

Electronic Supplementary Information (ESI) for

Methyl tunnelling of adsorbed methoxy on an alumina catalyst

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Experimental

η -Alumina (Ineos Chlor Ltd., catalyst reference: 25867/19A: BET surface area = 275 m² g⁻¹, average pore diameter = 39 Å, average pore volume = 0.18 cm³ g⁻¹) and γ -alumina (Ineos Chlor Ltd., catalyst reference: 25867/18A: BET surface area = 189 m² g⁻¹, average pore diameter = 146 Å, average pore volume = 0.70 cm³ g⁻¹) were activated by heating to 623 K under flowing helium (BOC, 99.999%) for 150 min in an Inconel cell using a gas manifold [1] that was specifically designed for the preparation of the large, ~10 g, catalyst samples required for inelastic neutron scattering. After cooling to ambient temperature, the samples were transferred to indium wire sealed thin walled cylindrical aluminium cells in an argon glovebox. After the background data were recorded, the sample was heated to 473 K, and exposed to a flow of helium that had passed through a Dreschel bottle, that contained methanol (Sigma-Aldrich \geq 99%) for one hour. The cell was then purged with helium at 473 K for a further hour and then allowed to cool to room temperature. This procedure produces a saturated layer of methoxy on the catalyst [2]. Isotopically labelled methoxy was generated by using CD₃OH (Aldrich, 99.8% D) or CH₃OD (Aldrich, 98% D) in place of CH₃OH. Low energy inelastic neutron scattering (QENS) spectra were recorded using the OSIRIS [3] and IRIS [4] spectrometers at ISIS [5]. On OSIRIS for each sample the following profiles were recorded: a high resolution (25 μ eV) measurement with the graphite 002 (PG002) reflection which covered the range -0.5 to +1.0 meV and a lower resolution (99 μ eV) measurement with the graphite 004 reflection in the offset mode (PG004 offset) which covered the range -1.0 to +8.0 meV. On IRIS for the sample prepared using CH₃OD, a high resolution (17.5 μ eV) measurement was undertaken with the graphite 002 reflection in the offset mode (PG002 offset) which covered the range -0.3 to +1.3 meV. Neutron vibrational (INS) spectra, 500 – 4000 cm⁻¹, were recorded after the OSIRIS or IRIS measurements to confirm the presence of chemisorbed methoxy using the MAPS [6] and MERLIN [7] spectrometers at ISIS [5] with various incident energies, E_i. For the isotopic samples, the 0 – 2000 cm⁻¹ region was also recorded with TOSCA [8].

Calculation of the tunnelling and librational energies

The initial methoxy-alumina model was the one used previously for normal mode calculations [2]. The atomic coordinates were optimised prior to rotation of the methyl group. For rigid body rotation, the total energy was calculated for each rotation angle and the average barrier height was calculated from the energy differences for a number of orientations in a complete turn. To allow relaxation during rotation, one torsion angle of a C–H bond with respect to the substrate was fixed and the atomic coordinates were optimised for each rotation angle. The average rotation angle was calculated from the resulting torsion angles of the three C–H bonds. For rigid body rotation the barrier height was ~65 meV, while allowing for structural relaxation reduced the barrier height to ~40 meV.

All energy calculations and geometry optimisations were performed using density functional theory as implemented in the CASTEP code [9,10]. The GGA PBE functional was used with ultrasoft pseudopotentials and a plane wave cut-off energy of 260 eV. The *k*-point sampling in the cell in which *a* = *b* = 5.6 Å and *c* = 12.0 Å (*c* being elongated to model the

alumina surface) was (3,3,1). All calculations were converged with respect to the plane wave cut-off and the k -point sampling.

