Supporting Information: Quantifying Effects of Active Site Proximity on Rates of Methanol Dehydration to Dimethyl Ether over CHA Zeolites through Microkinetic Modeling

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#### Section S.1. Microkinetic Model Parameter Inputs and Simulation Outputs

**Table S1**: DFT-evaluated parameters for isolated sites, next-nearest neighbor (NNN) paired acid sites, and next-<br/>next-nearest neighbor (NNNN) paired acid sites in the 6-MR of CHA. Rate constants are presented evaluated at a<br/>temperature of 415 K. [a] Pre-exponential factors and rate constants for parameters with this note are in units of s<sup>-1</sup>.[b] Pre-exponential factors and rate constants for parameters with this note are in units of (Pa s)<sup>-1</sup>.

Parameter	A <sub>iso</sub> (s <sup>-1</sup> /(Pa s) <sup>-1</sup> )	E <sub>a,iso</sub> (kJ/mol)	k <sub>iso</sub> (T) (s <sup>-1</sup> /(Pa s) <sup>-1</sup> )	$\begin{array}{c} A_{pair,NNN} \\ (s^{\text{-1}}/(Pa \ s)^{\text{-1}}) \end{array}$	E <sub>a,pair,NNN</sub> (kJ/mol)	$k_{pair,NNN}(T)$ (s <sup>-1</sup> /(Pa s) <sup>-1</sup> )	$\begin{array}{c} A_{pair,NNNN} \\ (s^{\text{-1}}/(Pa \; s)^{\text{-1}}) \end{array}$	E <sub>a,pair,NNNN</sub> (kJ/mol)	$k_{pair,NNNN}(T)$ (s <sup>-1</sup> /(Pa s) <sup>-1</sup> )
$k_{mon}{}^{b}$	$3.92\cdot 10^2$	0	$3.92\cdot 10^2$	$4.50\cdot 10^2$	0	$4.50\cdot 10^2$	$3.99\cdot 10^2$	0	$3.99\cdot 10^2$
k-mon <sup>a</sup>	$3.13\cdot 10^{16}$	121.2	$1.75 \cdot 10^1$	$2.85\cdot10^{16}$	115.4	$8.49 \cdot 10^1$	$3.09\cdot 10^{16}$	119.2	$3.08 \cdot 10^1$
$k_{dim}{}^{b}$	$6.38\cdot10^2$	0	$6.38 \cdot 10^{2}$	$3.61 \cdot 10^2$	0	$3.61 \cdot 10^{2}$	$1.12\cdot 10^3$	0.0	$1.12 \cdot 10^3$
k-dim <sup>a</sup>	$2.26\cdot 10^{16}$	81.4	$1.28 \cdot 10^{6}$	$3.30\cdot10^{16}$	80.1	$2.71 \cdot 10^6$	$1.55\cdot 10^{16}$	91.2	$5.17\cdot 10^4$
$k_{\text{conc,dim}}{}^a$	$8.64 \cdot 10^{12}$	137.0	$4.99 \cdot 10^{-5}$	$8.64 \cdot 10^{12}$	127.0	$9.01\cdot10^{-4}$	$8.64 \cdot 10^{12}$	134.6	$9.95\cdot10^{-5}$
k-conc,dim <sup>a</sup>	$8.64 \cdot 10^{12}$	113.5	$4.51 \cdot 10^{-2}$	$8.64 \cdot 10^{12}$	140.4	$1.83 \cdot 10^{-5}$	$8.64 \cdot 10^{12}$	130.0	$3.72\cdot10^{-4}$
$k_{h2o,des,dim}{}^a$	$2.38\cdot 10^{15}$	30.6	$3.32\cdot10^{11}$	$5.21\cdot 10^{15}$	66.0	$2.59\cdot 10^7$	$8.28\cdot 10^{15}$	70.0	$1.28\cdot 10^7$
k-h2o,des,dim <sup>b</sup>	$1.87\cdot 10^4$	0	$1.87\cdot 10^4$	$5.77 \cdot 10^3$	0	$5.77 \cdot 10^3$	$2.88 \cdot 10^3$	0	$2.88 \cdot 10^3$
k <sub>dme,des</sub> <sup>a</sup>	$1.80\cdot 10^{16}$	112.3	$1.32\cdot 10^2$	$1.58\cdot 10^{16}$	110.0	$2.26\cdot 10^2$	$2.48\cdot 10^{16}$	116.5	$5.38\cdot 10^1$
k-dme,des <sup>b</sup>	$8.95\cdot 10^2$	0	$8.95 \cdot 10^2$	$1.09 \cdot 10^3$	0	$1.09 \cdot 10^{3}$	$5.54 \cdot 10^2$	0	$5.54 \cdot 10^2$
k <sub>elim</sub> <sup>a</sup>	$8.64 \cdot 10^{12}$	129.5	$4.28\cdot10^{4}$	$8.64 \cdot 10^{12}$	128.8	$5.30\cdot10^{-4}$	$8.64 \cdot 10^{12}$	131.8	$2.22\cdot 10^{4}$
k-elim <sup>a</sup>	$8.64 \cdot 10^{12}$	76.8	$1.84 \cdot 10^{3}$	$8.64 \cdot 10^{12}$	100.5	$1.93\cdot 10^{0}$	$8.64 \cdot 10^{12}$	84.0	$2.34\cdot 10^2$
k <sub>h2o,des</sub> <sup>a</sup>	$7.26\cdot 10^{14}$	28.3	$1.97\cdot 10^{11}$	$7.93\cdot 10^{15}$	64.7	$5.74 \cdot 10^{7}$	$8.82\cdot 10^{15}$	49.2	$5.65 \cdot 10^{9}$
k-h2o,des <sup>b</sup>	$1.11 \cdot 10^{5}$	0	$1.11 \cdot 10^{5}$	$3.07 \cdot 10^{3}$	0	$3.07 \cdot 10^{3}$	$2.62 \cdot 10^3$	0	$2.62 \cdot 10^3$
k <sub>meoh,ads</sub> <sup>b</sup>	$1.20\cdot 10^4$	0	$1.20\cdot 10^4$	$4.72 \cdot 10^{2}$	0	$4.72 \cdot 10^{2}$	$4.13 \cdot 10^{2}$	0	$4.13 \cdot 10^{2}$

