Supporting Information for:

QM/MM study of the reactivity of zeolite bound methoxy and carbene groups

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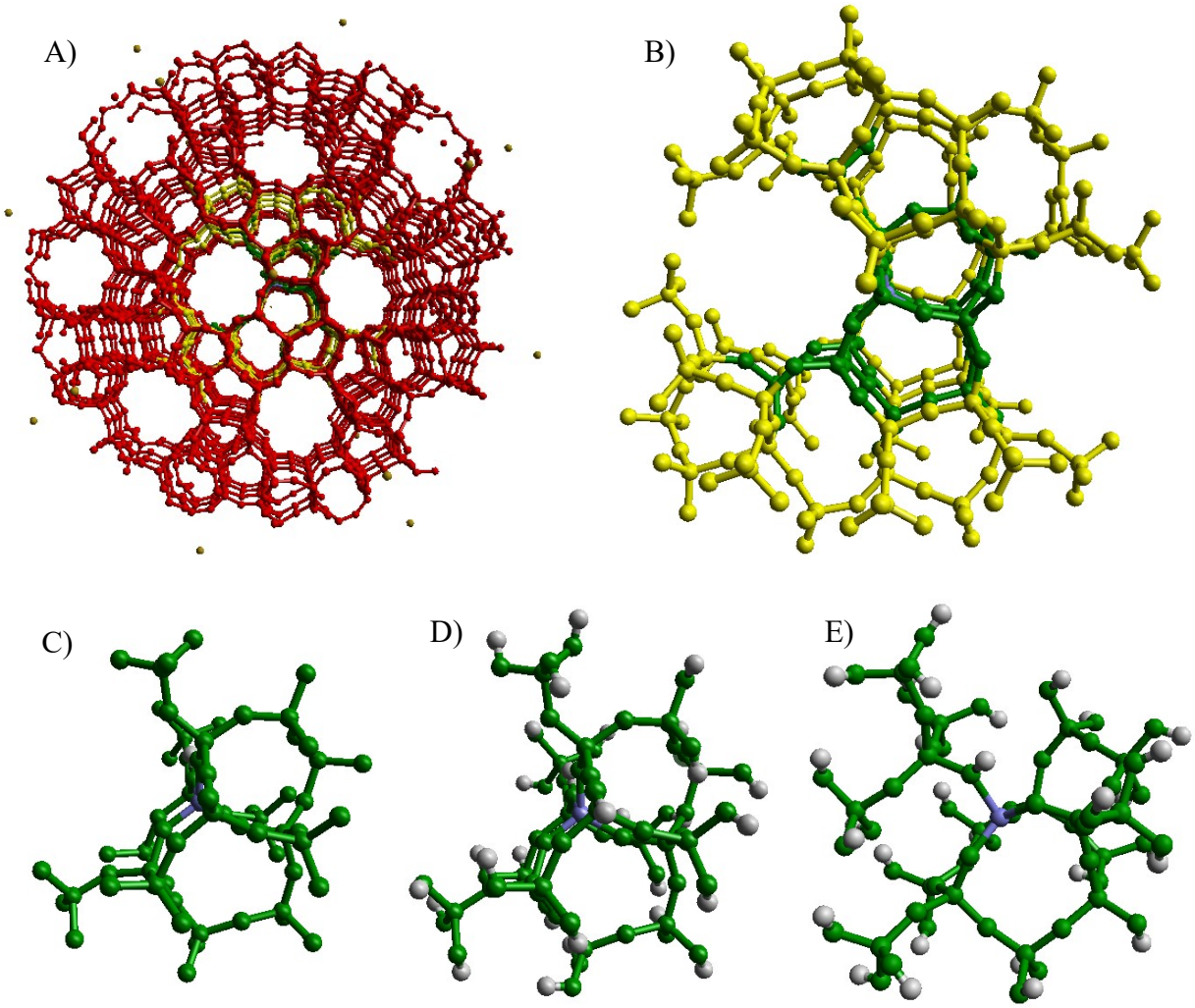
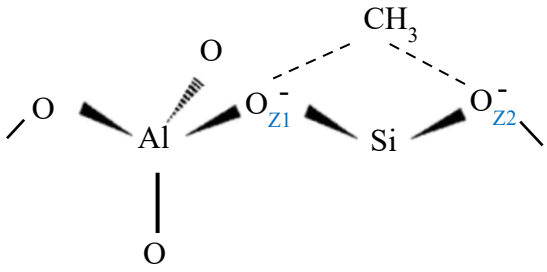


Figure S1. Illustration of H-ZSM-5 embedded cluster model of T12 Brønsted acid site, specifically, A) complete model – fixed MM region (red atoms), relaxed MM region (yellow atoms), QM region (green atoms), B) relaxed MM and QM regions, C) active site - QM region (side view, unterminated), D) active site – QM region (side view, hydrogen terminated), E) active site – QM region (front view, hydrogen terminated).

