Supporting Information:

Computational QM/MM investigation of the adsorption of MTH active species in H-Y and H-ZSM-5

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KEYWORDS: Methanol-to-Hydrocarbons, methanol zeolites, H-ZSM-5, H-Y, QM/MM

Table S1. Comparison of energies between the single point (SP) and optimised (Opt) models with B97-D and geometric parameters between the B97-3 optimised models used for the SP calculation and the B97-D optimised models, as defined in the main manuscript. $d(H_{zeo}\text{-}O_{MeOH})$ is the distance between the zeolite acid site and the oxygen of the methanol (Å).

	E_{ads}		$d(H_{zeo}\text{-}O_{MeOH})$	
Method	SP	Opt	SP	Opt
H-Y	-100	-96	1.50	1.39
H-ZSM-5 [I2]	-120	-122	1.50	1.41
H-ZSM-5 [Z6]	-115	-114	1.44	1.37
H-ZSM-5 [M7]	-114	-113	1.51	1.38

Table S2. Results obtained from vibrational frequency calculations of the bi-dentate H-Y model with differing numbers nearest neighbours (NN) included in the finite-difference displacements. E_{corr} ZPE, E_{vib}, S_{ads}, representing the correction to the electronic energy in order to obtain the thermodynamic enthalpy, the zero-point energy, the vibrational energy (as calculated using partition function) and the adsorption entropy. All values are presented in kJ/mol except $S_{ads,}$ which is in units of kJ/mol/K. The vibrational frequency, $v(O_{zeo}\text{-}H_{zeo})$, is given of the O-H group of the model (cm^{-1}).

	E_{corr}	ZPE	E_{vib}	S_{ads}	$v(O_{zeo}\text{-}H_{zeo})$
2NN	-17	8	16	0.140	3789
3NN	-17	8	16	0.138	3789
4NN	-18	8	16	0.138	3789
5NN	-19	7	16	0.141	3789

Table S3. Total basis set superposition error (BSSE) for all the systems (kJ/mol). * labels represent a bi-molecular systems, with the second molecule around the adsorbed methanol given.

	H-Y	H-ZSM-5 [I2]	H-ZSM-5 [Z6]	H-ZSM-5 [M7]
Methanol (end-on)	-3	-5	-5	-3
Methanol (side-on)	-3	-4	-3	-2
Methoxy – Water	-2	-2	-1	-2
* Methanol (mono-dentate)	-1	-5	-3	-3
* Methanol (bi-dentate)	-8	-9	-6	-5
* Methanol (tri-dentate)	-7	-6	-7	-5
* Water (bi-dentate)	-6	-6	-4	-3
* Water (mono-dentate)	-4	-6	-5	-5
* Methane (mono-dentate)	-3	-5	-5	-5

Table S4. Comparison of energy contributions for the stability of CH_3OH adsorbed in H-Y and H-ZSM-5[I2] (kJ/mol). E_{ads}, E_{int} and E_{dist} correspond to adsorption, interaction and distortion energies, respectively, as defined the main manuscript. $d(H_{zeo}\text{-}O_{zeo})$ is the length of the O-H bond at the zeolite acid site (Å).

Site	Adsorbate(s)	Configuration	E_{dist}	E_{int}	E_{ads}	$d(H_{zeo}\text{-}O_{zeo})$
H-Y	Methanol	"Side-on"	33	-103	-70	1.04
		"End-on"	27	-104	-77	1.05
	Bi-methanol	Bi-dentate	443	-605	-162	1.82
		Tri-dentate	373	-525	-152	1.65
	Methanol/H_2O	Mono-dentate	37	-139	-102	1.06
		Bi-dentate	411	-553	-142	1.73
	Methanol/CH_4	Bi-dentate	34	-111	-77	1.05
H-ZSM-5 [I2]	Methanol	"Side-on"	18	-104	-86	1.05
		"End-on"	19	-110	-91	1.05
	Bi-methanol	Bi-dentate	375	-535	-160	1.67
		Tri-dentate	303	-456	-153	1.53
	Methanol/H_2O	Mono-dentate	220	-318	-98	1.39
		Bi-dentate	351	-497	-146	1.64
	Methanol/CH_4	Bi-dentate	18	-98	-70	1.05

Table S5. Long-range molecular interaction distances for methanol adsorbed in the zeolite framework (Å). Molecular configurations and definitions of "short" and "long" are given in the main text; no directionality is considered in the interactions

	"Side-on"				"End-on"		
Site	short		long		short	long	
	-OH	$-CH_3$	-OH	$-CH_3$	-OH	-OH	$-CH_3$
H-Y	-	2.45; 2.94	3.57; 3.68	3.27; 3.62; 3.74	2.50; 2.93	3.01; 3.31; 3.35; 4.00	3.54; 3.80; 3.80
H-ZSM-5 [I2]	-	2.74	3.20; 3.42; 3.94	3.35; 3.61; 3.87; 3.97; 3.67; 3.87; 3.99	2.13; 2.73	3.66	3.63; 3.68; 3.89; 3.72; 3.98
H-ZSM-5 [Z6]	2.58; 2.88	2.72; 2.76; 2.79	3.86; 3.87; 3.96	3.19; 3.35; 3.58; 3.61; 3.89; 3.99; 3.14; 3.37; 3.56; 3.81; 3.83	2.49; 2.67	3.15; 3.87	3.08; 3.33; 3.24; 3.46; 3.47; 3.05; 3.52; 3.58; 3.86
H-ZSM-5 [M7]	-	2.73	3.15; 3.20	3.24; 3.83; 3.16; 3.49; 3.68; 3.84; 3.96	2.10; 2.60	3.16; 3.41; 3.55	3.42; 3.73; 3.30; 3.20; 3.44; 3.65; 3.66; 3.52; 3.54; 3.49; 3.69; 3.48

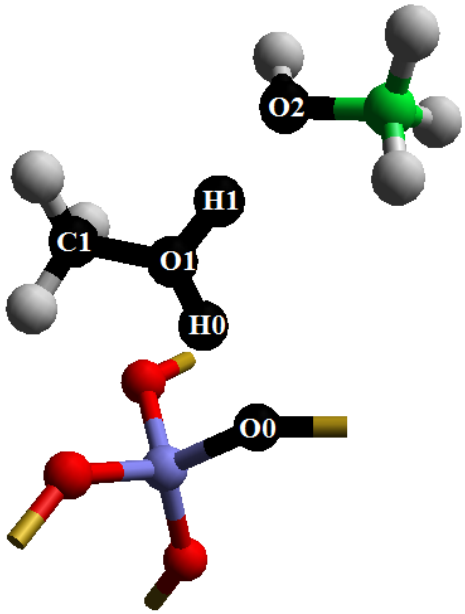


Figure S1. Schematic representation of atomic labels when computing bond distances: H0-O0 represents the distance between the Brønsted proton to the zeolite framework, H0-O1 represents the distance between the Brønsted proton to the oxygen of the first methanol, H1-O2 represents the distance between the hydrogen of the first methanol and the oxygen of the second methanol.

