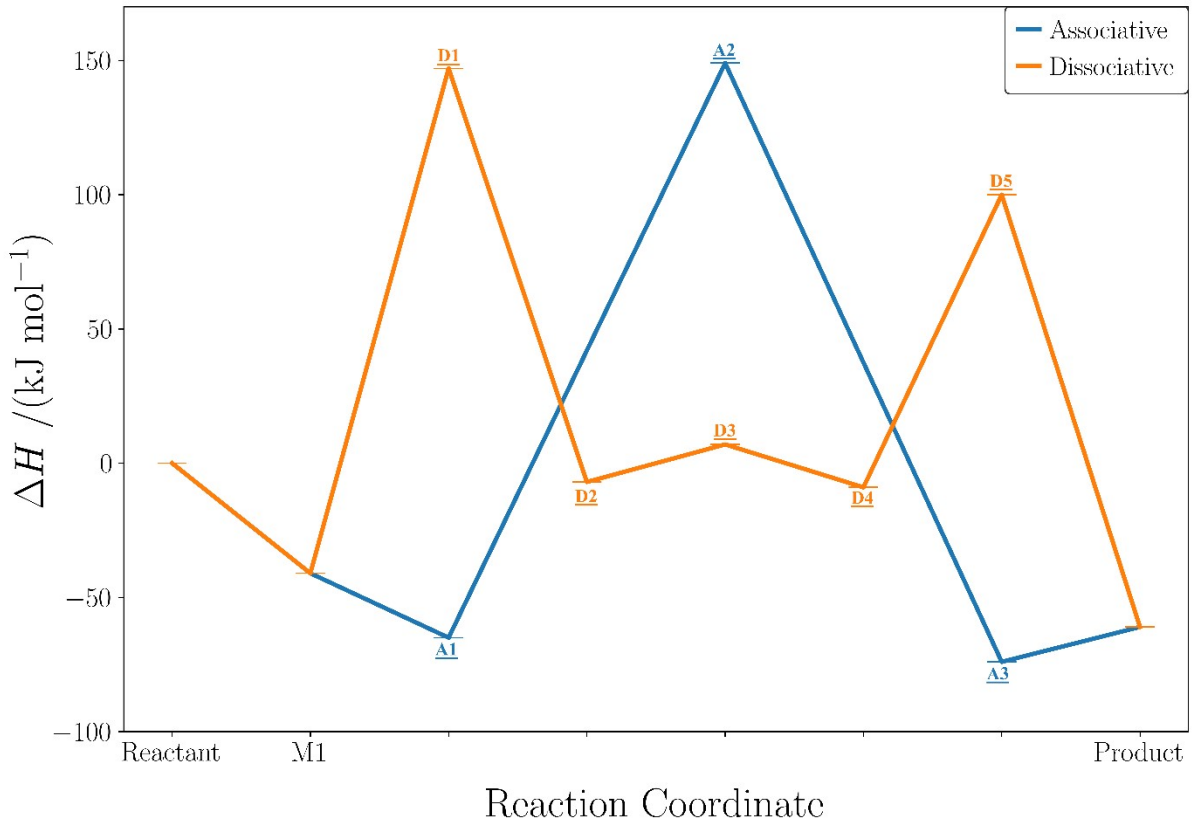
Supplementary information

1. Calculations of pathways for an S_N2 mechanism similar to that in work on CHA zeolite.[1]

We have also modelled the dehydration of methanol to DME by an S_N2-like mechanism as suggested in the above paper.[1] Our calculated intrinsic barriers for this geometry in both the associative and dissociative pathways are shown below in SI Figure 1 and are considerably higher than those for the mechanisms we propose in the main text.

