Supporting Information

Theoretical Study of Adsorption of C1-C4 Primary Alcohols in H-ZSM-5

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<u>Note</u>: XYZ coordinates of stationary points studied in this work could be obtained from the authors.

S.1. Views of Silicalite and H-ZSM-5 Unit Cells

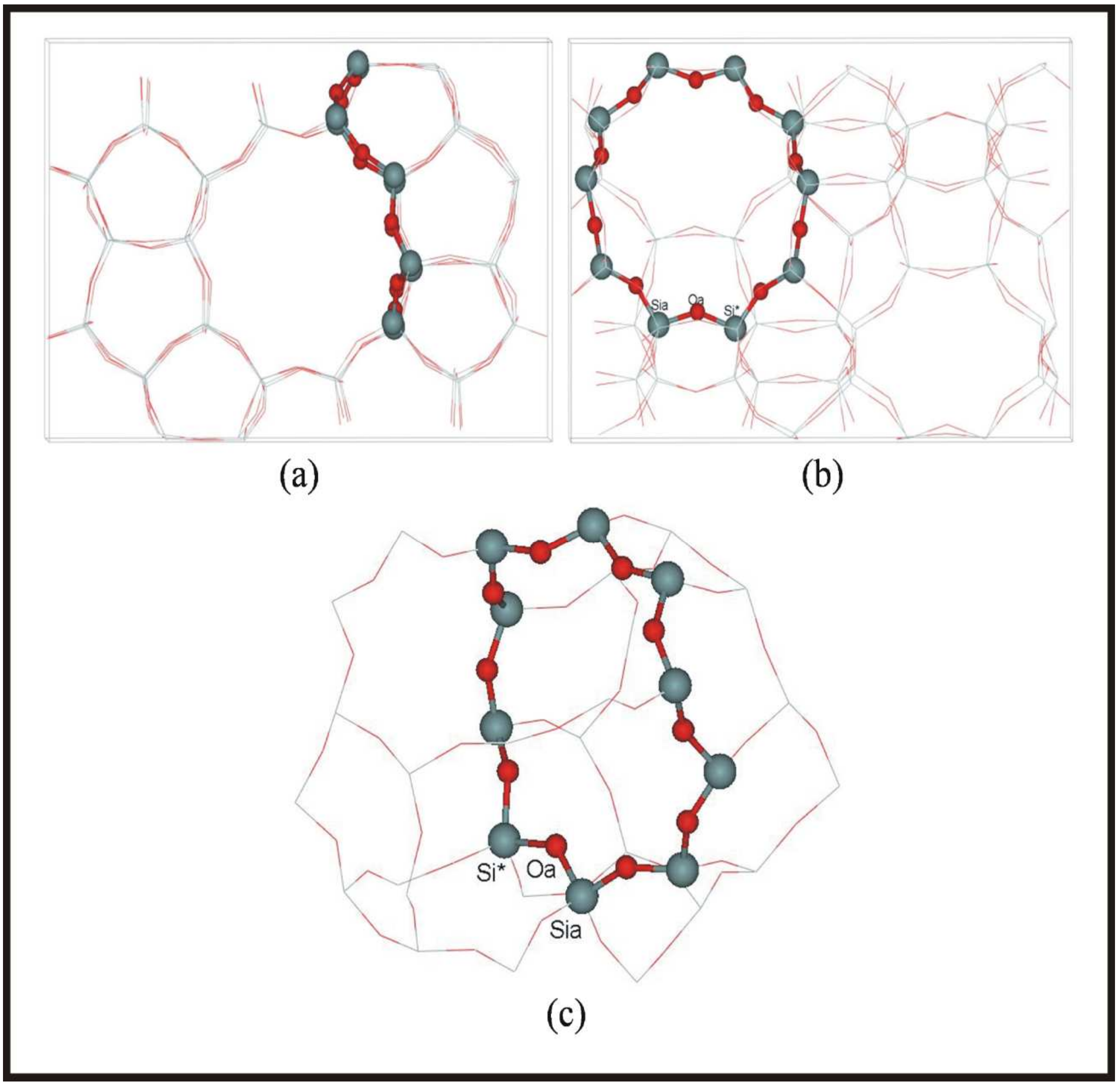


Figure S.1.1. Views of silicalite unit cell along the straight channel in the [010] direction (pannel a) and along the zigzag channel in the [100] direction (pannel b). Hilighted atoms define the 10-T intercrossing ring between the two channels. Si^*-O_a-Si_a indicates the bridging position Si12-O24-Si12 for Al substitution at Si* with Si* = Si12, O_a = O24, Si_a = Si12, respectively. The intersection space between the channels (pannel c) is devided into two parts by the 10-T ring: left part belongs to the straight channel while the right part belongs two the zigzag channel. The overall composition of unit cell is $Si_{96}O_{192}$. Code colors used: oxygen (red), and silicon (grey).