Assignment of the spectrum of adsorbed methoxy

We assign the spectrum shown in Figure 2 of the main text as being due to adsorbed methoxy. The methodology we adopt to generate methoxy (a flow of methanol vapour entrained in helium carrier gas passed over the catalyst at 473 K) is one that has been successfully used previously [11]. However, the presence of residual surface hydroxyl groups means that the distinction between physisorbed methanol and methoxy + hydroxyls is not as clear-cut as previously. To address the possibility of physisorbed methanol, we repeated the preparation except that the sample was exposed to methanol at room temperature and not purged. This results in physisorbed methanol as shown by the comparison with the pure solid shown in Fig. S1. In particular, the O–H stretch at 3230 cm^{-1} and the in-plane C–O–H bend at 740 cm^{-1} are diagnostic of intact methanol. Fig. S2 shows the bending region in more detail and it can be seen that the bending mode occurs at the same position, 740 cm^{-1} , for both solid and physisorbed methanol. (The bandshape is different because solid methanol is crystalline and the physisorbed species is amorphous).

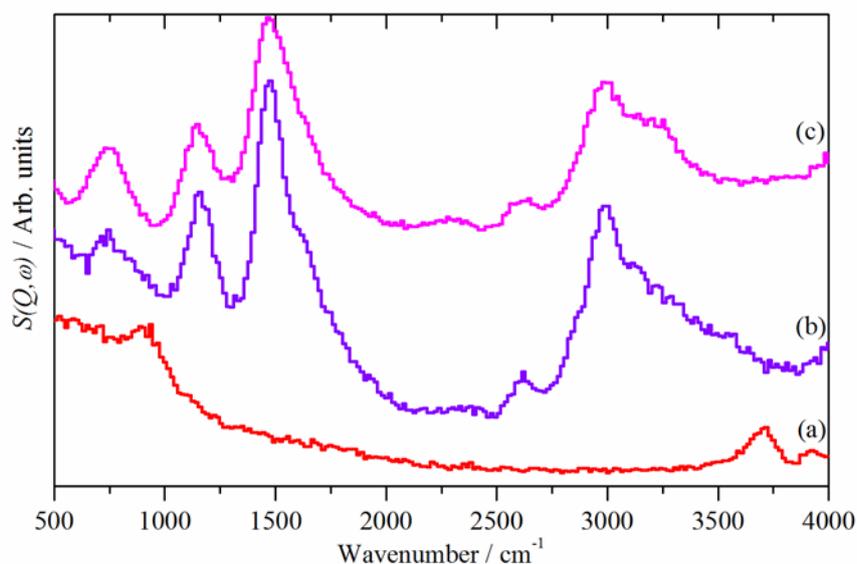


Fig. S1 INS spectra at 12 K of: (a) clean γ -alumina, (b) physisorbed CH_3OH on γ -alumina and (c) solid methanol. Spectra recorded using MAPS with $E_i = 4840\text{ cm}^{-1}$.

On heating to 473 K in a flow of helium, there is a significant change in the spectrum, Fig. S2. There is an overall decrease in intensity, consistent with removal of physisorbed material (compare (b) and (c) which are plotted on the same ordinate scale), but more significantly, the in-plane C–O–H bend at 740 cm^{-1} has vanished (compare (a) and (b)) and there is only the alumina hydroxyl bend at 885 cm^{-1} remaining. All of this is completely consistent with the initial spectra, Fig. S1b and S2b, being a mixture of physisorbed methanol and chemisorbed methoxy, on heating the methanol desorbs and the methoxy remains.