Table S6. Summary of the distances between atoms for the bimethanol configuration with all values presented in Å. Labels are as given in Figure S1.

Site	d(H0-O0)	d(H0-O1)	d(O2-H1)	d(O1-C2)
	Mono-dentate			
H-Y	1.42	1.06	2.57	1.47
H-ZSM-5 [I2]	1.69	0.97	2.78	1.47
H-ZSM-5 [Z6]	1.41	0.96	2.22	1.45
H-ZSM-5 [M7]	1.47	0.96	2.34	1.45
	Bi-dentate			
H-Y	1.82	0.99	1.33	1.46
H-ZSM-5 [I2]	1.67	1.00	1.45	1.46
H-ZSM-5 [Z6]	1.52	1.03	1.55	1.46
H-ZSM-5 [M7]	1.67	1.00	1.40	1.46
	Tri-dentate			
H-Y	1.73	1.00	1.51	1.47
H-ZSM-5 [I2]	1.53	1.02	1.5	1.46
H-ZSM-5 [Z6]	1.6	1.02	1.49	1.45
H-ZSM-5 [M7]	1.49	1.03	1.52	1.46

Table S7. Distances in the bi-methanol configurations between methanol and the zeolite framework. 'H1' and 'H2' represent hydrogen bonds of the -OH groups and 'HC1' and 'HC2' representing the hydrogen bonds of the $-CH_3$ groups, respectively, from the first and second methanol molecule (Å).

Site	H1	H2	HC1	HC2
	Mono-dentate			
H-Y	2.13	-	-	-
H-ZSM-5 [I2]	1.52; 2.56	2.75	-	2.45; 2.52
H-ZSM-5 [Z6]	-	2.20; 2.89	2.68	2.93
H-ZSM-5 [M7]	-	-	2.78; 2.80	2.70; 2.88
	Bi-dentate			
H-Y	2.77	2.07; 2.79	-	2.90; 2.66
H-ZSM-5 [I2]	2.65	2.19; 2.92	2.87	2.34; 2.71; 2.93
H-ZSM-5 [Z6]	-	2.33; 2.58	2.79	2.01; 2.20; 2.60; 2.13; 2.26; 2.60; 2.89
H-ZSM-5 [M7]	-	1.95; 2.78	2.63; 2.91	2.46; 2.48
	Tri-dentate			
H-Y	-	-	2.38; 2.81	3.00
H-ZSM-5 [I2]	-	2.20, 2.75, 3.02	2.55; 2.65	2.82; 2.06, 2.47, 2.78
H-ZSM-5 [Z6]	-	2.65, 3.00	2.63, 2.95; 3.00	-
H-ZSM-5 [M7]	-	2.81, 3.00	2.55, 2.94	2.24, 2.43; 2.43, 2.67

Table S8. Comparison of the relative Mulliken partial charges located on each atom presented the in first column, of bi-methanol system in H-Y, with the hydrogen atoms of the OH group of the methanol highlighted by the '*' sign.

	Mono-dentate	Tri-dentate	Bi-dentate
Al	0.03	0.04	0.06
O0	0.10	0.07	0.08
O	0.02	0.04	0.04
O	-0.01	-0.01	-0.01
O	0.08	0.01	0.09
H0	-0.12	-0.07	-0.10
C1	0.00	0.03	-0.01
H1	-0.03	-0.08	-0.05
H1	0.01	-0.08	-0.01
H1	-0.02	-0.08	-0.06
O1	0.04	-0.08	0.04
H1*	-0.02	-0.09	-0.11
C2	0.01	0.01	0.04
H2	-0.08	-0.05	-0.08
H2	-0.04	-0.03	-0.03
H2	-0.10	-0.07	-0.09
O2	-0.08	0.09	-0.06
H2*	0.00	-0.02	-0.02