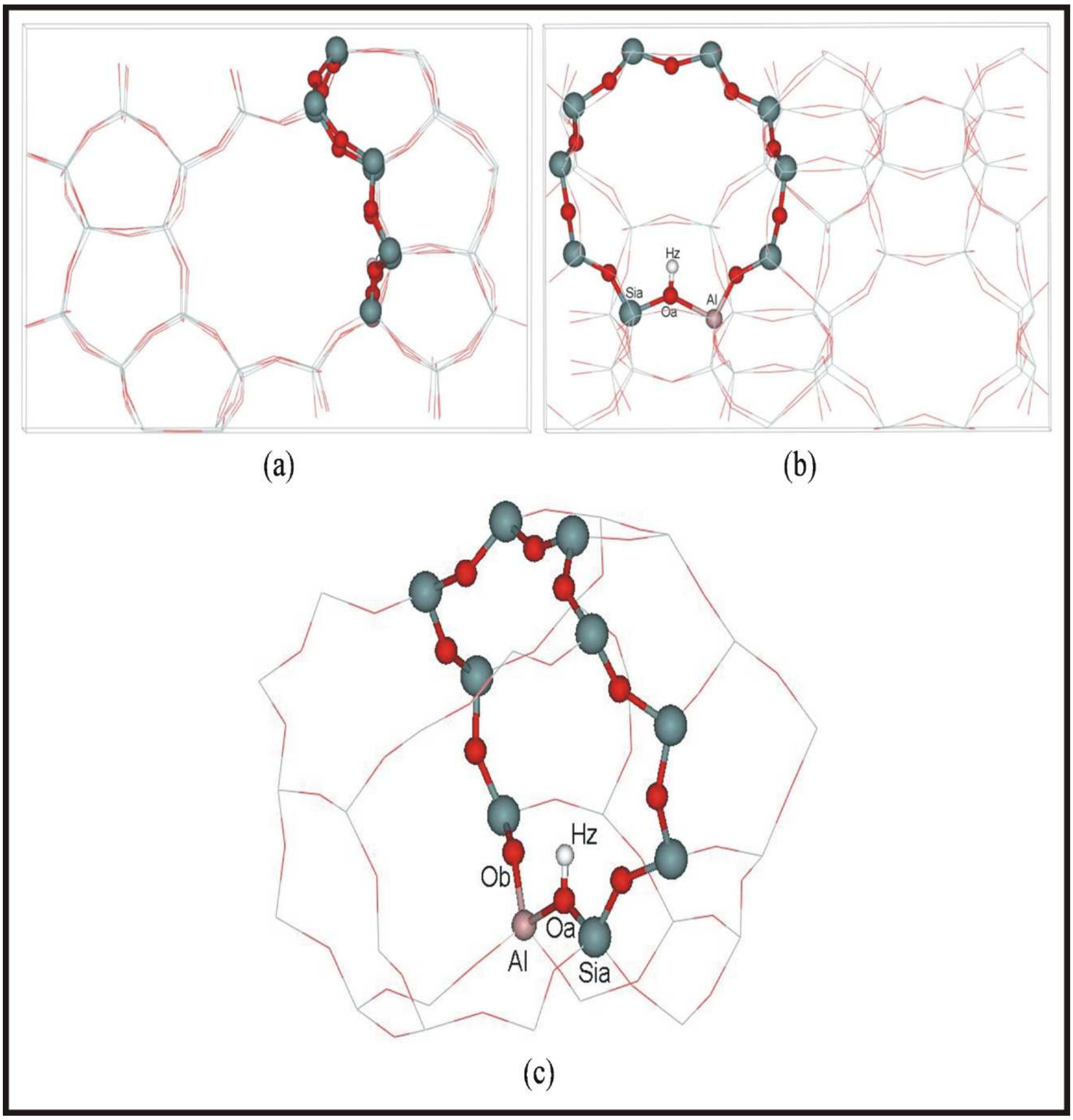


Figure S.1.2. Views of H-ZSM-5 unit cell along the straight channel in the [010] direction (pannel a) and along the zigzag channel in the [100] direction (pannel b). Hilighted atoms define the 10-T intercrossing ring between the two channels. Si_a = Si12, O_a = O24, Al = Al12, and O_b = O20, respectively. The intersection space between the channels (pannel c) is devided into two parts by the 10-T ring: the left part belongs to the straight channel while the right part belongs two the zigzag channel. The oveall composition of unit cell is $HAlSi_{95}O_{192}$. Code colors used: oxygen (red), silicon (grey), hydrogen (white), aluminum (pink).

S.2. Geometrical Parameters of C1-C4 Primary Alcohols Physisorbed in Silicalite

It is obvious that there are no significant changes in structure of the alcohol compounds upon adsorption, e.g. the alcohol OH bond is elongated by only 0.3 % at most while the O-C* bond length remains largely unchanged (Table S.2). The rather weak interaction between one oxygen of the zeolite lattice (O_a) and the hydroxyl hydrogen (H) of the alcohol is clearly demonstrated by long interatomic distances (d[H---O_a] = 215.9-229.6 pm).

Table S.2. Geometrical parameters (pm)^a of physisorbed complexes of C1-C4 primary alcohols at the straight (str) and zigzag (zig) channels in silicalite

	H-O	O-C*	H---O_a
Methanol	97.2	143.0	
Str_O_a	97.5	142.8	222.0
Zig_O_a	97.5	142.9	229.6
Ethanol	97.3	143.6	
Str_O_a	97.5	143.6	222.3
Zig_O_a	97.5	143.6	226.2
1-Propanol	97.2	143.5	
Str_O_a	97.4	143.4	220.8
Zig_O_a	97.5	143.5	223.0
1-Butanol	97.2	143.6	
Str_O_a	97.5	143.4	215.9
Zig_O_a	97.4	143.4	228.9

S.3. Geometrical Parameters of C1-C4 Primary Alcohols Physisorbed over the BAS $O_bAl[O_aH_z]$ of H-ZSM-5

