Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Molecular behaviour of methanol and dimethyl ether in H-ZSM-5 as a function of Si/Al ratio: a quasielastic neutron scattering study

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Electronic supplementary information (ESI)

S1. QENS analysis of methanol in ZSM-5 (36)

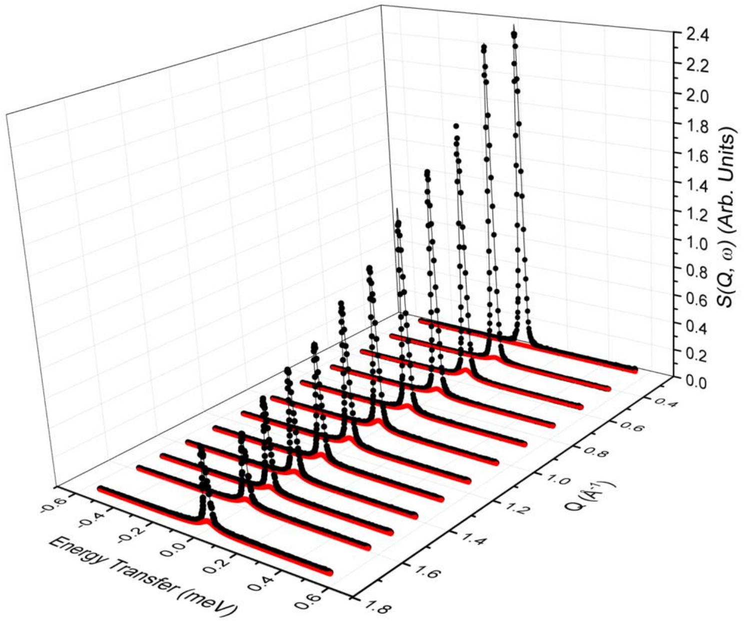

Fig. S1: QENS spectra as a function of momentum transfer vector Q for methanol in ZSM-5 (36) at 293 K

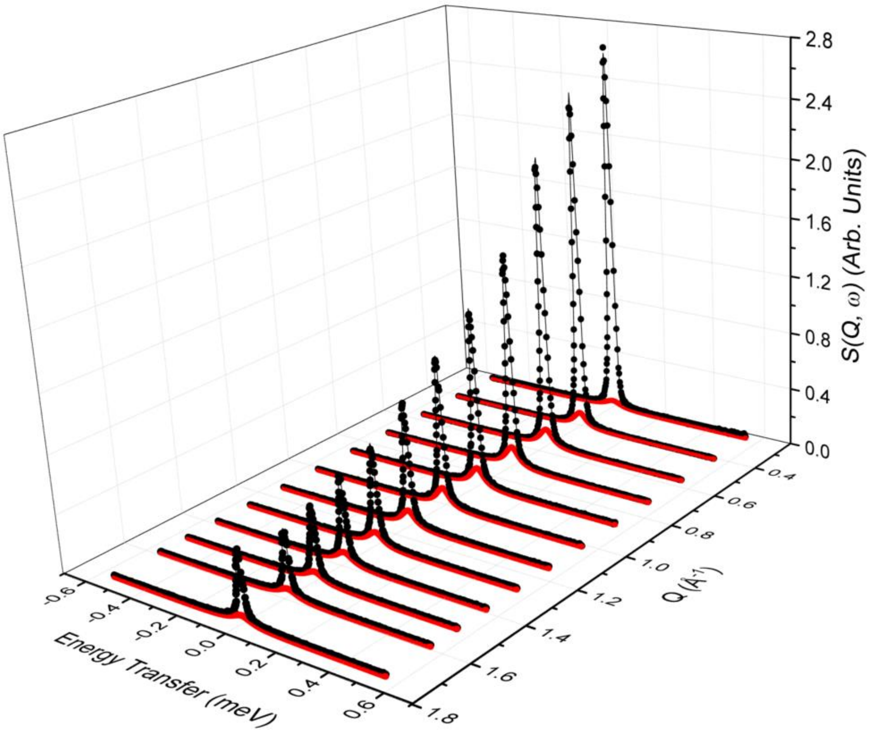

Fig. S2: QENS spectra as a function of momentum transfer vector Q for methanol in ZSM-5 (36) at 333 K