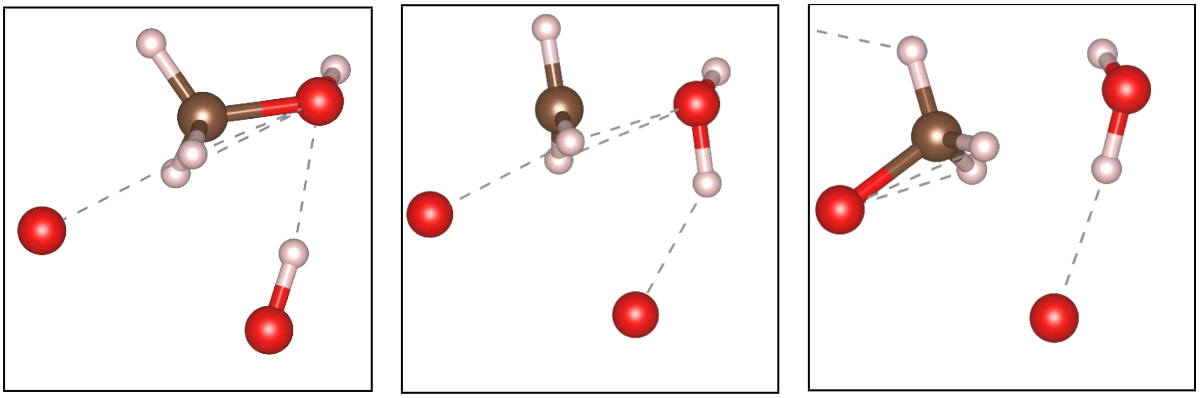


SI Figure 1 Calculated (DFT-D3) reaction coordinate diagram for the dehydration of methanol to DME by associative and dissociative mechanisms both involving concerted S_N2 backside attack as suggested in work on CHA zeolite (J.R. Di Iorio et al., Journal of Catalysis 380 (2019) 161–177)). Since the reaction pathway differs for each mechanism only Reactant, M1, and Product are labelled on the x-axis, axis and individual labels can be found on the diagram. Labels refer to reaction coordinate structures in SI Figures 2 and 3.

SI Table 1 – Comparing reaction enthalpies (H_{PBE+D3}; kJ mol^{-1}) of the dissociative mechanism proposed in our work and a dissociative mechanism involving the S_N2 step, calculated at the DFT-D3 level of theory.

Dissociative	**Reactant**	**M1**	**TS1**	**M2**	**Int**	**M3**	**TS2**	**Product**
S_N2	0	-41	147	-7	7	-9	100	-61
Mechanism proposed in our paper	0	-41	87	-7	7	-9	100	-61

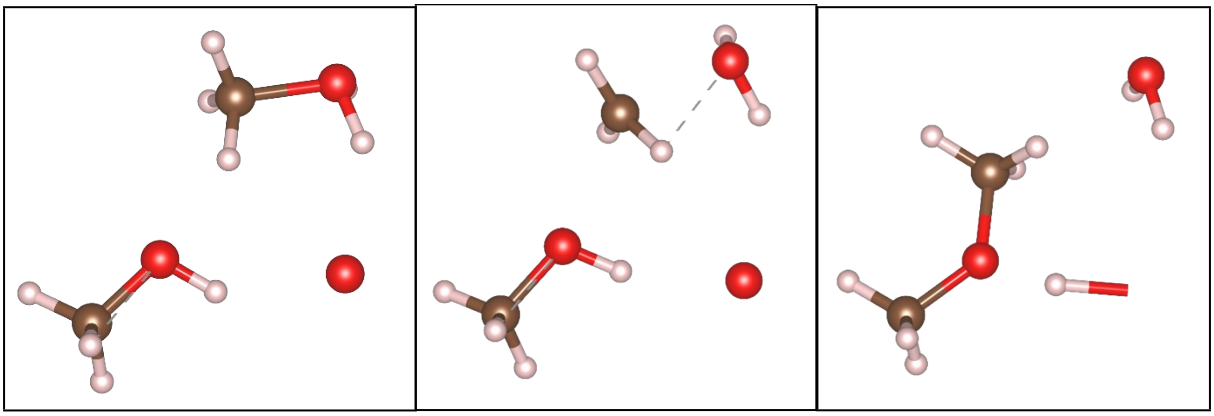
SI Figure 2 - Structures involved in the reaction coordinate for a dissociative mechanism with an S_N2-like transition state.



SI Table 2 - Comparing reaction enthalpies (H_{PBE+D3}; kJ mol^{-1}) of the associative mechanism proposed in our paper and an associative mechanism involving the S_N2 step, calculated at the DFT-D3 level of theory.