A)

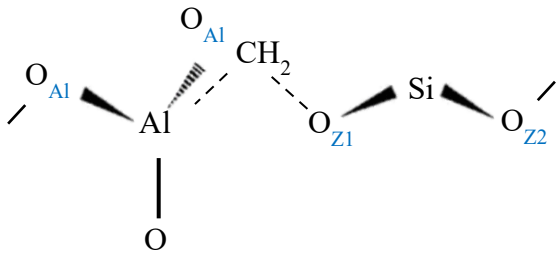


$CV_{biased} = CV2 - CV1$

$CV1 = CN(C, O_{Z1})$

$CV2 = CN(C, O_{Z2})$

B)



$CV_{biased} = CV2 - CV1$

$CV1 = CN(C\text{-}Al, O_{Z1})$

$CV2 = CN(C\text{-}Si, O_{Z2})$

$CV3 = CN(C, O_{ZAl})$ - constrained

Figure S2. Schematic representation of CVs employed in metadynamics simulations for A) methyl and B) carbene, as explained in Section 2.3 of the main manuscript.

Table S1. Cell parameters of unit cells at the end of NPT "production" simulations, with lattice vectors a, b and c given in Å, and inter-vector angles α, β and γ given in °.

Model	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)
Methyl	20.06	19.93	13.39	90.23	90.17	90.07
Carbene	20.06	20.00	13.44	90.39	89.74	89.67

Table S2. Extended set of results for methanol adsorbed on active sites with methyl oriented towards aluminium ($CH_3OH.O_{Al}$) and silicon ($CH_3OH.O_{Si}$) centres, as shown in Figure 1 of the main manuscript, alongside methoxy formation on oxygen closer to aluminium ($CH_3.H_2O.O_{Al}$) and silicon ($CH_3.H_2O.O_{Si}$). Geometric distances (d) and Mulliken charge (q) data are presented in Ångstroms and electronic charge (e), respectively.

			d (Å)		
	$Al\text{-}O_{Al}$	$O_{Al}\text{-}Si$	$O_{MeOH}\text{-}H_{ZeO}$	$O_{ZeO}\text{-}H_{ZeO}$	
$CH_3OH.O_{Al}$	1.85	1.66	1.50	1.03	
	$Si\text{-}O_{Si}$	O_{Si} -Si*	$O_{MeOH}\text{-}H_{ZeO}$	$O_{ZeO}\text{-}H_{ZeO}$	
$CH_3OH.O_{Si}$	1.82	1.67	1.48	1.03	
	$Al\text{-}O_{Al}$	$C\text{-}O_{Al}$	$C\text{-}O_{H2O}$		
$CH_3.H_2O.O_{Al}$	1.84	1.48	3.14		
	$Si\text{-}O_{Si}$	$C\text{-}O_{Si}$	$C\text{-}O_{H2O}$		
$CH_3.H_2O.O_{Si}$	1.77	1.51	3.05		
			q (e)		
	Al	O_{Al}	H_{ZeO}	O_{MeOH}	C
$CH_3OH.O_{Al}$	0.97	-0.61	0.44	-0.53	-0.25
	Si	O_{Si}	H_{ZeO}	O_{MeOH}	C
$CH_3OH.O_{Si}$	1.00	-0.61	0.43	-0.52	-0.24
	Al	O_{Al}	C		
$CH_3.H_2O.O_{Al}$	0.96	-0.53	-0.27		
	Si	O_{Si}	C		
$CH_3.H_2O.O_{Si}$	1.02	-0.49	0.27		

Table S3. Extended set of results for methyl (CH_3) group bonded on O_{Al*}. O_{Al}, O_{Si} sites. Geometric and charge observations are presented in Ångstroms and electronic charge (e), respectively. The specific charges of bonding sites were highlighted in bold.

