

Supporting Information for:

“QM/MM study of the stability of dimethyl ether in zeolites H-ZSM-5 and H-Y”

Stefan A. F. Nastase¹; C. Richard A. Catlow^{1,2,3}; Andrew J. Logsdail^{1*}

¹ *Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff
CF10 3AT, Wales, U.K.*

² *UK Catalysis Hub, Research Complex at Harwell, Rutherford Appleton Laboratory, Didcot,
OX11 0FA, UK*

³ *Department of Chemistry, University College London, Gordon Street, London, WC1H 0AJ,
UK*

* LogsdailA@cardiff.ac.uk

Transition state parameters analysis

The conversion of methanol adsorbed on the T12 [I2] site of H-ZSM-5 to methoxy bound zeolite and water was developed from previous work²⁹ and re-calculated. To test the effect of the size of the relaxed QM region on the value of the transition barrier, two calculations were performed, with one having the atoms of the entire QM region relaxed and another in which only the first nearest neighbours, starting from the center of QM region, were relaxed. This resulted in a difference of <10 kJ/mol between the two resulted transition states, indicating that the flexibility of the zeolite lattice would not significantly influence the stability of the transition state.

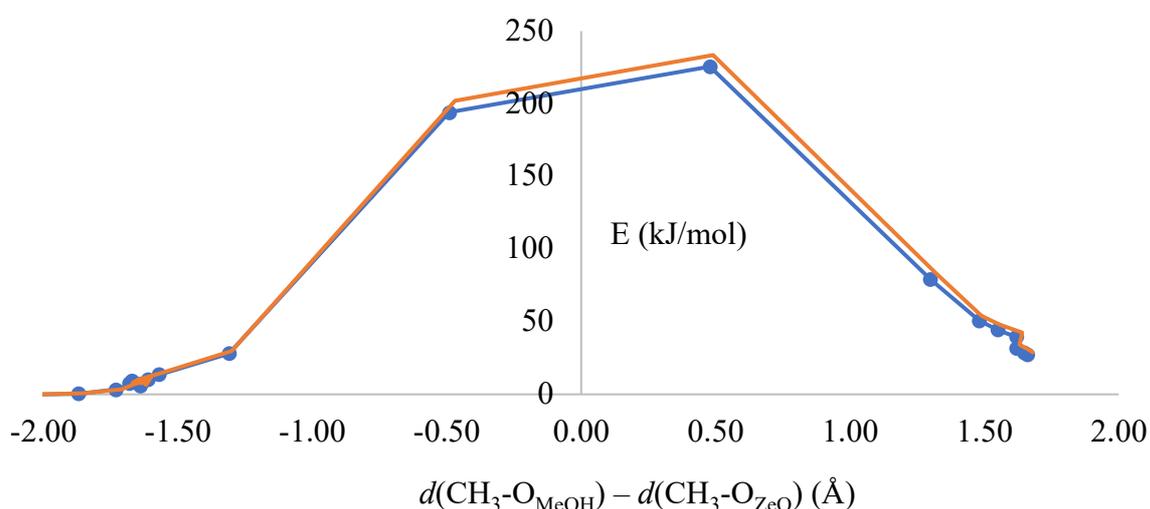


Figure S1. Plot between the difference of the bond length of methyl to oxygen of methanol and bond distance between methyl and oxygen of zeolite to which methyl was bonded, where the negative values describe the reactant state – methanol and the positive values describe the product state – methoxy and water, and the energy of each image of the NEB calculation relative to the reactant state, presented in Ångstroms and kJ/mol, respectively, of the calculations having the entire – blue and the first nearest neighbours - orange of the QM region relaxed. The lines are given to guide the eye.

Charge analysis of adsorbed DME models

Table S1. Comparison of the relative Mulliken partial charges for to isolated zeolite cluster and gas phase DME located on each atom presented the in first column, of DME adsorbed models, as provided in atomic units, with H_B – Brønsted proton, O_{DME} – oxygen of DME, C_1 – closest carbon of methyl to the active site, C_2 – furthest carbon of methyl to the active site, H_1 – closest hydrogen of C_1 methyl to the active site, H_2 – closest hydrogen of C_2 methyl to the active site.