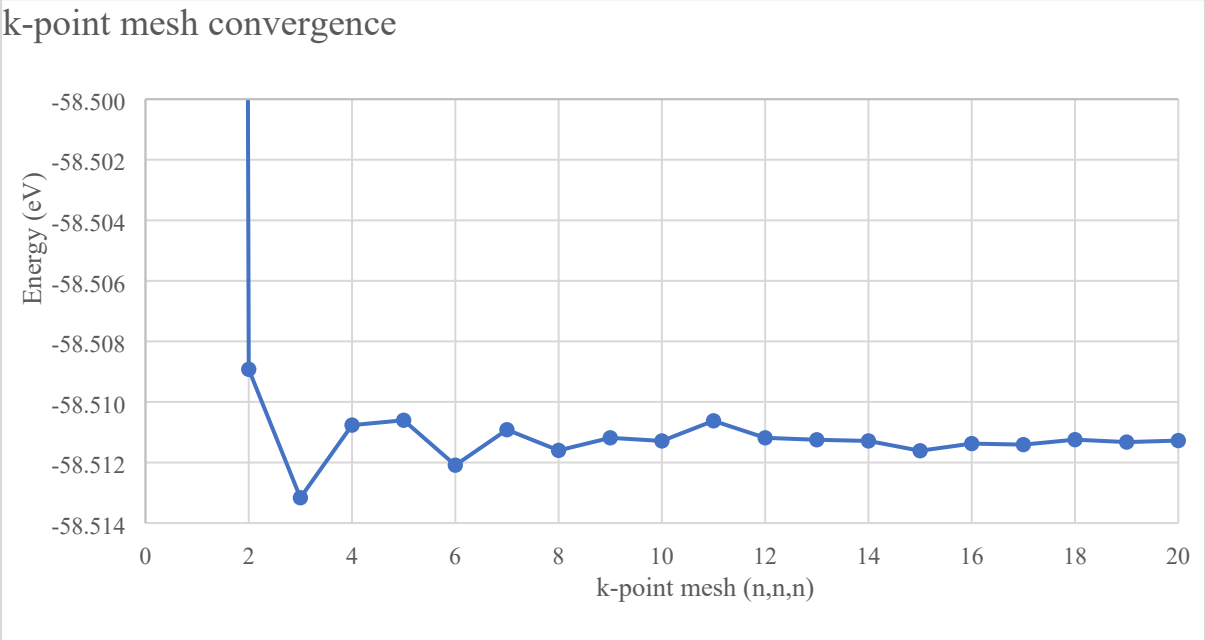
Associative	**Reactant**	**M1**	**M4**	**TS**	**M5**	**Product**
S_N2	0	-41	-65	149	-74	-61
Mechanism proposed in paper	0	-41	-65	38	-74	-61

SI Figure 3 - Structures involved in the reaction coordinate for an associative mechanism with an S_N2-like transition state.