k-meoh,ads <sup>a</sup>	$3.19\cdot 10^{15}$	41.1	$2.13\cdot10^{10}$	$2.76\cdot 10^{16}$	82.7	$1.08\cdot 10^6$	$3.02\cdot 10^{16}$	70.5	$4.08 \cdot 10^7$
$\mathbf{k}_{\mathrm{seq}}^{\mathrm{a}}$	$8.64 \cdot 10^{12}$	77.5	$1.52\cdot 10^3$	$8.64 \cdot 10^{12}$	94.9	$9.78\cdot 10^{0}$	$8.64 \cdot 10^{12}$	76.6	$1.96 \cdot 10^3$
k-seq <sup>a</sup>	$8.64 \cdot 10^{12}$	138.1	$3.59\cdot 10^{-5}$	$8.64 \cdot 10^{12}$	127.7	$7.37 \cdot 10^{-4}$	$8.64 \cdot 10^{12}$	125.0	$1.58 \cdot 10^{-3}$
$k_{trim}{}^{b}$	$1.37 \cdot 10^3$	0	$1.37 \cdot 10^{3}$	$1.66 \cdot 10^3$	0	$1.66 \cdot 10^{3}$	$5.89\cdot 10^2$	0	$5.89\cdot 10^2$
k <sub>-trim</sub> <sup>a</sup>	$1.18\cdot 10^{16}$	75.0	$4.27 \cdot 10^{6}$	$1.20\cdot 10^{16}$	74.5	$4.97\cdot 10^6$	$2.38\cdot 10^{16}$	89.2	$1.42\cdot 10^5$
$k_{\rm conc,trim}{}^{\rm a}$	$8.64 \cdot 10^{12}$	120.5	$5.38\cdot 10^{\text{-3}}$	$8.64 \cdot 10^{12}$	111.0	$9.22 \cdot 10^{-2}$	$8.64 \cdot 10^{12}$	140.9	$1.59\cdot 10^{\text{-5}}$
k-conc,trim <sup>a</sup>	$8.64 \cdot 10^{12}$	76.8	$1.87 \cdot 10^{3}$	$8.64 \cdot 10^{12}$	99.2	$2.81\cdot 10^{0}$	$8.64 \cdot 10^{12}$	110.6	$1.04 \cdot 10^{-1}$
$k_{h2o,des,trim}{}^{a}$	$4.49\cdot 10^{15}$	12.7	$1.12\cdot 10^{14}$	$8.59\cdot 10^{15}$	40.8	$6.35\cdot10^{10}$	$8.59\cdot 10^{15}$	40.8	$6.35 \cdot 10^{10}$
k-h2o,des,trim <sup>b</sup>	$7.21 \cdot 10^3$	0	$7.21 \cdot 10^{3}$	$2.72\cdot 10^3$	0	$2.72\cdot 10^3$	$2.72 \cdot 10^3$	0	$2.72 \cdot 10^3$
$k_{meoh,des,trim}$ a	$1.34 \cdot 10^{16}$	78.6	$1.72 \cdot 10^{6}$	$1.34 \cdot 10^{16}$	78.6	$1.72 \cdot 10^{6}$	$1.59 \cdot 10^{16}$	78.6	$2.03 \cdot 10^{6}$