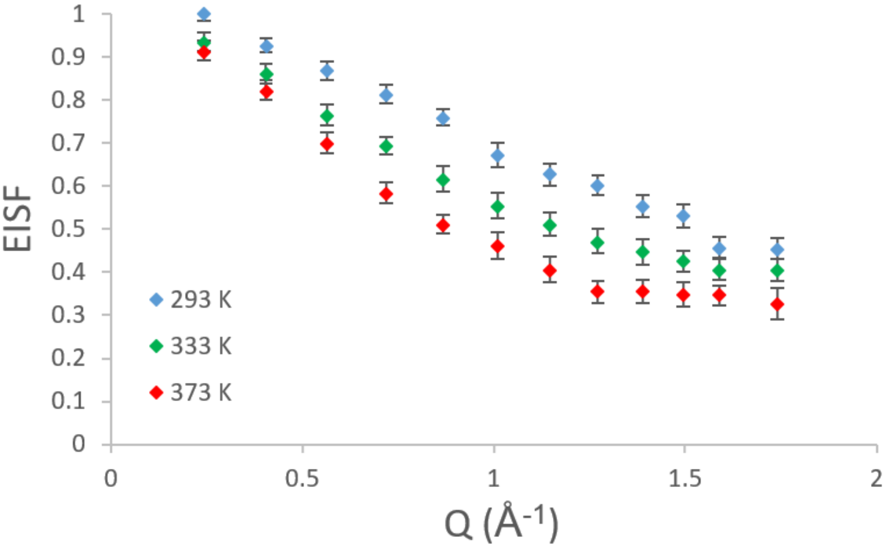

Fig S3. Experimental EISF plots of methanol in zeolite ZSM-5(36) at 293, 333 and 373 K

S1.1 Models for methanol motion

In this section we present the models used to characterise the localised motions of methanol, related to the geometries of motion of the protons in the molecule. First, the elastic incoherent structure factor (EISF) at 293 K is analysed.

Isotropic rotation is characterised by a molecule whose reorientation takes place through a series of small angle, random rotations so that no most probable orientation exists on a time average as depicted in Fig. S4a. The scattering law as derived by Sears[1] for this form of rotation has an EISF ($A_0(Q)$) given as:

$$A_0(Q) = j_0^2(Qr) \qquad \boldsymbol{eq.\ (S1)}$$

where r is the radius of rotation, and j_0 is the *0*th order spherical Bessel function given as:

$$j_0(Qr) = \frac{\sin(Qr)}{(Qr)} \qquad \boldsymbol{eq.\ (S2)}$$

The average radius of rotation of the 4 methanol protons as calculated from the centre of mass is 1.48 Å. The theoretical EISF for isotropic rotation with a radius of rotation of 1.48 Å is plotted against the experimental EISFs in Fig. S5 as the dashed black line. It is evident that the model falls far below all experimental points.

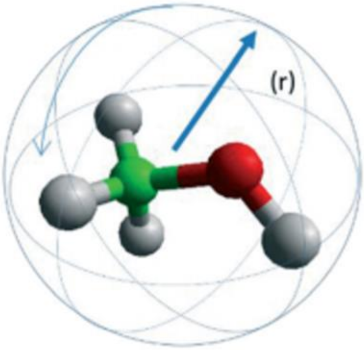

Fig. S4a: Isotropic rotation of a methanol molecule with a radius of rotation (r).