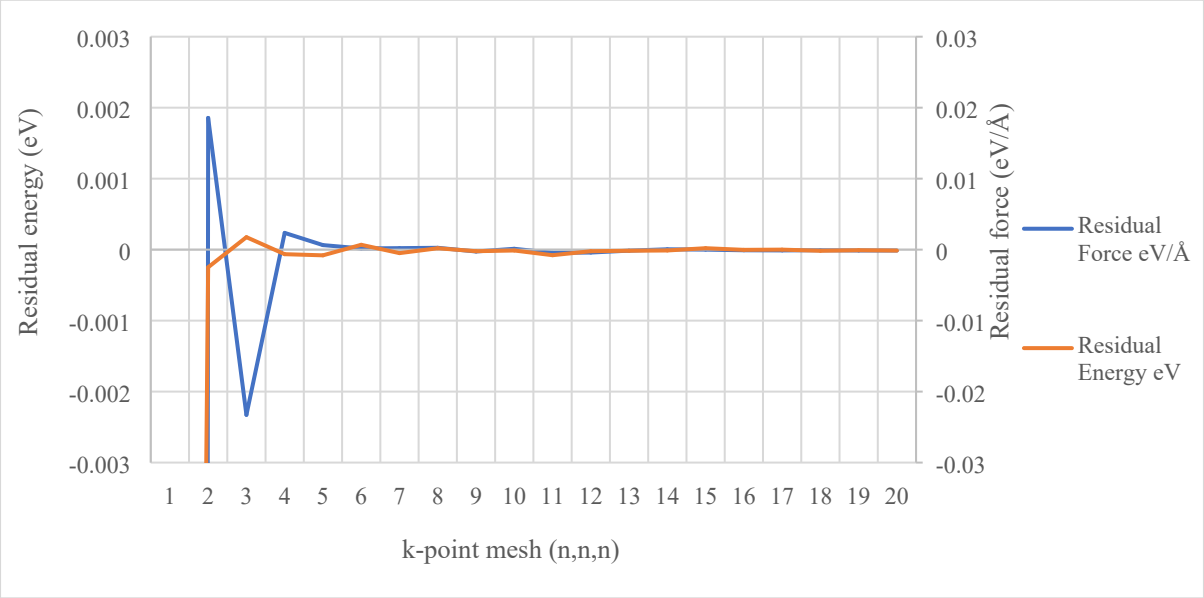


2. K-point sampling

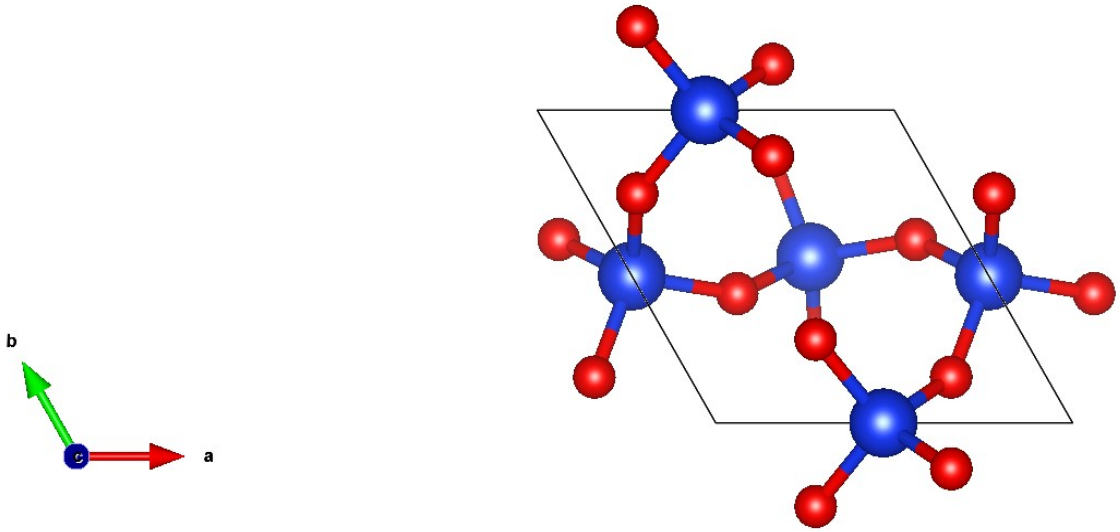
SI Figure 4 shows the calculated energies of a SiO_2 silicalite structure (Si Figure 6) with different k-point grids.



SI Figure 4 – k-point convergence of the SiO_2 structure with varying k-point grid.



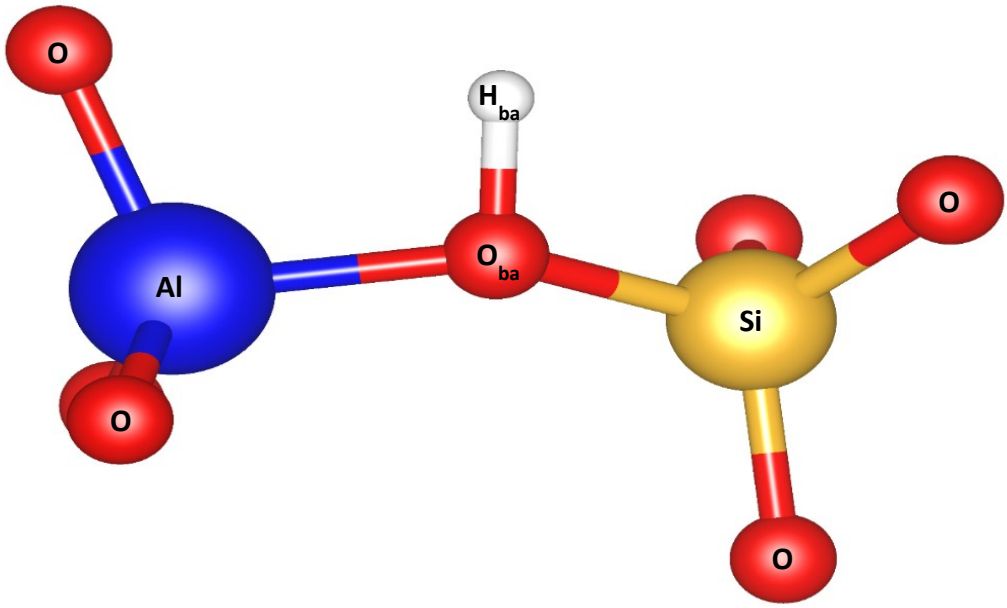
SI Figure 5 - Residual force and energy of the SiO_2 silicalite structure. The residual value was calculated as the value calculated with a 20x20x20 k-point grid minus that using the n x n x n k-point grid.