Important structural parameters of physisorbed complexes at the BAS $O_bAl[O_aH_z]$ are listed in Table S.3. The primary hydrogen bond (HB) H_z---O in the 1-HB complexes is much longer than that in the 2-HB complexes (142.1-153.7 vs. 126.2-130.9 pm). The latter complexes also possess a secondary HB between the hydroxyl hydrogen of alcohol and the adjacent aluminum-bound oxygen (d[H---O_b] = 188.1-212.6 pm). In contrast to the 1-HB complexes, the 2-HB complexes have the alcohol O-H bond (97.2-97.3 pm) strongly elongated as a consequence of the secondary H---Ob hydrogen bonding (d[H-O] = 98.4-99.8 vs. 97.1-97.3 pm). Upon the adsorption of the alcohol, the zeolite H_z-O_a bond is elongated by 6.4 to 19.5 pm, depending on the adsorption mode. For the 2-HB structures, the elongation amounts to 15.8-19.5 pm and is significantly larger than that predicted by cluster-model calculations for methanol physisorbed complexes.(1,2) For the case of methanol, cluster models have predicted the formation of a 2-HB physisorbed complex with rather short H_z-O_a bond and long H_z---O hydrogen bond. Sauer et al. have employed both cluster[1] and periodic models[3,4,5] to study the adsorption of methanol over several zeolites. Using cluster models of different size at the HF, MP2 levels of theory, they initially reported an extension of 3.0-8.0 pm upon adsorption of methanol. These authors also observed that the O_a-H_z bond elongation increases with increasing cluster sizes.[1] Recently, these authors reported periodic/MD calculations of methanol adsorption in chabazite,[3,4] theta-1,[4] ferrierite[4] and H-ZSM-5.[4,5] The elongation of the zeolite O_a-H_z bond was thereby predicted as 19.0, 12.0, 14.0 and 16.0 pm, respectively.