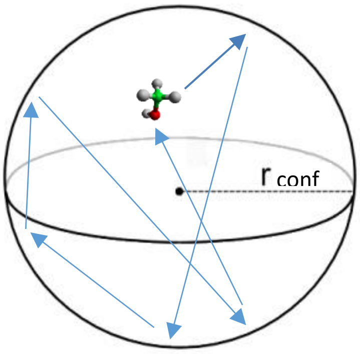

Fig. S4b: Translational motion of methanol confined to a spherical volume of radius, r_{conf}

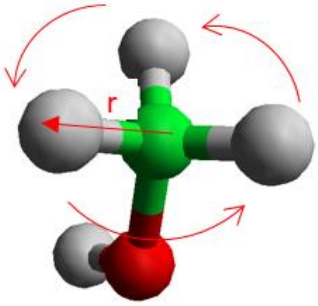

Fig. S4c: Methyl rotation described by a three-site jump model around a circle (red arrows)

Another model is when methanol undergoes translational motion but localised to a confined, spherical volume. Volino and Dianoux[2] developed a model to describe a scattering molecule undergoing translational motions in a confined spherical volume of radius $r_{conf.}$ as shown in Fig. S4b. This scattering model is based on the general problem of a particle diffusing in a potential field of spherical symmetry, where the potential is low inside the sphere's volume but infinite outside of it. The EISF in this model is given as:

$$A_0(Q) = \left[\frac{3j_1(Qr_{conf})}{Qr_{conf}}\right]^2 \qquad \boldsymbol{eq.(S3)}$$

where j_1 is the spherical Bessel function of the first kind, order 1, given by:

$$j_1(Qr_{conf}) = \frac{sin(Qr_{conf})}{(Qr_{conf})^2} - \frac{cos(Qr_{conf})}{(Qr_{conf})} \qquad \boldsymbol{eq.(S4)}$$

r_{conf} is the radius of the sphere to which the diffusion is confined to. The radius considered in this study is 2.75 Å (to represent half the diameter of a ZSM-5 channel of 5.5 Å). The model is plotted with the experimental EISF in Fig. S5 as the solid black line (r = 2.75 Å). The model also falls well below the experimental points at all Q Values.

The next consideration is that of a methanol molecule which is fixed through adsorption to the zeolite surface, either through physisorption due to H-bonding *via* the O-H group to the catalyst surface, or due to methoxylation, such that the only motion observable is that of rotating methyl groups. A model which can be used to describe methyl rotation is the jump rotation model between three equidistant sites on a circle with a radius (r) as depicted in Fig. S4c.The elastic incoherent structure factor is given as:

$$A_0(Q) = \frac{1}{3}\left[1 + 2j_0(Qr\sqrt{3})\right] \qquad \boldsymbol{eq.(S5)}$$

where r is the radius of the circle on which the jumps take place, in this case 1.02 Å. This model is plotted against the experimental EISF in Fig. S5 as the dotted line. We note that when considering a H-bonded methanol molecule, this model requires the incorporation of an immobile fraction (discussed later with regard to other models) of 25% to represent the hydroxyl proton which is static due to being anchored to the zeolite structure. The model of three site rotation around a circle (with this static incorporation) falls above the experimental points at virtually all Q values, suggesting there is more dynamical disorder in the system than that simply represented by methanol bound to the acidic sites. While the shape appears to match that of the data points, it still falls outside of the error bars when the necessary immobile fraction is considered, and thus the use of this model alone cannot describe the system.

The model of uniaxial rotation[3] may also be used to describe this mode of adsorption/methyl motion, where the methyl protons undergo continuous rotation around a circle. This model cannot be used for powder samples typical for porous material studies, because no expression exists for the average angle θ between the axis of rotation and the direction of Q. However, one may consider a jump rotation over N sites around circle similar to the 3-site model discussed earlier. With a sufficiently large N (> 7) the scattering function does not change as N increases. The approximation of jump rotation over N sites may then be used to approximate continuous rotation, as given in eq. S6.

$$A_0(Q) = \frac{1}{N}\sum_{n=1}^{N} j_0\left[2Qr_u \sin\left(\frac{n\pi}{N}\right)\right] \qquad \boldsymbol{eq.(S6)}$$

As with the 3-site jump rotation model. This model necessitates the incorporation of an immobile fraction of 0.25 to account for the hydroxyl proton being static in this model, described in eq. S7. The model EISF for uniaxial rotation with the radius of gyration of the methyl group is very similar to the 3-site rotation, and as such is not able to fit the data.