k. meoh.des.trim <sup>b</sup>	$1.39 \cdot 10^{3}$	0	$1.39 \cdot 10^{3}$	$1.39 \cdot 10^{3}$	0	$1.39\cdot 10^3$	$1.08 \cdot 10^{3}$	0	$1.08 \cdot 10^{3}$
$k_{tet}^{b}$	$1.22 \cdot 10^{3}$	0	$1.22 \cdot 10^{3}$	$5.72 \cdot 10^2$	0	$5.72 \cdot 10^{2}$	$4.87\cdot 10^2$	0	$4.87\cdot 10^2$
k-tet <sup>a</sup>	$1.47 \cdot 10^{16}$	71.0	$1.70 \cdot 10^7$	$2.43 \cdot 10^{16}$	60	$6.81 \cdot 10^{8}$	$2.70\cdot 10^{16}$	60.2	$7.21 \cdot 10^{8}$
$k_{\text{conc,tet}}^{a}$	$8.64 \cdot 10^{12}$	146.0	$3.68 \cdot 10^{-6}$	$8.64 \cdot 10^{12}$	131.5	$2.46\cdot10^{4}$	$8.64 \cdot 10^{12}$	122.8	$3.00 \cdot 10^{-3}$
k-conc,tet <sup>a</sup>	$8.64 \cdot 10^{12}$	78.5	$1.14 \cdot 10^{3}$	$8.64 \cdot 10^{12}$	100.9	$1.72\cdot 10^{0}$	$8.64 \cdot 10^{12}$	77.3	$1.61 \cdot 10^{3}$
$k_{h2o,des,tet}{}^a$	$7.56\cdot 10^{15}$	27.9	$2.30\cdot 10^{12}$	$1.45 \cdot 10^{16}$	56.0	$1.31\cdot 10^9$	$1.45\cdot 10^{16}$	56.0	$1.31\cdot 10^9$
k-h2o,des,tetb	$3.30\cdot10^3$	0	$3.30\cdot10^3$	$1.24\cdot 10^3$	0	$1.24 \cdot 10^3$	$1.24 \cdot 10^{3}$	0	$1.24 \cdot 10^{3}$
$k_{\text{meoh,des,tet}}^{a}$	$1.37 \cdot 10^{16}$	35.8	$4.23 \cdot 10^{11}$	$1.37 \cdot 10^{16}$	35.8	$4.23 \cdot 10^{11}$	$1.37\cdot 10^{16}$	35.8	$4.23 \cdot 10^{11}$
k. meoh,des,tet <sup>b</sup>	$1.36 \cdot 10^{3}$	0	$1.36 \cdot 10^{3}$	$1.36 \cdot 10^{3}$	0	$1.36 \cdot 10^{3}$	$1.36 \cdot 10^{3}$	0	$1.36 \cdot 10^{3}$
$k_{pent}{}^{b}$	$1.05\cdot 10^3$	0	$1.05 \cdot 10^{3}$	$5.72 \cdot 10^2$	0	$5.72 \cdot 10^2$	$4.87\cdot 10^2$	0.0	$4.87 \cdot 10^2$
k-pent <sup>a</sup>	$1.62 \cdot 10^{16}$	71.0	$1.87 \cdot 10^{7}$	$2.43 \cdot 10^{16}$	60.0	$6.81 \cdot 10^8$	$2.70 \cdot 10^{16}$	60.2	$7.21 \cdot 10^{8}$