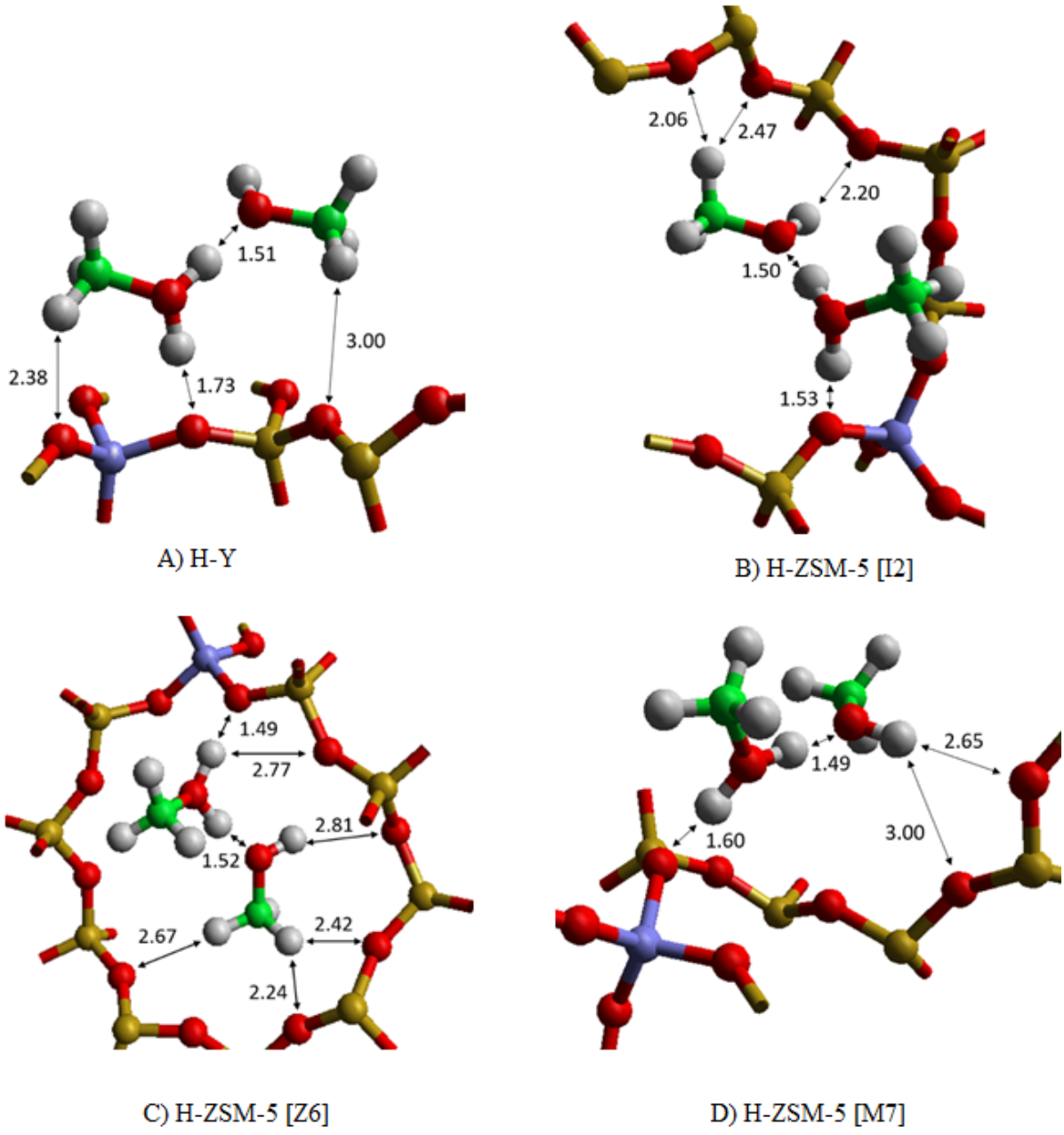


Figure S2. The adsorbed B97-3 optimised geometries of the tri-dentate bi-methanol. Hydrogen bonds distances are illustrated with double-headed arrows (Å). The atom colours are as in Figure 3 of the main manuscript.

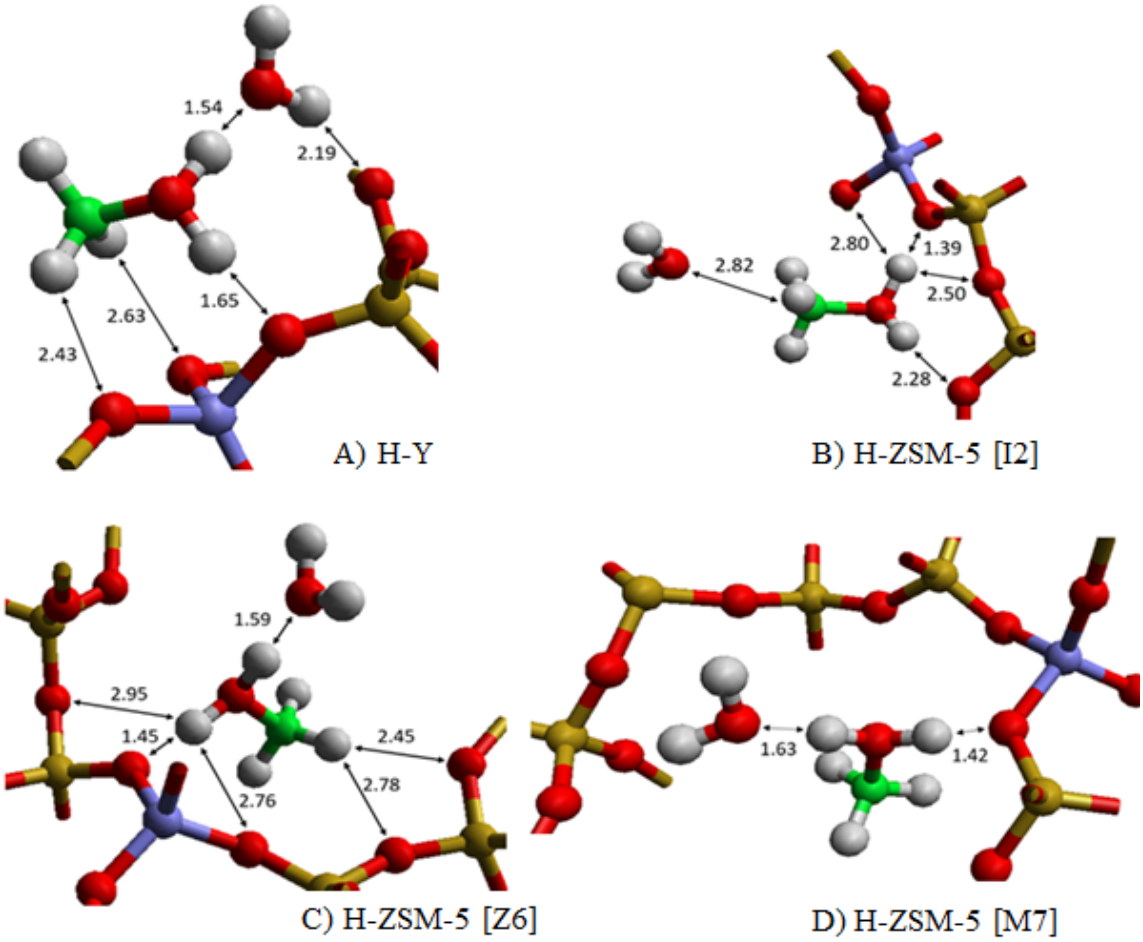


Figure S3. The B97-3 optimised geometries of the CH_3OH/H_2O models in a mono-dentate configuration, with zeolite pores as labelled and hydrogen bonds distances given with double-headed arrows (Å). The atom colours are as in Figure 3 of the main manuscript.