While the isotropic/methyl/uniaxial rotation models and confined diffusion model alone are not able to provide an adequate fit to the experimental data, previous work in zeolites[4-6] has shown that the incorporation of a static fraction of molecules (either too sterically hindered by the zeolite pores, or interacting too strongly with the pore wall/acidic sites to move over the measured timescale) is necessary in order to describe the system correctly. We therefore incorporate an immobile fraction into the calculation of the model EISF, to gain an effective EISF as:

$$A_{0\_eff}(Q) = p_x A_0(Q) + (1 - p_x) \qquad \boldsymbol{eq.(S7)}$$

Here, p_x is the fraction of mobile molecules, and $A_0(Q)$ is each EISF as shown in eqs. S1, S3 and S5. In Fig. S6 we plot these effective EISFs against the experimental data obtained at 293 K with the optimal p_x (as obtained by a least squares fitting procedure). We note that the effective EISF of isotropic rotation with p_x = 0.57 fits the data best. This suggests that our dominant mode of motion observed at 293 K in H-ZSM-5 (Si/Al = 36) is that of isotropic rotation with a static fraction of ~43%.

The isotropic rotation model was also validated upon studying the broadenings of the Lorentzian component used to fit the scattering function. The broadenings, plotted in Fig. S7, show that they are independent of Q in line with rotational motions being observed. These widths can be used to calculate the rotational diffusion coefficient D_R as outlined in refs.[6] and [7] and leading to a D_R value of 2.6×10^{10} s^{-1}.

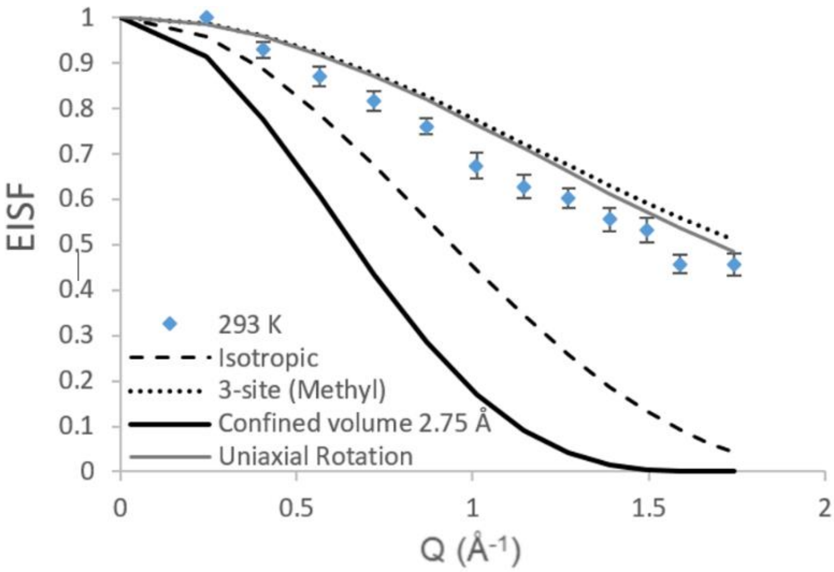

Fig S5. Experimental EISF plot of methanol in ZSM-5 at 293 K against different theoretical EISF models.