In going from C1 to C4 alcohol, it is observed that in the zigzag channel the 2-HB complexes of 1-propanol and 1-butanol have rather longer H_z-O_a bonds (116.2-117.2 pm) and shorter primary H_z---O HBs (126.2-127.8 pm) while the complexes of methanol and ethanol have comparable structural parameters (d[H_z-O_a] = 114.3-114.8 pm and d[H_z---O] = 130.0-130.2 pm). This result may be ascribed to strong pore confinement effects and/or steric constraints exerted by the narrower zigzag channel on the longer hydrocarbon chains of 1-propanol and 1-butanol. In the straight channel, however, all 2-HB complexes have H_z-O_a bonds and H_z---O HBs of similar length (d[H_z-O_a] = 113.5-114.5 pm and d[H_z---O] = 130.0-130.9 pm). Apparently, the more open straight channel does not exhibit noticeable steric constraints for the adsorption of C1-C4 primary alcohols.

It is found that the methanol 2HB_str_O_aH_z and 2HB_zig_O_aH_z complexes with their O-C* bond tilted out of the O_aOO_b plane (α = 44-51^o) have stronger interactions with the BAS as compared to the 2HB_i_O_aH_z complex with its O-C* bond lying in the "3-O" plane (α = 4^o). Clearly, the 2HB_str_O_aH_z and 2HB_zig_O_aH_z complexes have longer O_a-H_z bonds (113.9-114.3 vs. 106.7 pm), shorter primary (130.2-130.3 vs. 142.7 pm) and secondary (188.1-191.6 vs. 193.3 pm) HBs (Table S.3). For ethanol, 1-propanol, and 1-butanol, we also located 2-HB physisorbed structures with the O-C* bond shifting out of the "3-O" plane (α = 39-51^o) as minima on the potential energy surface. In a periodic-DFT study of methanol adsorption, Shah et al.[6] predicted chemisorbed methoxonium over chabazite and a 2-HB physisorbed species over sodalite.

Considering the geometrical difference of the two zeolites, these authors suggested that if methanol is in an open cage such as that of the sodalite framework, physisorption is favored. However, when methanol can lie in a ring such as the eight-ring of chabazite, the charge transfer due to chemisorption is stabilized by the electronic potential and/or interactions with the far side of the ring. This idea was also shared by Stich et al.[7], who found a methoxonium lying planar in the eight-ring channel of ferrierite. However, Sauer et al. found physisorbed methanol as the most stable species over several zeolites (theta-1, ferrierite, chabazite, and H-ZSM-5) having 8- or 10-ring channels.[3,4]

Table S.3. Geometrical parameters (distances in pm and angles in degree)[a] of physisorbed complexes of C1-C4 primary alcohols at the straight (str) and zigzag (zig) channels of H-ZSM-5

	H_z-O_a	H-O	O-C*	H_z---O	H---O_b	Angle α[b]
Unloaded H-ZSM-5	97.7					
Methanol		97.2	143.0			
1HB_str_O_aH_z	104.5	97.1	144.8	150.5	355.1	48
2HB_str_O_aH_z	113.9	99.1	145.1	130.3	191.6	44
1HB_zig_O_aH_z	104.4	97.3	144.8	151.2	367.3	49
2HB_zig_O_aH_z	114.3	99.5	145.3	130.2	188.1	51
2HB_i_O_aH_z	106.7	98.4	144.0	142.7	193.3	4
Ethanol		97.3	143.6			
1HB_str_O_aH_z	104.9	97.3	146.0	150.0	365.1	45
2HB_str_O_aH_z	114.5	99.1	146.8	130.7	195.0	43
1HB_zig_O_aH_z	104.1	97.2	146.2	153.7	359.4	39
2HB_zig_O_aH_z	114.8	99.2	146.4	130.0	191.7	40
1-Propanol		97.2	143.5			
1HB_str_O_aH_z	105.8	97.2	146.0	145.4	358.9	42
2HB_str_O_aH_z	114.2	99.8	146.4	130.0	203.0	41
1HB_zig_O_aH_z	106.2	97.2	1.462	145.2	363.6	47
2HB_zig_O_aH_z	117.2	99.2	146.8	126.2	196.9	46
1-Butanol		97.2	143.6			
1HB_str_O_aH_z	107.1	97.3	146.6	143.9	361.0	41
2HB_str_O_aH_z	113.5	98.4	146.5	130.9	212.6	39
1HB_zig_O_aH_z	107.7	97.4	146.4	142.1	381.0	41
2HB_zig_O_aH_z	116.2	99.3	146.5	127.8	189.5	41

[b] Angle α is defined as the angle between O-C* bond and O_aOO_b plane.