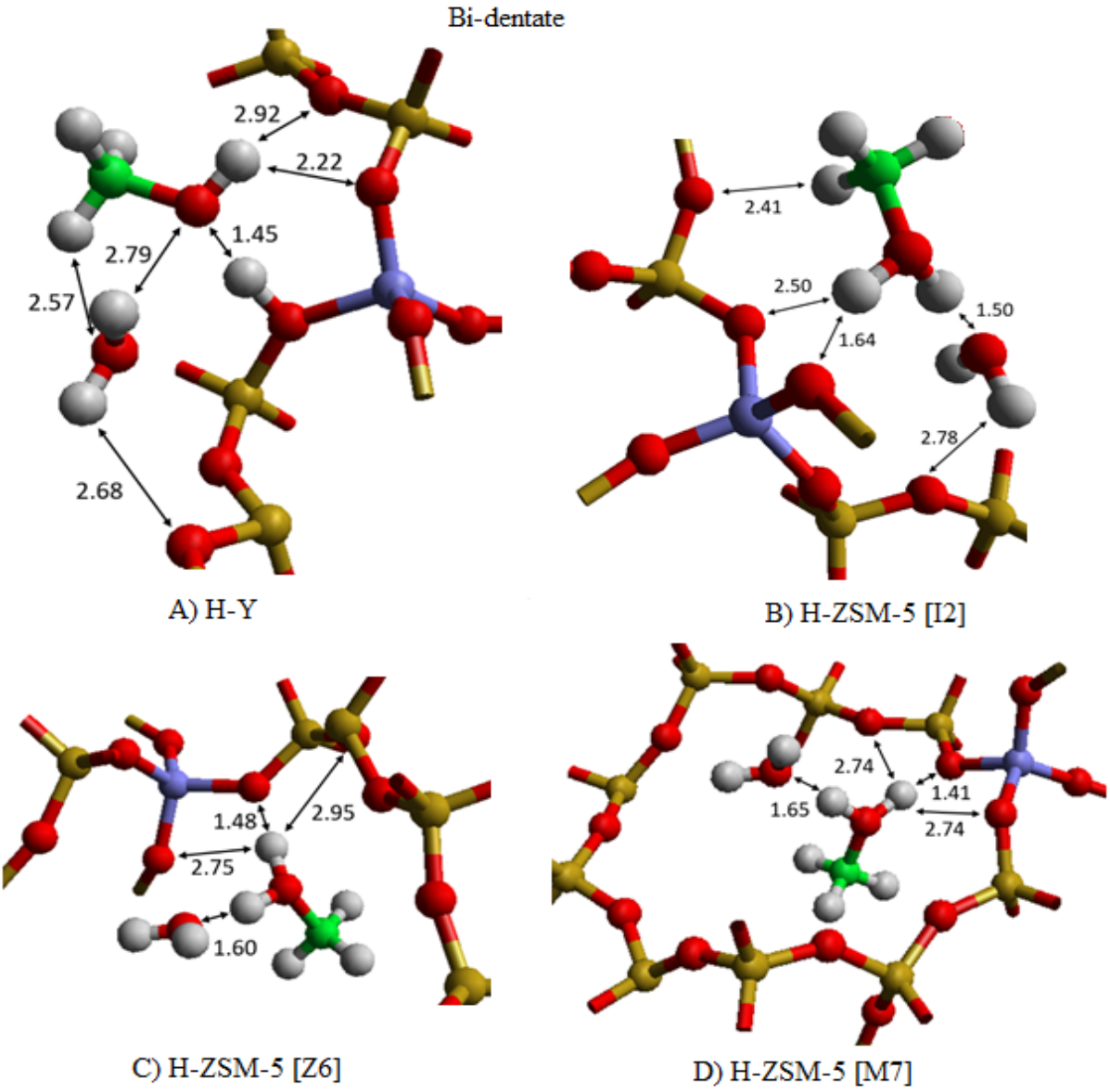


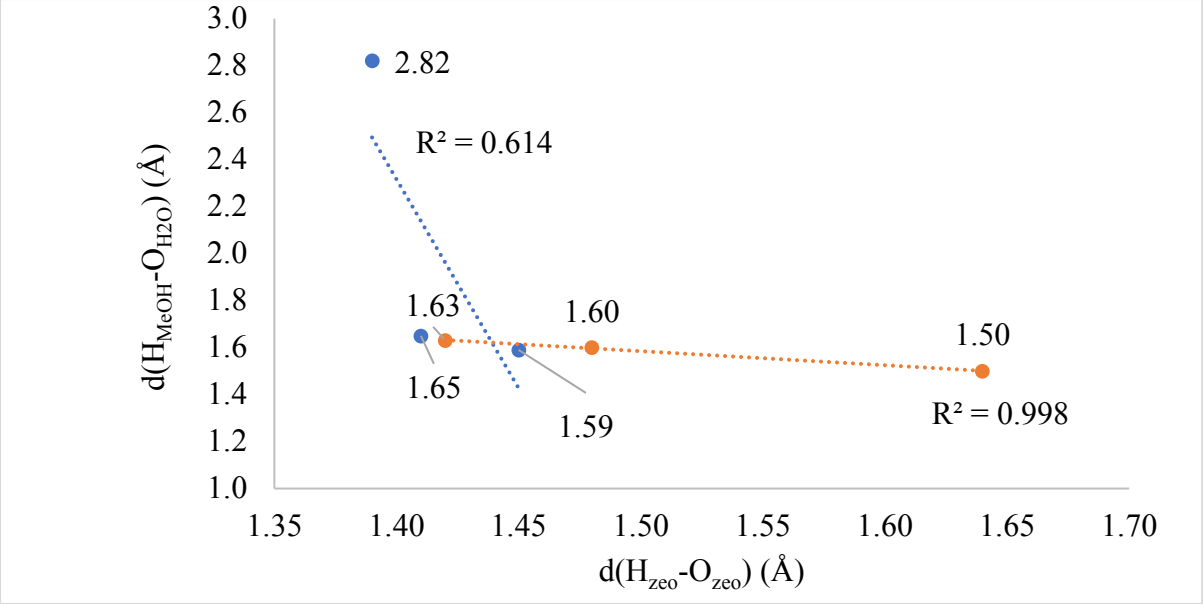
Figure S4. The B97-3 optimised geometries of the CH_3OH/H_2O models in a bi-dentate configuration, with zeolite pores as labelled and hydrogen bonds distances given with double-headed arrows (Å). The atom colours are as in Figure 3 of the main manuscript.