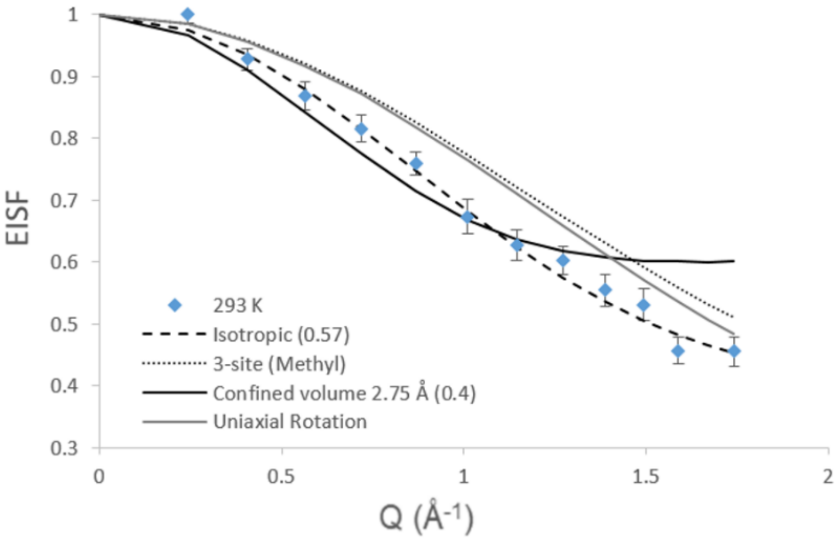

Fig S6. The experimental EISF of methanol in H-ZSM-5 at 293 K, plotted against the models of localised motions after fitting with an immobile fraction. The optimum p_x value is shown in the legend in brackets.

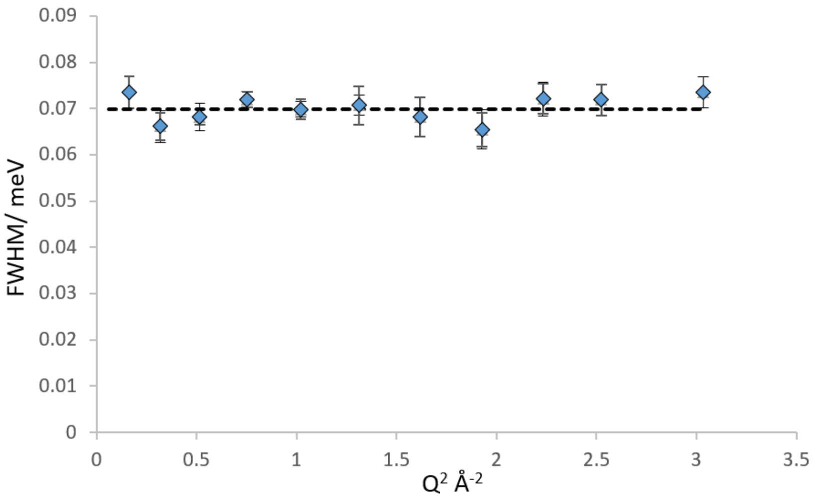

Fig S7. FWHM at 293 K as a function of Q^2 of methanol in H-ZSM-5 (36).

The rotational diffusion coefficient is lower than that obtained at 325 K in previous work studying methanol in ZSM-5[6] potentially reflecting both the lower temperature in this study and also the presence of mesopores in the above reference generated by framework damage due to the MTH process taking place.

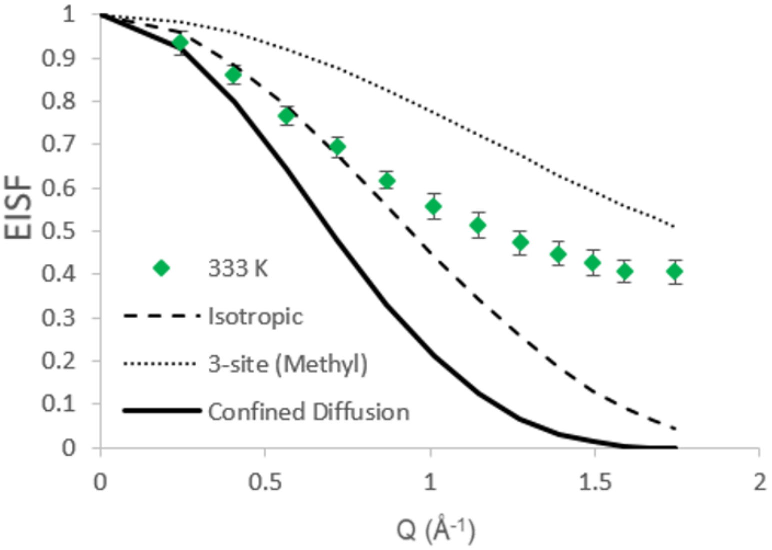

Fig S8. Experimental EISF plot of methanol in ZSM-5 at 333 K against different theoretical EISF models.