S.4. Geometrical Parameters of C1-C4 Primary Alcohols Chemisorbed over the BAS $O_bAl[O_aH_z]$ of H-ZSM-5

Important geometrical parameters and formal charges of stationary chemisorbed complexes are reported in Table S.4. For the chemisorbed oxoniums an average O-H distance is defined as

$$d_1^{avg} = \frac{d[H_z-O] + d[H-O]}{2} \qquad (1)$$

while for the hydrogen bonds between the oxonium ions and the zeolite an average O···H distance is defined as

$$d_2^{avg} = \frac{d[H_z \cdots O_a] + d[H \cdots O_b]}{2} \qquad (2)$$

The chemisorbed complexes are characterized by two HBs of inappreciably different length ($d[H_z---O_a]$ = 143.8-152.3 pm; $d[H---O_b]$ = 140.6-154.4 pm) and possess two equivalent covalent OH bonds (d[Hz-O] = 105.1-107.5 pm; d[H-O] = 104.7-109.0 pm), indicating the complete proton transfer from the BAS to the alcohol. Analogous to 2-HB physisorbed complexes, the O-C* bond in the chemisorbed complexes is significantly tilted out of the “3-O” plane ($\alpha = 47\text{-}61^{o}$). In addition, Bader charge analysis allocated a total charge of +0.75 to +0.78 to the oxonium fragments. A similar charge of +0.77 on the methoxonium in chabazite was obtained by Shah et al.[6]

The methoxonium ion has a rather longer average O-H bond length (d_1^{avg} = 107.3-107.4 pm) as compared to the other oxonium ions that have comparable average O-H bond lengths (d_1^{avg} = 105.7-106.2 pm). The moderate increase in O-H bond length in going from methanol to the other alcohols may be attributed to the difference in proton affinity of the alcohols. Methanol (PA = -754 kJ mol^{-1})[8] is somewhat less prone to protonation then the C2-C4 alcohols (PA = -776 kJ mol^{-1} to -789 kJ mol^{-1}).[8] In literature, periodic-DFT studies reported methoxonium ions having O-H bond lengths ranging from 105.0-108.0 pm[3,6] and are in agreement with the values obtained in this study. The existence of both 2-HB physisorbed and chemisorbed complexes as minima over the potential energy surface with a significantly broad range of H_z-O_a bond length/distance (113.5-152.3 pm) reveals that the zeolite proton fluctuates between the framework and the alcohol while the hydroxyl proton is well localized near the alcohol oxygen (d[H-O]: 98.4-109.0 pm). This observation is supported by the OH radial distributions obtained from ab initio MD simulations for methanol adsorption over several zeolites.[3,4,7,9]

To interpret the effect of symmetry in O-H bond length on the energy and on the harmonic stretching frequencies of the H_z-O-H group of the oxonium ions, chemisorbed complexes with more symmetric O-H bonds were also located for methanol and 1-butanol in the zigzag channel (Table S.4). In contrast to methoxonium_zig (d[Hz-O] = 105.8 pm, d[H-O] = 109.0 pm), methoxonium_zig_sym has a more symmetric structure (d[Hz-O] = 107.3 pm, d[H-O] = 107.2 pm). A similar difference in O-H bond lengths is also observed for butoxonium_zig (d[Hz-O] = 107.5 pm, d[H-O] = 104.7 pm) and butoxonium_zig_sym (d[Hz-O] = 105.9 pm, d[H-O] = 105.4 pm).