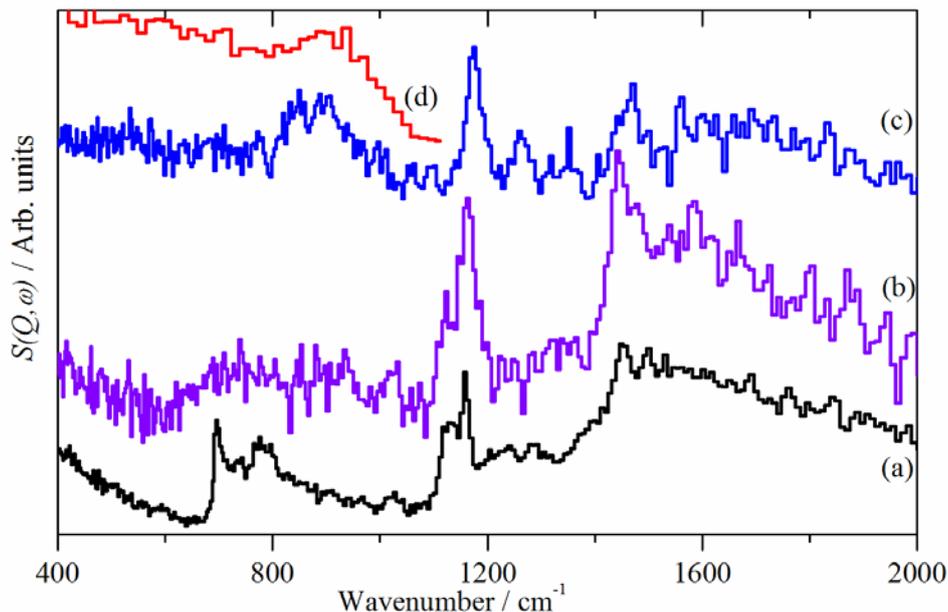


Fig. S2 INS spectra at 12 K of: (a) solid methanol, (b) physisorbed CH₃OH on γ -alumina (c) same sample as (b) after heating in flowing helium at 473 K. ((a), (b) and (c) were recorded with TOSCA, (b) and (c) are plotted on the same ordinate scale) and (d) clean γ -alumina (recorded using MAPS with $E_i = 2420$ cm⁻¹).

Figs. S3 and S4 show INS spectra for the formation of methoxy and methoxy-D3, respectively, on γ -alumina.

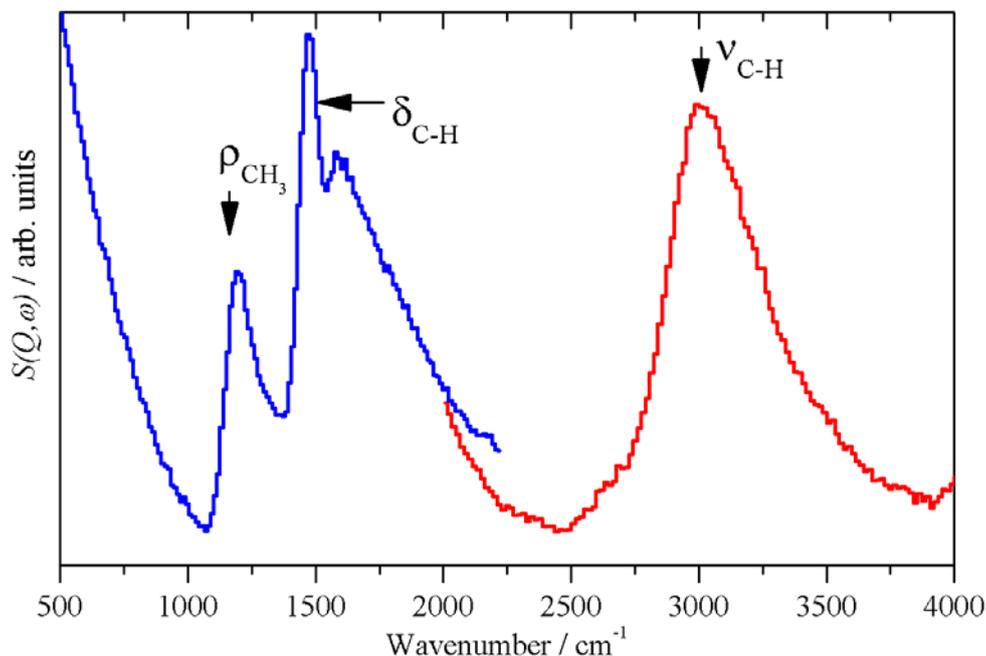


Fig. S3 INS spectra of the reaction of CH₃OD with γ -alumina recorded using MERLIN. Right (red): $E_i = 4840$ cm⁻¹, Left (blue): $E_i = 2420$ cm⁻¹. Note the presence of methoxy and the absence of hydroxyls.