Table S9. Summary of geometric observables for the water models, presented in Å. The notations given are described in detail in Figure S2, except with 'H-O2' representing the smallest hydrogen-bond formed between any hydrogen from the methanol (methyl or hydroxyl) and the oxygen of the water molecule.

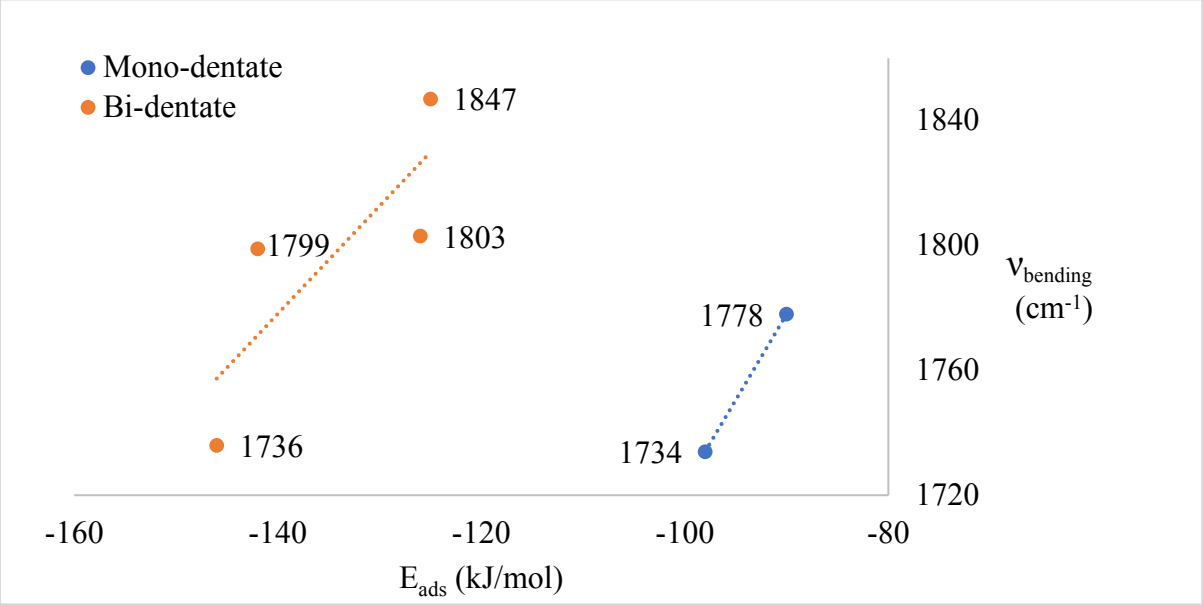
Site	H0-O0	H0-O1	O1-H1	H-O2	O1-C1
	Mono-dentate				
H-Y	1.06	1.45	0.96	2.57	1.44
H-ZSM-5 [I2]	1.39	1.08	0.97	2.82	1.48
H-ZSM-5 [Z6]	1.45	1.04	1.01	1.59	1.46
H-ZSM-5 [M7]	1.41	1.06	1.00	1.65	1.45
	Bi-dentate				
H-Y	1.65	1.01	1.02	1.54	1.47
H-ZSM-5 [I2]	1.64	1.00	1.03	1.5	1.46
H-ZSM-5 [Z6]	1.48	1.04	1.00	1.6	1.46
H-ZSM-5 [M7]	1.42	1.06	1.00	1.63	1.45

Table S10. Summary of bond distances (Å) and the number of "short" distances for bi-molecular CH_3OH/H_2O models. $-OH_{MeOH}$ and $-CH_3$ identify H-bond interactions with the H atoms of the methanol hydroxyl and methyl, respectively, and $-OH_{H2O}$ denotes interaction by hydrogen-bonds formed to the H_2O. For the distances, d, the parent structure of the relevant atoms, either zeolite (zeo), methanol (MeOH) or water (H_2O), is given in subscript after the atomic label. The adsorption energy is also given, presented in kJ/mol.

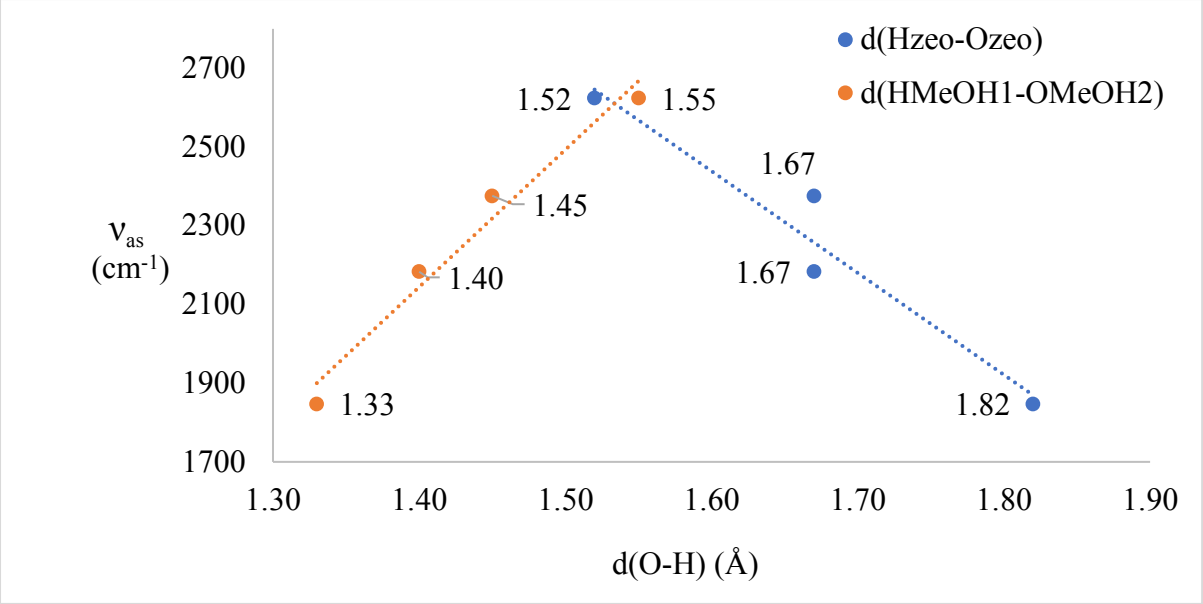
	$d(H_{zeo}\text{-}O_{zeo})$	$d(H_{MeOH}\text{-}O_{H2O})$	$-OH_{MeOH}$	$-CH_3$	$-OH_{H2O}$	E_{ads}
	Mono-dentate					
H-Y	1.06	2.57	2	3	2	-90 (-20)
H-ZSM-5 [I2]	1.39	2.82	2	1	4	-84 (-3)
H-ZSM-5 [Z6]	1.45	1.59	-	3	1	-133 (-51)
H-ZSM-5 [M7]	1.41	1.65	-	1	-	-123 (-42)
	Bi-dentate					
H-Y	1.65	1.54	-	2	2	-134 (-65)
H-ZSM-5 [I2]	1.64	1.5	-	3	5	-134 (-53)
H-ZSM-5 [Z6]	1.48	1.6	-	2	2	-148 (-54)
H-ZSM-5 [M7]	1.42	1.63	-	-	2	-126 (-45)