	d (Å)					
	O_{Al*}-Al	Al-O_{Al}	O_{Al}-Si	Si-O_{Si}	O_{Si*}-Si*	O-C
$CH_3.O_{Si}$	1.71	1.76	1.57	1.81	1.69	1.52
$CH_3.O_{Al}$	1.70	1.85	1.69	1.61	1.60	1.47
$CH_3.O_{Al*}$	1.89	1.70	1.59	1.62	1.60	1.48
	q (e)					
	O_{Al*}	Al	O_{Al}	O_{Si*}	C	
$CH_3.O_{Si}$	-0.59	0.96	-0.59	**-0.45**	-0.22	
$CH_3.O_{Al}$	-0.56	0.94	**-0.51**	-0.50	-0.25	
$CH_3.O_{Al*}$	**-0.53**	1.00	-0.59	-0.49	-0.30	

Table S4. Extended set of results when two methyl (CH_3) groups are bonded on O_{Al*} and O_{Al} ($2CH_3.O_{Al}$) and on O_{Al*} and O_{Si} ($2CH_3.O_{Si}$) sites, with geometric and charge observables are presented in Ångstroms and electronic charge (e), respectively. The specific charges of bonding sites were highlighted in bold.

	E_{bond}	E_{mig}					
$2CH_3.O_{Al}$	-358						
$2CH_3.O_{Si}$	-277	81					
	d (Å)						
	O_{Al*}-Al	Al-O_{Al}	O_{Al}-Si	Si-O_{Si}	O_{Si}-Si*	O_{Al*}-C	O_{Al}-C
$2CH_3.O_{Al}$	1.85	1.85	1.71	1.60	1.62	1.49	1.49
$2CH_3.O_{Si}$	1.86	1.72	1.57	1.77	1.71	1.48	1.52
	q (e)						
	O_{Al*}	Al	O_{Al}	O_{Si}	C_{Al*}	C_{Al}	
$2CH_3.O_{Al}$	-0.55	1.07	**-0.54**	-0.49	-0.30	-0.34	
$2CH_3.O_{Si}$	-0.59	0.99	-0.60	**-0.45**	-0.29	-0.20	

Table S5. Extended set of results for a carbene (CH_2) moiety formed from the methyl conversion on O_{Al}, bonded in the proximity of Al and Si and formed from the methyl conversion on O_{Si}, bonded in the proximity of Si and Si, with geometric and charge data presented in Ångstroms and electronic charge (e), respectively. The specific charges bonding sites were highlighted in bold.*

	d (Å)							
	O_{Al*}-Al	O_{Al*}-H	Al-O_{Al}	O_{Al}-Si	Si-O_{Si}	O_{Si}-Si*	Al-C	C-O_{Al}
H.CH_2.Al	1.91	0.97	1.94	1.63	1.60	1.59	1.95	1.54
H.CH_2.Si	1.85	0.96	1.75	1.76	1.64	1.59	1.89	1.55
	q (e)							
	O_{Al*}	H	Al	O_{Al}	O_{Si}	C		
H.CH_2.Al	-0.61	0.40	1.05	**-0.45**	-0.46	-0.56		
H.CH_2.Si	-0.62	0.41	1.05	-0.53	**-0.49**	-0.48		

Table S6. Extended set of results for a carbene (CH_2) moiety formed from the methyl conversion on O_{Si}, bonded in the proximity of Si and Si and formed from the methyl conversion on O_{Si}, bonded in the proximity of Si and Si*, with geometric and charge data presented in Ångstroms and electronic charge (e), respectively.*

	E_R							
H.CH_2.Si	103							
H.CH_2.Si*	239							
	d (Å)							
	O_{Al*}-Al	O_{Al*}-H	Al-O_{Al}	O_{Al}-Si	Si-O_{Si}	O_{Si}-Si*	Si-C	C-O_{Si}
H.CH_2.Si	1.7	0.97	1.88	1.70	1.61	2.78	1.86	1.42
H.CH_2.Si*	1.72	0.97	1.75	1.56	1.95	1.65	1.82	1.50
	q (e)							
	O_{Al*}	H	Al	O_{Al}	O_{Si}	C	O*	
H.CH_2.Si	-0.59	0.40	1.06	-0.64	-0.36	-0.39	-0.49	
H.CH_2.Si*	-0.57	0.39	0.98	-0.56	-0.39	-0.41	-0.61	