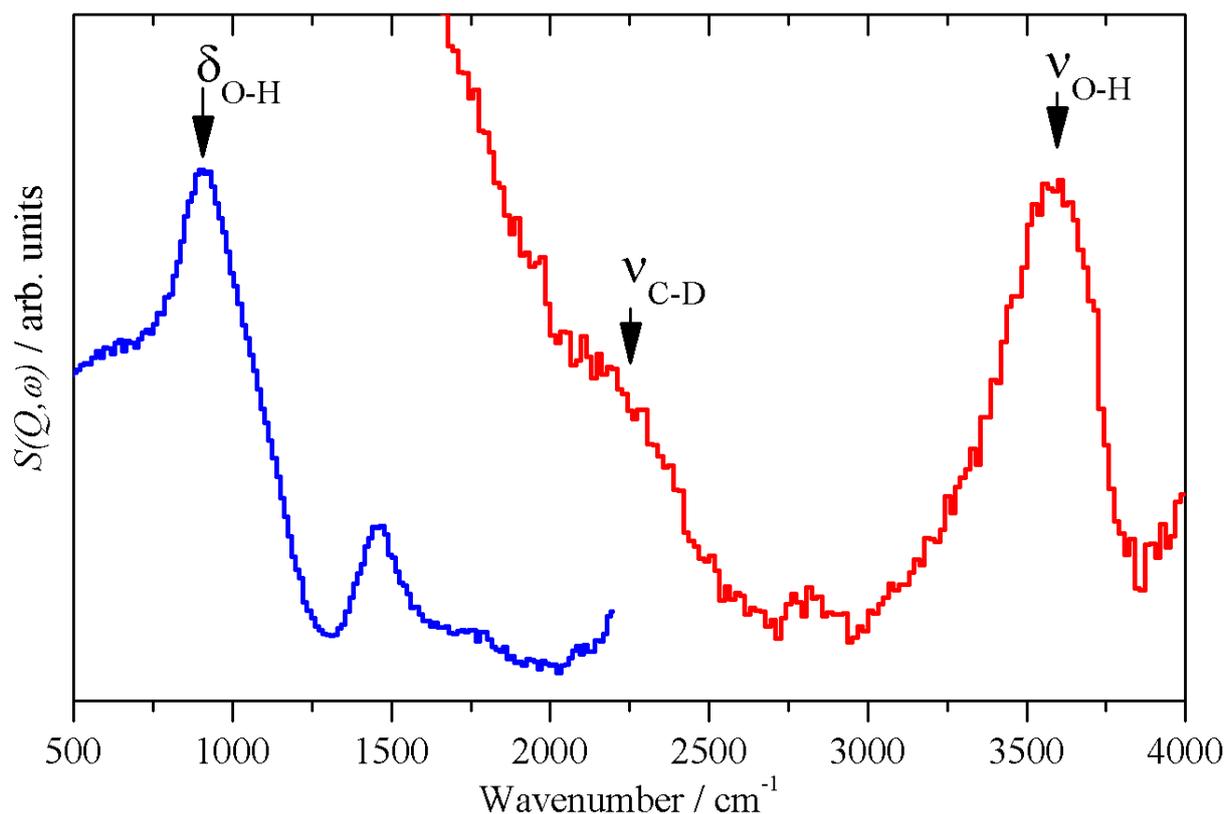


Fig. S4 INS spectra of the reaction of CD_3OH with γ -alumina recorded using MERLIN. Right (red): $E_i = 4840 \text{ cm}^{-1}$, Left (blue): $E_i = 2420 \text{ cm}^{-1}$. Note the absence of methoxy (it is present as $\text{CD}_3\text{O}\equiv$ and the presence of hydroxyls.

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