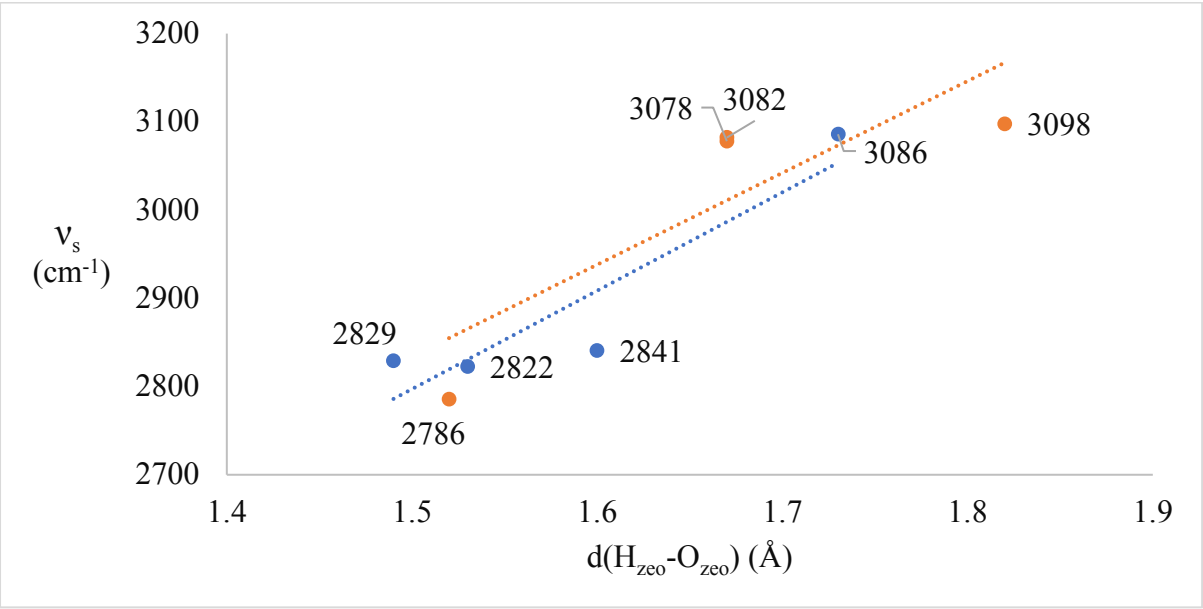
Graph S1. Distance between framework proton and oxygen, $d(H_{zeo}\text{-}O_{zeo})$, plotted against distance between the two molecular species in the pore, $d(H_{MeOH}\text{-}O_{H2O})$. Blue data points identify mono-dentate arrangements whereas orange denotes bidentate.



Graph S2. Plot between the adsorption energy of the two methanol molecules E_{ads} (kJ/mol) of bi-methanol system and H-O-H$^+$ bending vibrational frequency ($\nu_{bending}$, cm^{-1}).



Graph S3. Distance d(O-H), representing the distance between the two methanol molecules ($d(H_{MeOH1}\text{-}O_{MeOH2})$, orange line) and the distance between the zeolite framework and the main adsorbent ($d(H_{zeo}\text{-}O_{zeo})$, blue line), plotted against the asymmetric O-H stretch vibrational frequency (ν_{as}, cm^{-1}).



Graph S4. Plot between distance between the zeolite framework and the main adsorbent $d(H_{zeo}\text{-}O_{zeo})$ (Å) and O-H symmetric stretch vibrational frequency (ν_s, cm^{-1}).

Electronic Parameters Analysis

We calculated the chemical hardness (η), chemical potential (μ), band gaps (δ) and electronegativity (χ) of the empty clusters, given in Table S11, using the following equations[1]:

$$\eta = -\frac{(IP - EA)}{2} \quad ; \quad \mu = -\frac{(IP + EA)}{2} \quad ; \quad \delta = (IP - EA) \quad ; \quad \chi = -\mu$$

Where IP (ionisation potential) and EA (electron affinity), presented in Table S12, are approximated as IP = $-E_{HOMO}$ and EA = $-E_{LUMO}$, where E_{HOMO} and E_{LUMO} are the HOMO and LUMO energies of the corresponding empty clusters.[2,3]