Figure S1: Comparison of model output and experimental values for the full range of MeOH partial pressures for untuned NNN DFT values, assuming a distribution of 7.4% NNN sites and 92.6% inactive NNNN sites, for 0% total paired acid sites (red, ●), 18% paired acid sites (green, ♦), 30% paired acid sites (blue, ▲), and 44% paired acid sites (pink, ■). Markers with error bars are the experimental data from Di Iorio et al. [1] adjusted as described in Section S.2. The crosses identify the output of individual microkinetic model runs at the given paired acid site percentages at methanol partial pressures matching each experimental data point. The dashed lines connecting microkinetic model outputs are presented to guide the eye.



**Figure S2**: Comparison of model output and experimental values for the full range of MeOH partial pressures for untuned NNN DFT values, assuming a distribution of 100% NNN sites, for 0% total paired acid sites (red,  $\bullet$ ), 18% paired acid sites (green,  $\bullet$ ), 30% paired acid sites (blue,  $\blacktriangle$ ), and 44% paired acid sites (pink,  $\blacksquare$ ). Markers with error bars are the experimental data from Di Iorio et al. [1] adjusted as described in Section S.2. The crosses identify the output of individual microkinetic model runs at the given paired acid site percentages at methanol partial pressures matching each experimental data point. The dashed lines connecting microkinetic model outputs are presented to guide the eye.



Figure S3: Comparison of model output and experimental values for the full range of MeOH partial pressures for untuned NNNN DFT values, assuming a distribution of 100% NNNN sites, for 0% total paired acid sites (red, ●), 18% paired acid sites (green, ◆), 30% paired acid sites (blue, ▲), and 44% paired acid sites (pink, ■). Markers with error bars are the experimental data from Di Iorio et al. [1] adjusted as described in Section S.2. The crosses identify the output of individual microkinetic model runs at the given paired acid site percentages at methanol partial pressures matching each experimental data point. The dashed lines connecting microkinetic model outputs are presented to guide the eye.



Figure S4: Comparison of model output and experimental values for the full range of MeOH partial pressures for maximally tuned NNNN DFT values, assuming a distribution of 100% NNNN sites, for 0% total paired acid sites (red, ●), 18% paired acid sites (green, ♦), 30% paired acid sites (blue, ▲), and 44% paired acid sites (pink, ■).
Markers with error bars are the experimental data from Di Iorio et al. [1] adjusted as described in Section S.2. The crosses identify the output of individual microkinetic model runs at the given paired acid site percentages at methanol partial pressures matching each experimental data point. The dashed lines connecting microkinetic model outputs are presented to guide the eye.

**Table S2**: DRC Sensitivity Coefficients for 0% paired acid site percentage. Values that round to 0.00 are red or dark orange depending on their original value, transitioning to yellow from 0.01 to 0.15, and eventually becoming green for values up to 1.00.

MeOH Partial				
Pressure (kPa)	iso,conc,dim	iso,elim	iso,seq	iso,conc,trim
0.04	0.00	0.96	0.01	0.02
0.1	0.00	0.87	0.01	0.12
0.25	0.01	0.53	0.00	0.46
0.5	0.01	0.22	0.00	0.77
1	0.00	0.07	0.00	0.93
1.5	0.00	0.03	0.00	0.97
2.5	0.00	0.01	0.00	0.99
4	0.00	0.00	0.00	0.99
6	0.00	0.00	0.00	1.00
10	0.00	0.00	0.00	1.00
15	0.00	0.00	0.00	1.00
25	0.00	0.00	0.00	1.00
50	0.00	0.00	0.00	1.00

Table S3: DRC Sensitivity Coefficients for 18% paired acid site percentage.