SI Figure 6: SiO_2 silicalite structure used for k-point convergence testing

3. Functional

The experimental bond lengths at the BAS, shown in SI Figure 7, and the lattice parameters of ZSM-5 were used as a test of the accuracy of the functional chosen (PBE+D3BJ). A comparison of theory and experiment are in SI Table 1. The calculated bond lengths and lattice parameters are within 2 % of the experimental.



SI Figure 7 - The Brønsted acid site structure. The key atoms are labelled. Colour key: red, oxygen, yellow, silicon, blue, aluminium, white, hydrogen.

SI Table 1 – Si-O, Si-O_{ba}, Al-O, Al-O_{ba} and H_{ba}-O_{ba} bond lengths (Å), lattice parameters (Å) and cell volume (Å^3) for H-ZSM-5 zeolite, $_{ba}$ denotes an atom at the Brønsted acid site. An asterisk (*) denotes an average.

	bond lengths (Å)					lattice parameters (Å)			
	Si-O	**Si-O_{ba}**	**Al-O**	**Al-O_{ba}**	**H_{ba}-O_{ba}**	***a***	***b***	***c***	**Cell Volume (Å^3)**
This work	1.60	1.70	1.69	1.83	1.00	20.09	19.74	13.14	5211.28
Crystal Structure	1.61	1.67	1.70	1.78	1.06	20.09	19.74	13.14	5211.28
Exp[2]	1.59*					20.07	19.92	13.41	5361.24
Exp[3]					1.01*				
Exp[4]	1.59*								
Exp[5]						19.86	19.74	12.95	5076.87
Exp[6]						20.07	19.93	13.41	5367.95

4. Enthalpies calculated with PBE+D3, ΔMP2, and ΔCCSD(T) corrections for each promoter

The tables (SI Table 2 – SI Table 8) show the contribution of each individual QM method to the overall final enthalpies for the stages in the associative mechanism for each promoter.

SI Table 2 - Reaction enthalpies (ΔH; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl formate, values calculated with the hybrid multilevel QM scheme.

Dissociative mechanism	**Reaction coordinate**								
	Reactant	**M1**	**P2**	**TS1**	**M5**	**Int**	**M3**	**TS2**	**Product**
ΔH_{Final}	0	-45	-30	192	-59	-22	-42	113	-85
H_{PBE+D3}	0	-41	-39	166	-47	7	-9	100	-65
ΔH_{MP2}	0	0	15	31	-8	-21	-24	25	-18
$\Delta H_{CCSD(T)}$	0	-4	-6	-5	-4	-8	-9	-12	-2

SI Table 3 - Reaction enthalpies (ΔH; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the associative mechanism of methanol dehydration to dimethyl ether with methyl formate, values calculated with the hybrid multilevel QM scheme.

Associative mechanism	**Reaction coordinate**										
	Adsorption		**Reaction 1**				**Reaction 2**				
	Reactant	**P1**	$P1^{\ddagger}$	**P1***	$P1^{*\ddagger}$	**P3**	**P4**	$P4^{\ddagger}$	**P5***	$P5^{*\ddagger}$	**Product**
ΔH_{Final}	0	-73	-6	-55	-28	-90	-104	-49	-90	-22	-92
H_{PBE+D3}	0	-70	-25	-50	-48	-79	-77	-55	-68	-34	-71
ΔH_{MP2}	0	0	18	-2	16	-13	-26	10	-21	9	-20
$\Delta H_{CCSD(T)}$	0	-3	1	-3	4	2	-1	-4	-1	3	-1

SI Table 4 - Reaction enthalpies (ΔH; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl acetate, values calculated with the hybrid multilevel QM scheme.