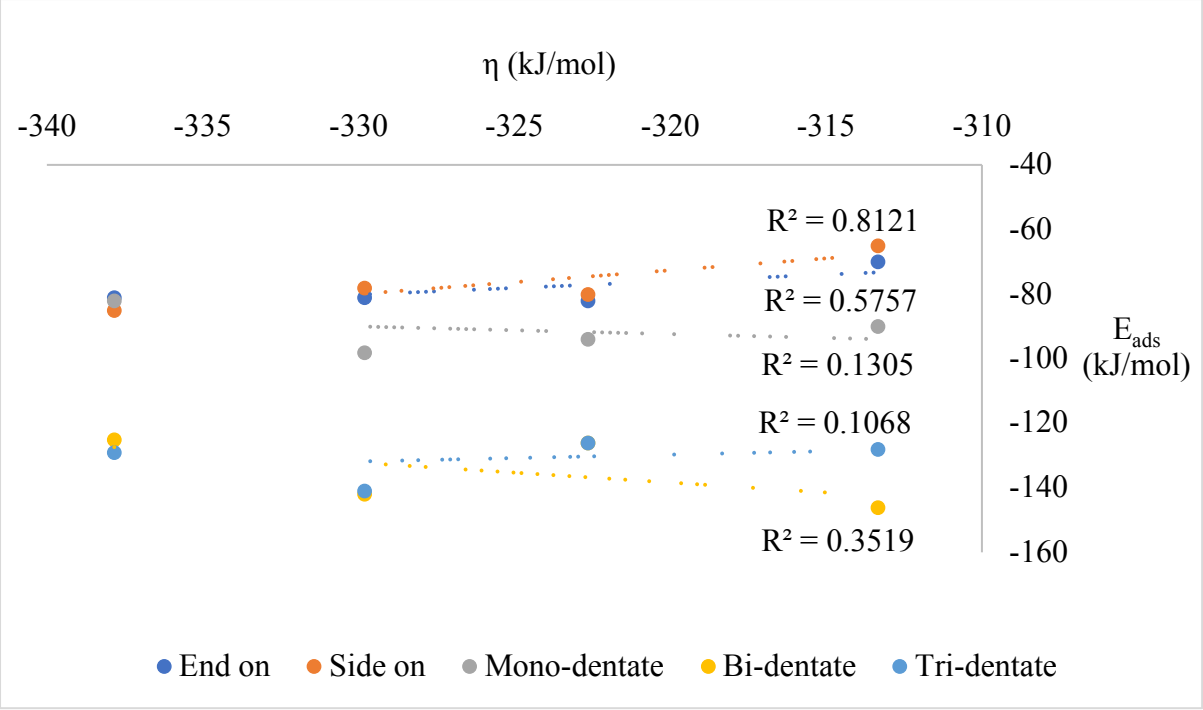
Table S11. Summary of chemical hardness (η), chemical potential (μ), band gaps (δ) and electronegativity (χ) of the empty clusters. All values given in kJ/mol.

	H-Y	H-ZSM-5 [I2]	H-ZSM-5 [Z6]	H-ZSM-5 [M7]
η	-313	-330	-323	-338
μ	-654	-622	-619	-620
δ	627	660	645	676
χ	654	622	619	620

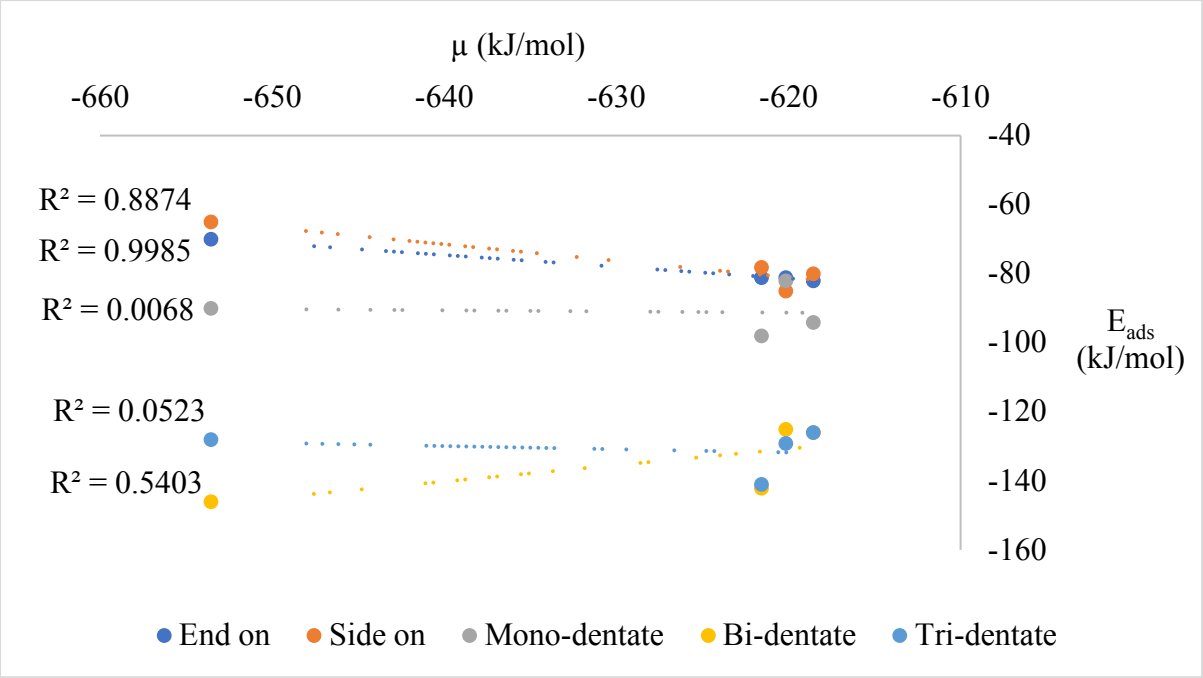
Table S12. Summary of HOMO-LUMO energies, ionization potential (IP) and electron affinity (EA) of empty zeolite clusters. All values given in kJ/mol.

H-Y		H-ZSM-5 [I2]		H-ZSM-5 [Z6]		H-ZSM-5 [M7]	
HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
-967	-340	-951	-292	-941	-296	-958	-282
IP	EA	IP	EA	IP	EA	IP	EA
967	340	951	292	941	296	958	282