	H-Y	H-ZSM-5 (T12 [I2])	H-ZSM-5 (T4 [Z6])	H-ZSM-5 (T1 [M7])
H_B	-0.005	0.003	0.028	0.010
O_{DME}	0.013	-0.035	-0.002	0.010
C_1	-0.016	0.041	0.035	0.038
C_2	0.023	0.004	0.000	0.027
H_1	-0.071	-0.061	-0.051	-0.071
H_2	-0.081	-0.081	-0.061	-0.061

Geometric and thermodynamic correlations

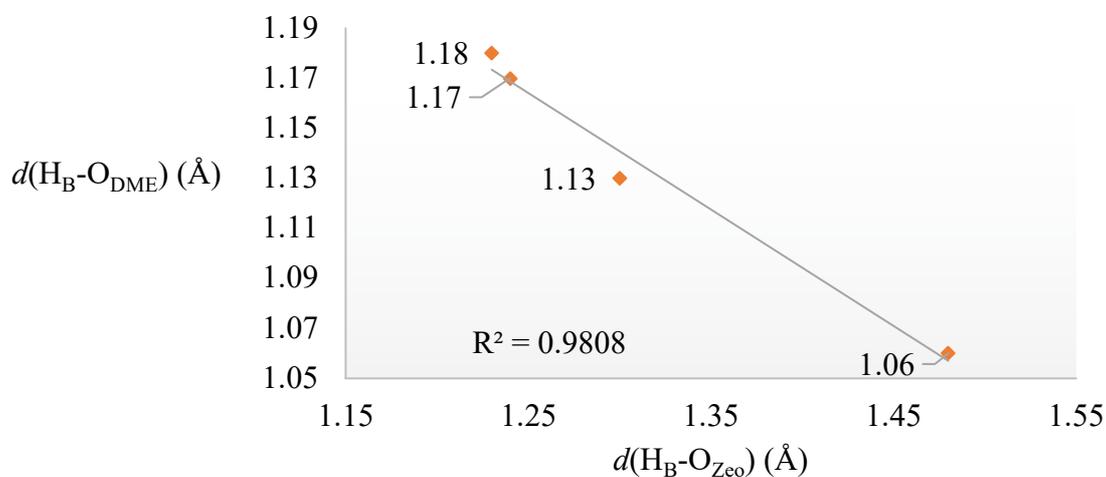


Figure S2. Comparison of the distance from the Brønsted proton to the zeolite oxygen, $d(\text{H}_B\text{-O}_{\text{Zeo}})$, and from the same proton to the DME oxygen, $d(\text{H}_B\text{-O}_{\text{DME}})$. The distances of $d(\text{H}_B\text{-O}_{\text{DME}})$ also provided in the plot in Ångstrom. The line of best fit has an R^2 of 0.9808 to quantify the low deviation in the fit

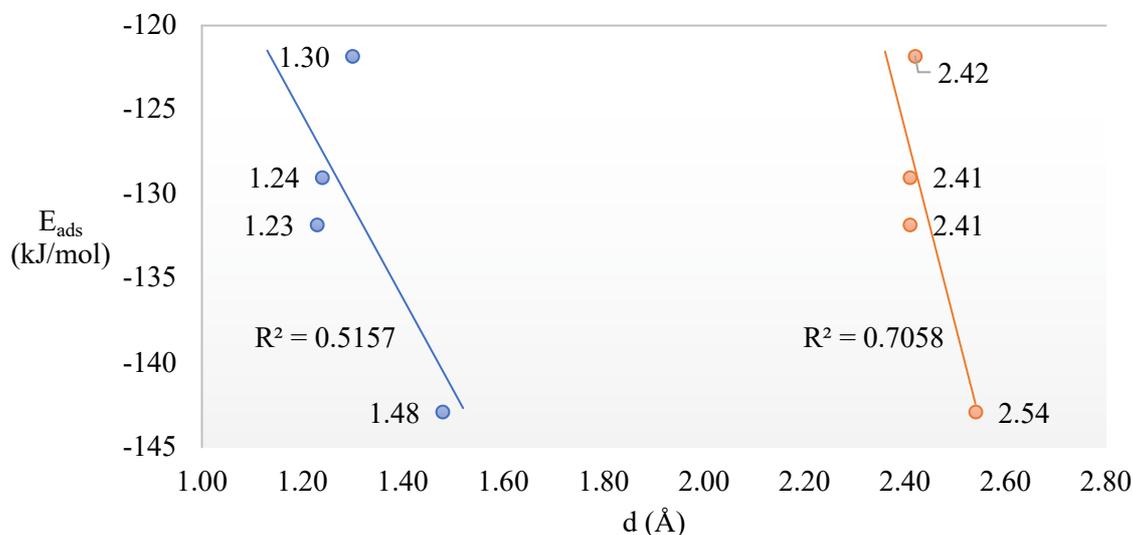


Figure S3. Comparison of the the adsorption energy (E_{ads}) of DME and the distances (d) between the zeolite active site and the Brønsted proton, $d(\text{O}_{\text{Zeo}}\text{-H}_B)$ - blue, and between the zeolite active site and the DME molecule, $d(\text{O}_{\text{Zeo}}\text{-O}_{\text{DME}})$ - orange. Energies and distances are presented in kJ/mol and Ångstrom, respectively. The lines of best fit are given with an R^2 to quantify error in the fit (Blue: $R^2 = 0.5157$; Orange: $R^2 = 0.7058$)