	Reaction coordinate										
	Adsorption		**Reaction 1**				**Reaction 2**				
	Reactant	**P1**	$P1^{\ddagger}$	**P1***	$P1^{*\ddagger}$	**P3**	**P4**	$P4^{\ddagger}$	**P5***	$P5^{*\ddagger}$	**Product**
ΔH_{Final}	0	-82	-33	-99	-50	-100	-114	-64	-119	-48	-120
$\Delta H_{\text{PBE+D3}}$	0	-83	-52	-91	-63	-96	-94	-75	-97	-56	-93
ΔH_{MP2}	0	0	21	-10	12	-4	-18	12	-23	8	-27
$\Delta H_{\text{CCSD(T)}}$	0	1	-2	2	1	0	-2	-1	1	0	0

SI Table 5 - Reaction enthalpies (ΔH; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl propionate, values calculated with the hybrid multilevel QM scheme.

	Reaction coordinate										
	Adsorption		**Reaction 1**				**Reaction 2**				
	Reactant	**P1**	$P1^{\ddagger}$	**P1***	$P1^{*\ddagger}$	**P3**	**P4**	$P4^{\ddagger}$	**P5***	$P5^{*\ddagger}$	**Product**
ΔH_{Final}	0	-94	-48	-123	-58	-124	-131	-87	-132	-71	-138
$\Delta H_{\text{PBE+D3}}$	0	-94	-71	-112	-77	-112	-110	-106	-123	-83	-114
ΔH_{MP2}	0	0	20	-11	19	-13	-19	23	-7	11	-21
$\Delta H_{\text{CCSD(T)}}$	0	0	3	0	0	1	-2	-4	-2	1	-3

SI Table 6 - Reaction enthalpies (Δ*H*; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl *n*-butyrate, values calculated with the hybrid multilevel QM scheme.

	Reaction coordinate										
	Adsorption		Reaction 1				Reaction 2				
	Reactant	P1	$P1^{\ddagger}$	P1*	$P1^{*\ddagger}$	P3	P4	$P4^{\ddagger}$	P5*	$P5^{*\ddagger}$	Product
ΔH_{Final}	0	-104	-60	-132	-72	-130	-136	-95	-137	-84	-147
ΔH_{PBE+D3}	0	-104	-80	-122	-91	-120	-118	-113	-131	-95	-125
ΔH_{MP2}	0	0	20	-10	20	-10	-17	22	-5	10	-20
$\Delta H_{CCSD(T)}$	0	0	0	0	-1	0	-3	-4	-1	1	-2

SI Table 7 - Reaction enthalpies (Δ*H*; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl *n*-pentanote, values calculated with the hybrid multilevel QM scheme.

	Reaction coordinate										
	Adsorption		Reaction 1				Reaction 2				
	Reactant	P1	$P1^{\ddagger}$	P1*	$P1^{*\ddagger}$	P3	P4	$P4^{\ddagger}$	P5*	$P5^{*\ddagger}$	Product
ΔH_{Final}	0	-109	-66	-137	-76	-136	-148	-104	-150	-97	-152
ΔH_{PBE+D3}	0	-107	-85	-126	-95	-124	-122	-120	-135	-102	-129
ΔH_{MP2}	0	-3	20	-10	19	-12	-23	17	-14	4	-22
$\Delta H_{CCSD(T)}$	0	1	-1	-1	0	0	-3	-1	-1	1	-1

SI Table 8 - Reaction enthalpies (Δ*H*; kJ mol^{-1}) relative to the reactant of intermediates and transition states involved in the dissociative mechanism of methanol dehydration to dimethyl ether with methyl *n*-hexanoate, values calculated with the hybrid multilevel QM scheme.