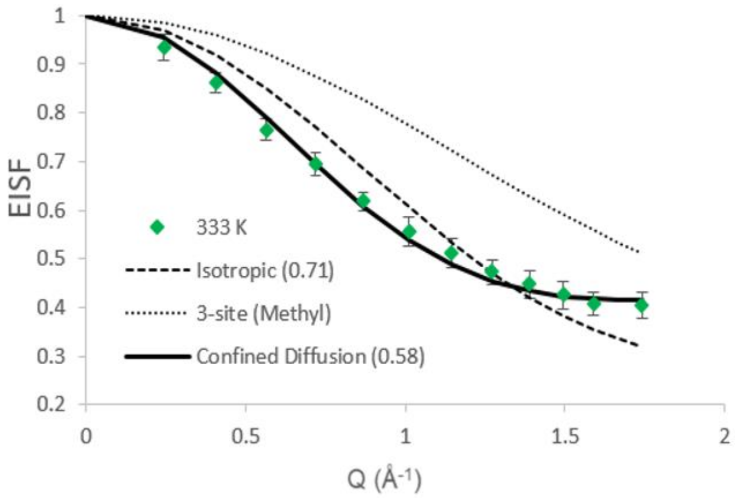

Fig S9. Experimental EISF plot of methanol in ZSM-5 at 333 K against different theoretical EISF models with the only a fraction of mobile molecules considered. The optimum p_x is shown in the legend in brackets.

S2. QENS analysis of methanol in ZSM-5 (135)

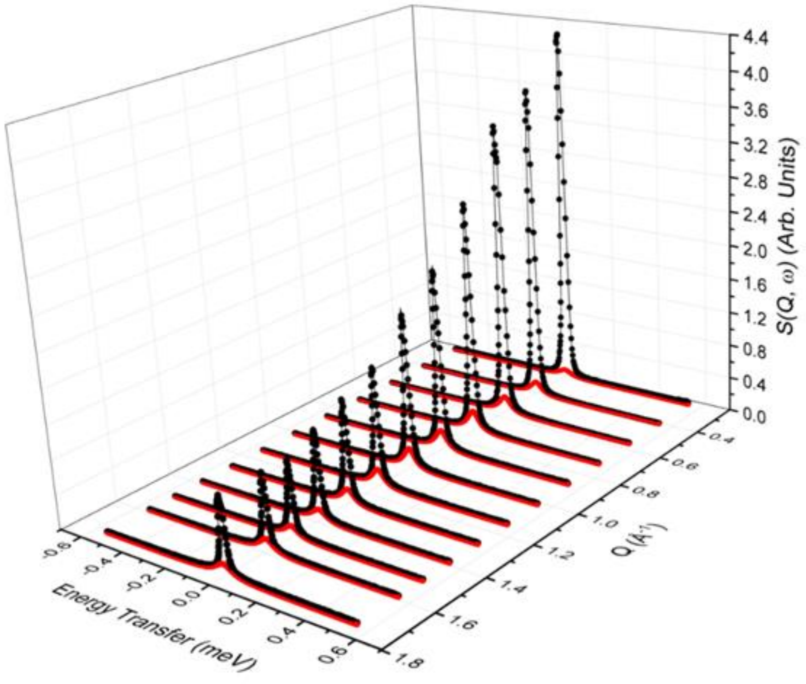

Fig. S10: QENS spectra as a function of momentum transfer vector Q for methanol in ZSM-5 (135) at 293 K

