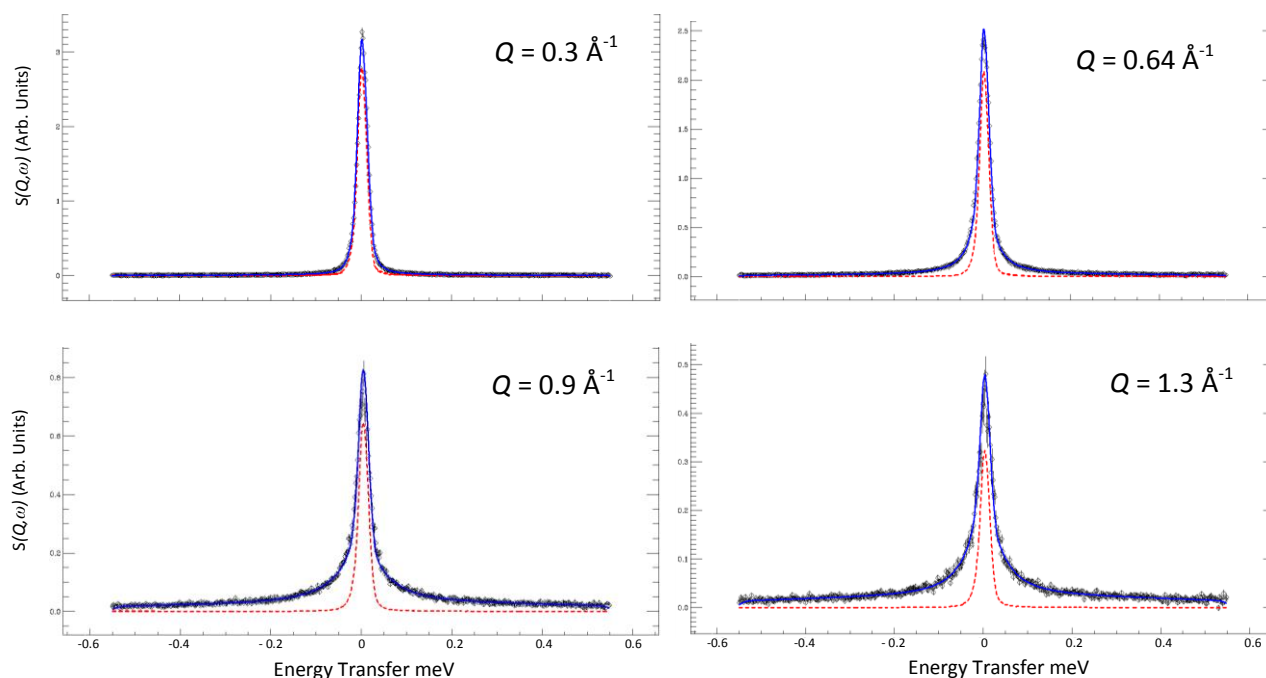


Figure S2. QENS spectra of methanol at 300 K in HY with the total peak fit (blue line). The red dotted line represents a delta function convoluted with the resolution function (measured at base temperature).

#### 4. Quantum mechanical simulations

The plane-wave density functional theory (DFT) calculations were performed using *ab-initio* plane-wave pseudopotential code CASTEP (version 7.03).<sup>8</sup> The Perdew-Wang 1991 (PW91)<sup>9</sup> Generalised Gradient Approximation (GGA) exchange-correlation functional was chosen for the calculations due to its reliability over a wide-range of materials. Norm-conserving pseudopotentials were employed at a cut-off energy of 830 eV. Calculations were performed at the gamma point in the Brillouin zone. The quasi-Newtonian Broyden-Fletcher-Goldfarb-Shanno (BFGS)<sup>10</sup> algorithm was used for the geometry optimisation of the system and forces. The optimizations were carried out until the energy, maximum force, maximum stress and maximum displacement were less than  $2.0 \times 10^{-6}$  eV/atom, 0.03 eV/Å, 0.05 GPa and 0.001 Å respectively. On the optimized structures the phonon vibrational frequencies were calculated by diagonalization of dynamical matrices computed using density functional perturbation theory (DFPT).<sup>11</sup> The calculated INS spectrum was generated from the phonon vibrational modes using the ACLIMAX<sup>12</sup> software designed for modelling INS spectra, thus enabling direct comparison with experimental data. ACLIMAX assumes a particular trajectory in  $(Q, \omega)$  space, which is different from that of MAPS. To enable a direct comparison with the experimental data, and abnormal Debye-Waller factor was used. The zeolite HY primitive cell containing 144 atoms was chosen as the host to reduce the computational cost (c.f. 288 atom ZSM-5 unit cell). However it is expected that the vibrational properties of the methoxy species are not sensitive to the host.

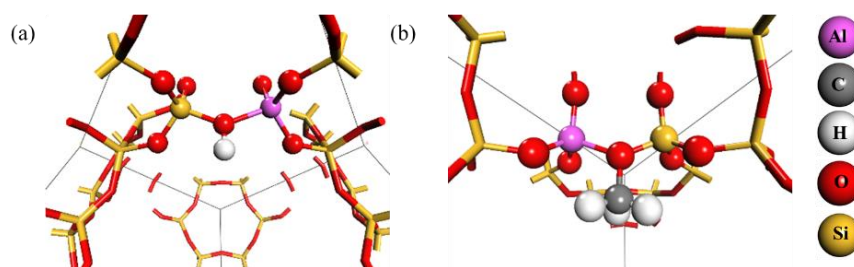


Figure S3. Optimized geometries of (a) protonated and (b) methylated active sites of FAU framework. All the other atoms in the framework were held fixed.

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