	Reaction coordinate										
	Adsorption		Reaction 1				Reaction 2				
	Reactant	P1	$P1^{\ddagger}$	P1*	$P1^{*\ddagger}$	P3	P4	$P4^{\ddagger}$	P5*	$P5^{*\ddagger}$	Product
ΔH_{Final}	0	-119	-71	-145	-80	-144	-156	-118	-162	-106	-166
ΔH_{PBE+D3}	0	-119	-90	-135	-103	-134	-122	-127	-140	-116	-139
ΔH_{MP2}	0	0	23	-9	25	-10	-28	10	-21	9	-26

$\Delta H_{CCSD(T)}$	0	0	-4	-1	-2	0	-6	-1	-1	1	-1

5. Geometric parameters

SI Table 9 – Bond lengths and angles involved in the transition state for the protonation of the promoter molecules, atom labels as in the left of Figure 9.

	bond lengths / (Å)			bond angles / (°)	
Promoter	**O1-H1**	**O2-H1**	**O1-O2**	**C1-O2-H1**	**O1-H1-O2**
methyl formate	1.41	1.27	2.76	160	167
methyl acetate	1.38	1.27	2.66	159	168
methyl propionate	1.39	1.26	2.66	156	168
methyl *n*-butyrate	1.40	1.27	2.66	155	163
methyl *n*-pentanoate	1.39	1.26	2.66	159	168
methyl *n*-hexanoate	1.39	1.27	2.64	156	168

SI Table 10 - Bond lengths involved in the transition state for the formation of DME, atom labels as in the right of Figure 9.

	bond lengths / (Å)					
Promoter	**O1-C1**	**C1-O2**	**O2-H1**	**H1-O3**	**O3-H2**	**H2-O4**
methyl formate	2.15	1.82	0.99	1.63	0.95	2.19
methyl acetate	2.07	1.81	1.00	1.61	0.96	2.20
methyl propionate	1.98	1.93	1.01	1.58	0.95	2.20
methyl *n*-butyrate	2.06	1.83	1.01	1.58	0.95	2.20
methyl *n*-pentanoate	2.07	1.83	1.02	1.59	0.99	2.15
methyl *n*-hexanoate	1.97	1.93	1.02	1.58	0.96	2.20

SI Table 11 - Bond lengths involved in the transition state for the re-esterification of the promoter, atom labels as in the left of Figure 9.

	bond lengths / (Å)					
Promoter	**O1-C1**	**C1-O2**	**O2-H1**	**H1-O3**	**O3-H2**	**H2-O4**
methyl formate	2.09	1.82	1.02	1.51	0.98	2.1
methyl acetate	1.9	2	1.01	1.56	0.98	2.1
methyl propionate	1.81	2.07	1.01	1.56	0.98	2.06
methyl *n*-butyrate	1.99	1.92	1.01	1.52	0.98	2.12
methyl *n*-pentanoate	1.92	1.99	1.02	1.55	0.98	2.06
methyl *n*-hexanoate	2.1	1.8	1.01	1.55	0.97	2.06

SI Table 12 - Bond lengths and angles involved in the transition state for the deprotonation of the promoter molecules, atom labels found as in the right of Figure 9.

	bond lengths / (Å)			bond angles / (˚)	
Promoter	**O1-H1**	**O2-H1**	**O1-O2**	**C1-O2-H1**	**O1-H1-O2**
methyl formate	1.29	1.4	2.67	161	165
methyl acetate	1.3	1.39	2.68	160	168
methyl propionate	1.27	1.39	2.64	158	168
methyl *n*-butyrate	1.26	1.39	2.63	157	169
methyl *n*-pentanoate	1.3	1.37	2.66	160	168
methyl *n*-hexanoate	1.27	1.39	2.64	155	167

SI Bibliography

1 J. R. Di Iorio, A. J. Hoffman, C. T. Nimlos, S. Nystrom, D. Hibbitts and R. Gounder, *J. Catal.*, 2019, **380**, 161–177.

2 D. H. Olson, G. T. Kokotallo and S. L. Lawton, *J. Phys. Chem.*, 1981, **85**, 646–648.

3 H. Huo, L. Peng and C. P. Grey, *J. Phys. Chem. C*, 2011, **115**, 2030–2037.

4 H. Van Koningsveld, *Acta Crystallographica Section B*, 1990, **46**, 731–735.

5 E. Dib, T. Mineva, E. Veron, V. Sarou-Kanian, F. Fayon and B. Alonso, *J. Phys. Chem. Lett.*, 2018, **9**, 19–24.

6 Y. Yokomori and S. Idaka, *Microporous and Mesoporous Materials*, 1999, **28**, 405–413.