Table S.4. Geometrical parameters (distances in pm and angles in degree)[a] and formal charge of chemisorbed complexes of C1-C4 primary alcohols at the straight and zigzag channel

	H_z---O_a	H---O_b	H_z-O	H-O	O-C*	d_1^{avg}	d_2^{avg}	α	q^a
Methanol									
Methoxonium_str	148.7	142.2	106.2	108.6	146.5	107.4	145.4	61	+0.76
Methoxonium_zig	148.9	140.6	105.8	109.0	145.9	107.4	144.7	54	+0.75
Methoxonium_zig_sym[b]	144.7	144.7	107.3	107.2	146.0	107.3	144.7	54	+0.75
Ethanol									
Ethoxonium_str	150.0	147.1	105.8	106.6	147.9	106.2	149.0	48	+0.78
Ethoxonium_zig	146.9	151.3	106.6	105.4	147.9	106.0	149.1	48	+0.77
1-Propanol									
1-Propoxonium_str	151.6	147.2	105.4	106.7	148.5	106.0	149.4	52	+0.78
1-Propoxonium_zig	151.1	149.8	105.4	106.2	148.1	105.8	150.5	47	+0.76
1-Butanol									
1-Butoxonium_str	152.3	146.0	105.1	107.1	148.3	106.1	149.2	55	+0.77
1-Butoxonium_zig	143.8	154.4	107.5	104.7	148.0	106.1	149.1	47	+0.78
1-Butoxonium_zig_sym[b]	149.2	151.3	105.9	105.4	148.1	105.7	150.3	47	+0.78

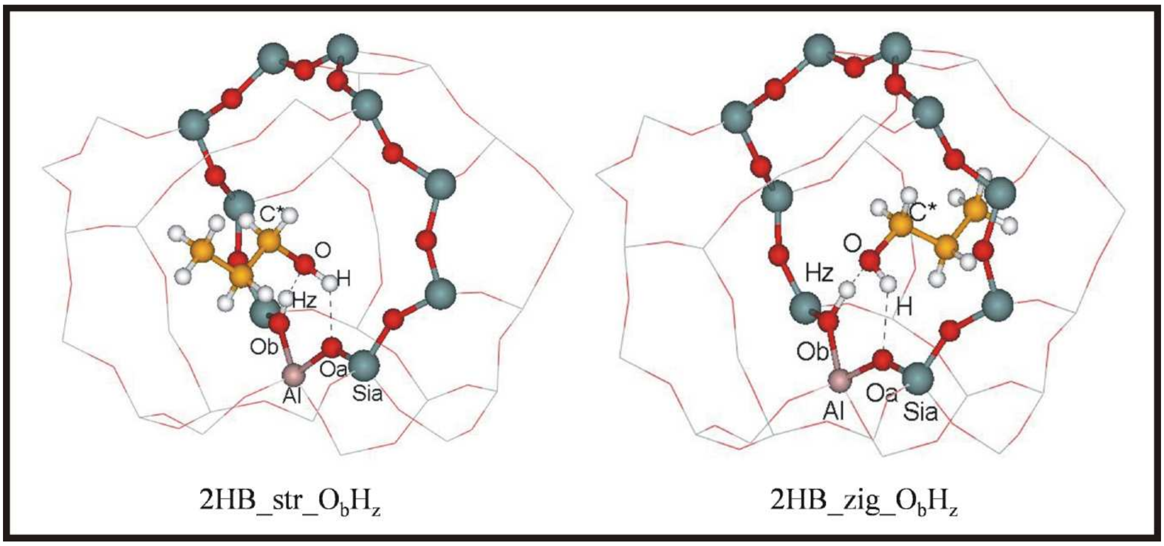
$d_1^{avg} = \frac{d[Hz-O] + d[H-O]}{2}$ and $d_2^{avg} = \frac{d[Hz\cdots Oa] + d[H\cdots Ob]}{2}$

[a] q: formal charge of the protonated alcohol (ROH_2^+, R: hydrocarbon chain) in H-ZSM-5.

[b] Chemisorbed complexes with more symmetric covalent OH bond length.

S.5. Geometrical Parameters and Physisorption Energies of C1-C4 Primary Alcohols Physisorbed over the BAS $O_aAl[O_bH_z]$ of H-ZSM-5

To put in evidence the proton exchange between two adjacent aluminum-bound oxygen atoms (O_a and O_b), 2-HB physisorption structures are additionally sampled at the other BAS $O_aAl[O_bH_z]$ with the zeolite proton attached to O_b. It was observed that the location of the zeolite proton (H_z) at O_a or O_b has no significant effect on the structural parameters and energetics of the 2-HB physisorbed complexes (see Tables S.5.1 and S.5.2 below).