MeOH Partial						
Pressure (kPa)	iso,elim	iso,seq	iso,conc,trim	pair,dme,des	pair,elim	pair,conc,trim
0.04	0.86	0.01	0.02	0.00	0.09	0.01
0.1	0.76	0.00	0.11	0.00	0.08	0.04
0.25	0.42	0.00	0.37	0.00	0.05	0.14
0.5	0.16	0.00	0.56	0.00	0.02	0.25
1	0.04	0.00	0.57	0.00	0.01	0.37
1.5	0.02	0.00	0.54	0.00	0.00	0.44
2.5	0.01	0.00	0.49	0.00	0.00	0.50
4	0.00	0.00	0.47	0.00	0.00	0.53
6	0.00	0.00	0.45	0.00	0.00	0.54
10	0.00	0.00	0.44	0.01	0.00	0.56
15	0.00	0.00	0.42	0.01	0.00	0.57
25	0.00	0.00	0.40	0.01	0.00	0.58
50	0.00	0.00	0.37	0.02	0.00	0.61

Table S4: DRC Sensitivity Coefficients for 30% paired acid site percentage.

MeOH Partial						
Pressure (kPa)	iso,elim	iso,seq	iso,conc,trim	pair,dme,des	pair,elim	pair,conc,trim
0.04	0.79	0.01	0.02	0.00	0.16	0.01
0.1	0.68	0.00	0.10	0.00	0.15	0.06

0.25	0.36	0.00	0.31	0.00	0.09	0.23
0.5	0.12	0.00	0.44	0.00	0.04	0.39
1	0.03	0.00	0.42	0.00	0.01	0.53
1.5	0.01	0.00	0.38	0.00	0.01	0.60
2.5	0.00	0.00	0.34	0.00	0.00	0.66
4	0.00	0.00	0.31	0.00	0.00	0.68
6	0.00	0.00	0.30	0.00	0.00	0.70
10	0.00	0.00	0.28	0.01	0.00	0.71
15	0.00	0.00	0.27	0.01	0.00	0.72
25	0.00	0.00	0.26	0.02	0.00	0.73
50	0.00	0.00	0.23	0.03	0.00	0.74

 Table S5: DRC Sensitivity Coefficients for 44% paired acid site percentage.

MeOH Partial						
Pressure (kPa)	iso,elim	iso,seq	iso,conc,trim	pair,dme,des	pair,elim	pair,conc,trim
0.04	0.69	0.01	0.02	0.00	0.26	0.02
0.1	0.58	0.00	0.08	0.00	0.23	0.10
0.25	0.28	0.00	0.25	0.00	0.12	0.33
0.5	0.09	0.00	0.32	0.00	0.05	0.53
1	0.02	0.00	0.29	0.00	0.02	0.67
1.5	0.01	0.00	0.25	0.00	0.01	0.73
2.5	0.00	0.00	0.22	0.00	0.00	0.77
4	0.00	0.00	0.20	0.00	0.00	0.80
6	0.00	0.00	0.19	0.01	0.00	0.81
10	0.00	0.00	0.18	0.01	0.00	0.81
15	0.00	0.00	0.17	0.01	0.00	0.82
25	0.00	0.00	0.16	0.02	0.00	0.82
50	0.00	0.00	0.14	0.03	0.00	0.83

# Section S.2. Benchmarking Methanol Dehydration Turnover Rates and Kinetic Parameters using Commercial MFI Samples

We previously measured methanol dehydration turnover rates (per H<sup>+</sup>) on two commercially sourced MFI samples (MFI(43,C) (CBV8014, Si/Al = 43, Zeolyst) and MFI(31,C) (CBV3024E, Si/Al = 31, Zeolyst) at 433 K [1] and compared these values with turnover rates reported by Jones et al. at 433 K [2] in order to benchmark our rate measurements. In our prior report [1], we observed that dimethyl ether (DME) formation rates (per H<sup>+</sup>) at 433 K were ~4x higher than those reported by Jones et al. [2], and these rates were calculated based on absolute response factors in the flame ionization detector (FID) in our gas chromatograph (GC) determined from direct injections of methane, methanol and DME standards into the heated GC inlet [1] (Table S6; "Prior work"). We recently re-calibrated the FID using methanol and DME response factors (relative to methane) determined by co-feeding methane along with methanol and DME standards at various concentrations via heated transfer lines into the GC sample valve (Table S6; "This work"), which resulted in relative RF values similar to those documented in the literature based on effective carbon number predictions (Table S6, "Literature") [3, 4].