S3. QENS spectra of DME in ZSM-5 (36)

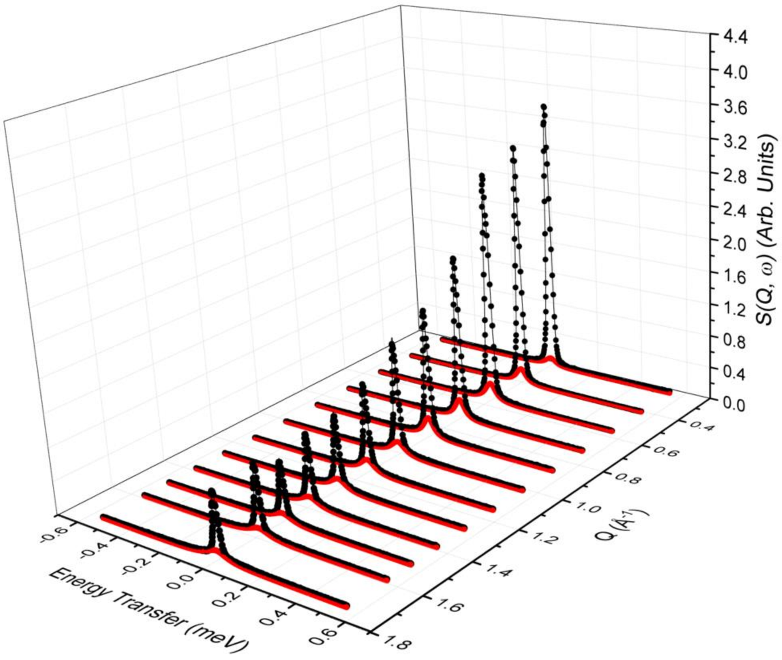

Fig. S11: QENS spectra as a function of momentum transfer vector Q for DME in ZSM-5 (36) at 293 K

The behaviour of dimethylether in the two ZSM-5 samples is considered next. Fig. S11 gives the QENS spectra of DME in ZSM-5 (36) catalysts. As with the methanol samples there is a very large elastic componant to all the spectra at all Q-values, indicating significant constraint/localisation of DME motion in the ZSM-5 pores. The models of localised molecular described above to fit the EISF were applied with immobile fractions applied as in eq. S4. An additional model which takes into account the symmetry of the DME molecule was also applied, which was that of the 2-site rotational model, where the DME molecules rotates through its C_{2v} axis as shown in Fig. S12 such that each methyl proton is in an equivalent position after a rotation of π Rad through this axis.

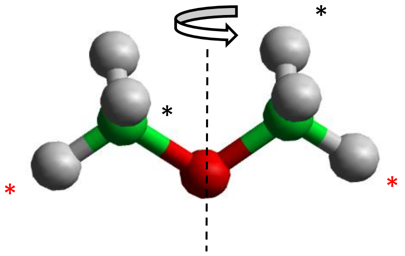

Fig. S12: Dimethyl ether rotation as around the C_{2V} axis with protons highlighted as per their relevant 2-site jump rotation model.

The model for this form of rotation is given by equation S8:

$$A_0(Q) = \frac{1}{2}\left[1 + j_0(Qd)\right] \qquad \boldsymbol{eq.}\ (\boldsymbol{S8})$$

where *d* is the distance between each equivalent site, i.e. the weighted average of the distance between the symmetrically equivalent protons marked with an asterisk (3.3 Å). The model appears to fit the lower and mid Q values well but lies above the experimental points at higher Q values. We note that the model of uniaxial rotation, using the same weighted average radius as the 2-site rotation model, gives an effective EISF almost identical to that of isotropic rotation when its optimal mobile fraction of 0.78 is used. The fit of the isotropic rotation model (where r in eq. S2 is the average distance of the proton from the centre of mass, 1.9 Å) with a mobile fraction of 0.58 provides a good fit to the data at low and mid Q values, however falls below the experimental points at the higher Q values, and the EISF model of methyl rotation is not able to fit the experimental data at any Q values (Fig. S13).