2HB_str_O_bH_z 2HB_zig_O_bH_z

Figure S.5. Representative H-ZSM-5-C_3H_7OH physisorbed complexes over the BAS $O_aAl[O_bH_z]$: 2HB_str_O_bH_z at the straight channel (left pannel) and 2HB_zig_O_bH_z at the zigzag channel (right pannel). Si_a = Si12, O_a = O24, Al = Al12, and O_b = O20, respectively.

Table S.5.1. Geometrical parameters (distances in Å and angles in degree)[a] of 2-HB physisorbed complexes over the BAS $O_aAl[O_bH_z]$ of H-ZSM-5

	H_z-O_b	H-O	O-C*	H_z---O	H---O_a	Angle α[b]
H-ZSM-5…Methanol						
2HB_str_O_bH_z	114.3	99.4	145.6	130.4	191.1	57
2HB_zig_O_bH_z	115.1	99.6	145.3	129.9	185.7	51
H-ZSM-5…Ethanol						
2HB_str_O_bH_z	114.7	99.3	146.8	130.1	193.9	48
2HB_zig_O_bH_z	116.0	99.3	146.5	128.4	190.6	38
H-ZSM-5…1-Propanol						
2HB_str_O_bH_z	114.2	99.2	146.1	130.7	190.6	36
2HB_zig_O_bH_z	116.5	98.8	146.9	127.0	205.7	46
H-ZSM-5…1-Butanol						
2HB_str_O_bH_z	113.8	99.1	146.0	130.6	190.0	33
2HB_zig_O_bH_z	118.6	99.1	147.1	124.7	198.9	41

[a] Atom labels and physisorbed complex notation are defined in Figure S.5.

[b] Angle α is defined as the angle between O-C* bond and O_aOO_b plane.

Table S.5.2. Physisorption energies (ΔE_{phys}, kJ mol^{-1}) of 2HB physisorbed complexes at the straight (str) and zigzag (zig) channel over the BAS $O_aAl[O_bH_z]$ of H-ZSM-5

	ΔE_{phys}			
	PBE		PBE-D	
	str	zig	str	zig
Methanol	-86	-83	-114	-116
Ethanol	-88	-84	-126	-132
1-Propanol	-88	-83	-138	-148
1-Butanol	-87	-80	-149	-162

S.6. Atomic Coeeficient and van der Waals Radii used for PBE-D Calcualtions

Table S.6. Atomic coeeficients (c_6, Jnm^6 mol^{-1}) and van der Waals radii (R_o, Å) taken from ref. 10 for H, C, O, Si and Al atoms.

Element	c_6	R_o
H	0.14	1.001
C	1.75	1.452
O	0.70	1.342
Si	9.23	1.716
Al	10.79	1.639

S.7. References

1. F. Haase and J. Sauer, *J. Am. Chem. Soc.*, 1995, **117**, 3780.
2. S. R. Blaszkowski and R. A. van Santen, *J. Phys. Chem.*, 1995, **99**, 11728.
3. S. Svelle, C. Tuma, X. Rozanska, T. Kerber and J. Sauer, *J. Am. Chem. Soc.*, 2009, **131**, 816.
4. F. Haase and J. Sauer, *Microporous Mesoporous Mater.*, 2000, **35-36**, 379.
5. F. Haase, J. Sauer and J. Hutter, *Chem. Phys. Lett.*, 1997, **266**, 397.
6. R. Shah, J. D. Gale and M. C. Payne, *J. Phys. Chem.*, 1996, **100**, 11688.
7. I. Stich, J. D. Gale, K. Terakura and M. C. Payne, *Chem. Phys. Lett.*, 1998, **283**, 402.
8. http://webbook.nist.gov/chemistry/
9. I. Stich, J. D. Gale, K. Terakura and M. C. Payne, *J. Am. Chem. Soc.* **1999**, 121, 3292.
10. Grimme, *J. Comput. Chem.*, 2006, **27**, 1787