	Prior work <sup>b</sup>	This work	Literature[3]	Literature[4]
Dimethyl ether	0.88	1.20	1 <sup>3</sup>	-
Methanol	2.49	0.95	$0.5^{3}$	$0.5, 0.75^4$

Table S6: Response factors (RF)<sup>a</sup> of DME and methanol (relative to methane) in the FID.

 ${}^{a}RF = (area / mole fraction)_{component} / (area / mole fraction)_{methane}$ 

<sup>b</sup>Response factor used in [1, 5-7].

<sup>3</sup>Response factor calculated based on the contribution of different functional groups to the effective carbon number (ECN) of a compound reported in Table I of [3].

<sup>4</sup>Response factor listed in Appendix A of [4]. There are two response factors for methanol listed in this literature report.

With these new relative response factors, we re-measured DME formation rates (per H<sup>+</sup>) at 433 K and 0–20 kPa CH<sub>3</sub>OH on MFI(43,C) to be within ~1.8x of the rates measured at 433 K on MFI(43,C) by Jones et al. [8] (Fig. S5). Rate data were measured between 393–456 K and fitted to a Langmuirian rate expression derived from the associative mechanism (Eq. S.1) [8] to estimate first-order and zero-order (in CH<sub>3</sub>OH pressure) rate constants as a function of temperature.

$$\frac{r_{DME}}{[L]} = \frac{k_{first}P_{CH_3OH}}{1 + \frac{k_{first}}{k_{zaro}}P_{CH_3OH}}$$
(S.1)

The Eyring equation was then used to estimate apparent activation enthalpies and entropies (Fig. S6), which are listed in Table S7 along with values reported by Di Iorio et al. [1] and Jones et al. [8] (Table S7). Activation enthalpies were identical, within experimental error, across all three reports. The differences in FID response factors between this work and Di Iorio et al. [1] led to more negative activation entropies estimated in this work (Table S7), and to activation Gibbs free energies that were within error of the values reported by Jones et al. [8]. These data indicate that methanol dehydration rates (433 K, per H<sup>+</sup>) measured with the new FID response factors were adequately benchmarked to this prior literature report [8]. Thus, from re-analysis of our previous data and repeated measurements of these data, the experimental methanol dehydration rate and rate constant values reported in our prior work [1, 5-7] should be divided by a factor of 3.6x before comparing to predictions of rates and rate constants from theoretical models.



Figure S5: Methanol dehydration rates (per H<sup>+</sup>) on MFI(43,C) measured at 433 K (black, ■) and rates reported by Jones et al. [8] (red, •). Solid lines are regressions of the data to Eq. (S.1).



**Figure S6**: First-order (closed) and zero-order (open) methanol dehydration rate constants (per  $H^+$ ) on MFI(43,C) measured as a function of temperature (393–456 K). Solid lines are regressions of the data to the Eyring equation.

 Table S7: Activation parameters for first-order and zero-order kinetic regimes, with apparent Gibbs free energies at 433 K on MFI(43,C) measured in prior work [1], this work, and reported by Jones et al. [8].

	Di Iorio et al. [1]	This work	Jones et al. [8]
$\Delta H_{\text{first}} (\text{kJ mol}^{-1})$	$48\pm5$	$46\pm7$	42 ±2
$\Delta H_{zero} (kJ mol^{-1})$	$93 \pm 5$	$87 \pm 14$	90 ±2
$\Delta S_{\text{first}} (J \text{ mol}^{-1} \text{ K}^{-1})$	$-149 \pm 8$	$-195 \pm 33$	-160 ±10
$\Delta S_{zero} (J \text{ mol}^{-1} \text{ K}^{-1})$	$-58 \pm 7$	$-84 \pm 16$	-75 ±2
$\Delta G_{\text{first}} (\text{kJ mol}^{-1})$	$112 \pm 10$	$130\pm16$	111 ±9
$\Delta G_{zero} \ (kJ \ mol^{-1})$	$119\pm10$	$123\pm15$	123 ±3

#### Section S.3. Statistics Mechanics Formulas Used to Calculate H, G, and S values

Enthalpies (H), Gibbs free energies (G), and entropies (S) are computed from DFTderived vibrational frequencies using statistical mechanics as a sum of their constitutive vibrational, translational, and rotational parts with the corresponding zero-point vibrational energy (ZPVE) and electronic energy at 415 K:

$$H = E_0 + ZPVE + H_{vib} + H_{trans} + H_{rot}$$
(S.2)

$$G = E_0 + ZPVE + G_{vib} + G_{trans} + G_{rot}$$
(S.3)