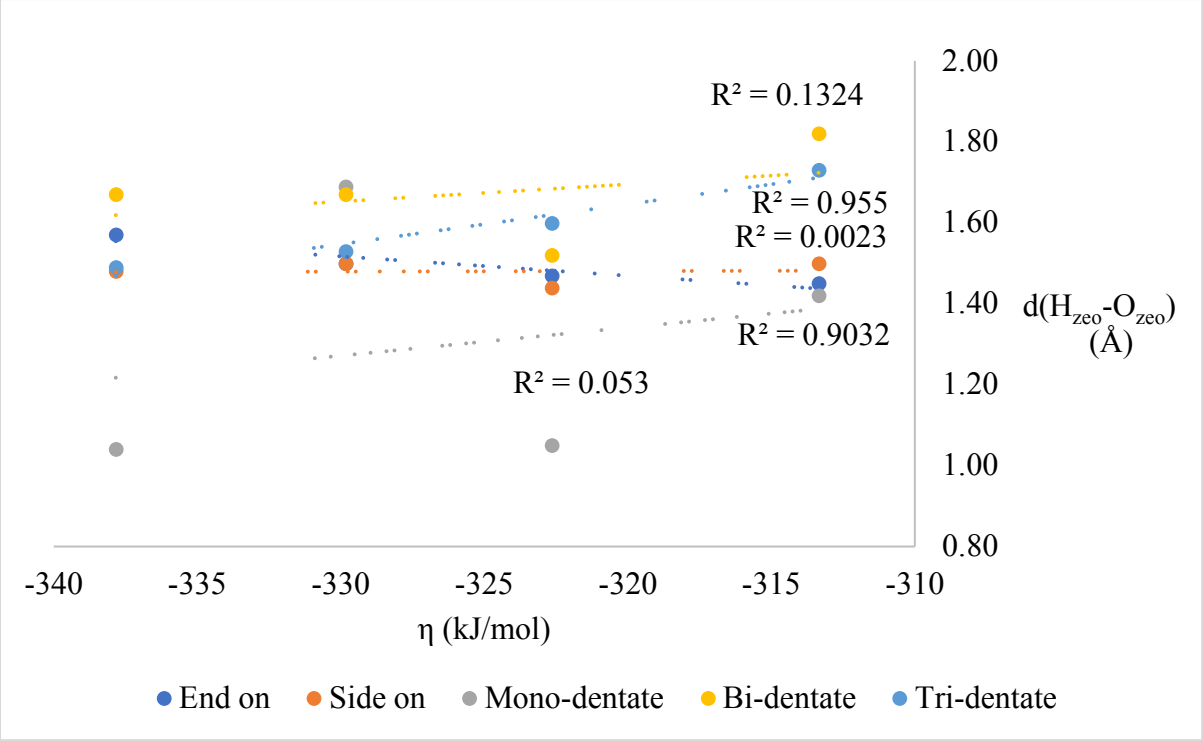
Graphs S5-8 analyse the relationship between chemical hardness or chemical potential and energetic or structural observables from our calculations. There is no obvious correlation between the parameters in these graphs, which highlights the complexity of the interactions involved and factors taking part in them, further validating the necessity to use state-of-the-art techniques to model them. We limited our analysis to just using the chemical hardness and potential because the other two parameters (band gap and electronegativity) were proportional to the initially mentioned electronic factors, as can be understood from the methodology.



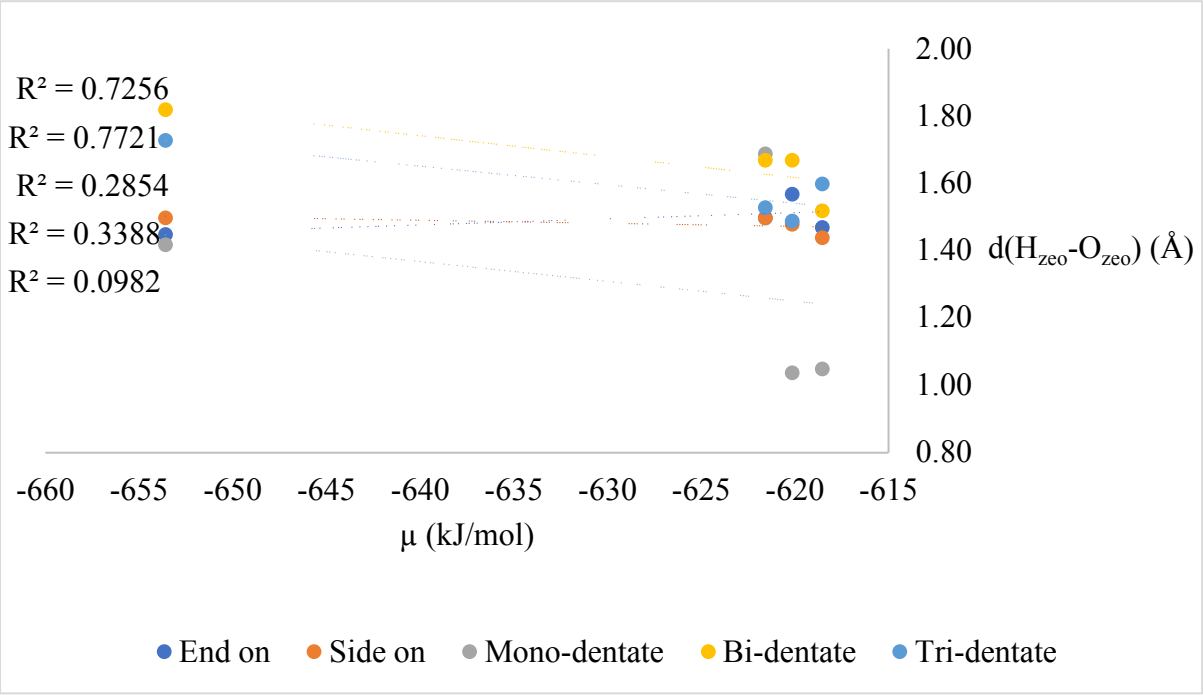
Graph S5. Plot between chemical hardness (η) (kJ/mol) of empty cluster and adsorption energy (E_{ads}) (kJ/mol) of single and bi-methanol models.



Graph S6. Plot between chemical potential (μ) (kJ/mol) of empty cluster and adsorption energy (E_{ads}) (kJ/mol) of single and bi-methanol models.



Graph S7. Plot between chemical hardness (η) (kJ/mol) of empty cluster and the distance between the zeolite framework and the main adsorbent d(H_{zeo}-O_{zeo}) (Å) of the single and bi-methanol models.



Graph S8. Plot between chemical potential (μ) (kJ/mol) of empty cluster and the distance between the zeolite framework and the main adsorbent d(H_{zeo}-O_{zeo}) (Å) of the single and bi-methanol models.

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(1) Julien, J.-P.; Maruani, J.; Mayou, D.; Delgado-Barrio, G. *Recent Adv. Theory Chem. Phys. Syst.* **2006**, *9*, 159–177.

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