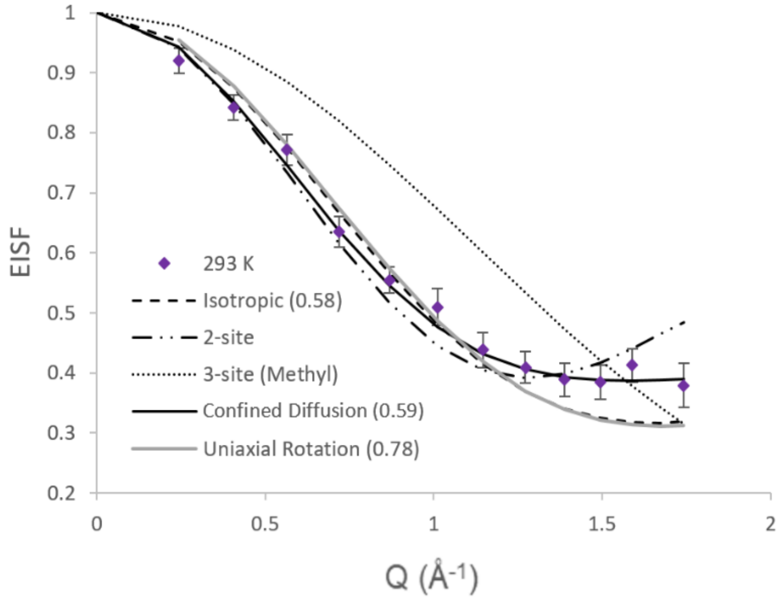

Fig S13. Experimental EISF plot of dimethyl ether in ZSM-5 (36) at 293 K against different theoretical EISF models.

S4. QENS spectra of DME in ZSM-5 (135)

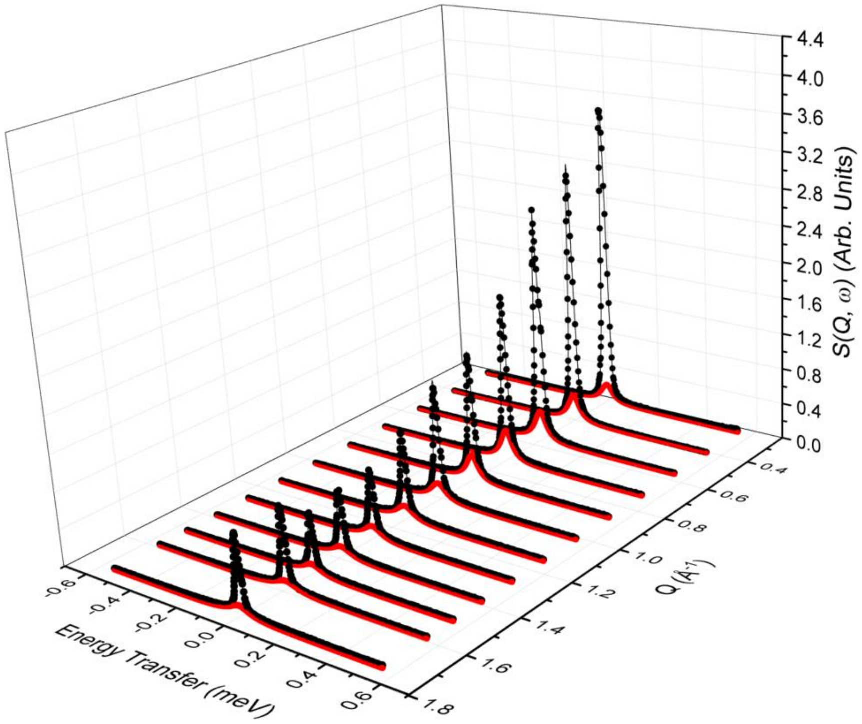

Fig. S14: QENS spectra as a function of momentum transfer vector Q for DME in ZSM-5 (135) at 293 K

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