Only adsorbates, protons, and AlO<sub>4</sub> tetrahedra were permitted to move during frequency calculations in zeolites and all motions of adsorbates were modeled as vibrations (i.e., translations and rotations were considered frustrated). The vibrational components—ZPVE,  $H_{vib}$ , and  $G_{vib}$ —were calculated as

$$ZPVE = \sum_{i} \left(\frac{1}{2}h\nu_{i}\right) \tag{S.4}$$

$$H_{vib} = \sum_{i} \frac{hv_i e^{-\frac{hv_i}{kT}}}{1 - e^{-\frac{hv_i}{kt}}}$$
(S.5)

$$G_{vib} = \sum_{i} \left( -kT \ln\left(\frac{1}{1 - e^{-\frac{hv_i}{kT}}}\right) \right)$$
(S.6)

Translational and rotational components were calculated for gas-phase species only, using similar formalisms:

$$H_{trans} = \frac{5}{2}kT \tag{S.7}$$

$$H_{rot,linear} = kT \tag{S.8}$$

$$H_{rot,nonlinear} = \frac{3}{2}kT \tag{S.9}$$

$$G_{trans} = -kT \ln\left(\left(\frac{2\pi mkT}{h^2}\right)^{\frac{3}{2}}V\right)$$
(S.10)

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$$G_{rot} = -kT \ln\left(\frac{\pi^{\frac{1}{2}}}{\sigma} \left(\frac{T^{3}}{\theta_{x} \theta_{y} \theta_{z}}\right)^{\frac{1}{2}}\right)$$
(S.11)

$$\theta_i = \frac{h^2}{8\pi k I_i} \tag{S.12}$$

where  $I_i$  is the moment of inertia about the *i* axis (where i = x, y, z) and  $\sigma$  is the symmetry number of the species [9].

## Section S.4. DFT-calculated Methanol Cluster Structures

Cluster size	Number of configurations				
Cluster size	NNN site-pair	NNNN site-pair			
2 CH <sub>3</sub> OH	637	242			
3 CH <sub>3</sub> OH	443	242			
4 CH <sub>3</sub> OH	219	145			
5 CH <sub>3</sub> OH	328	286			
6 CH <sub>3</sub> OH	431	656			
7 CH <sub>3</sub> OH	398	1302			
8 CH <sub>3</sub> OH	483	1147			
9 CH <sub>3</sub> OH	482	1315			
10 CH <sub>3</sub> OH	486	378			
11 CH <sub>3</sub> OH	483	458			
12 CH <sub>3</sub> OH	642	435			

 Table S8: The number of configurations tested for each respective cluster size on NNN and NNNN site pairs in this work.



**Figure S7**: The most stable structure on the NNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) one ( $\theta = 0.5$ ), (b) two ( $\theta = 1.0$ ), (c) three ( $\theta = 1.5$ ), and (d) four ( $\theta = 2.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.



**Figure S8**: The most stable structure on the NNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) five ( $\theta = 2.5$ ), (b) six ( $\theta = 3.0$ ), (c) seven ( $\theta = 3.5$ ), and (d) eight ( $\theta = 4.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.



**Figure S9**: The most stable structure on the NNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) nine ( $\theta = 4.5$ ), (b) ten ( $\theta = 5.0$ ), (c) eleven ( $\theta = 5.5$ ), and (d) twelve ( $\theta = 6.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.



**Figure S10**: The most stable structure on the NNNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) one ( $\theta = 0.5$ ), (b) two ( $\theta = 1.0$ ), (c) three ( $\theta = 1.5$ ), and (d) four ( $\theta = 2.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.



**Figure S11**: The most stable structure on the NNNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) five ( $\theta = 2.5$ ), (b) six ( $\theta = 3.0$ ), (c) seven ( $\theta = 3.5$ ), and (d) eight ( $\theta = 4.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.



**Figure S12**: The most stable structure on the NNNN site pair shown down the *c*-axis (left) and *b*-axis (right) of the CHA unit cell with (a) nine ( $\theta = 4.5$ ), (b) ten ( $\theta = 5.0$ ), (c) eleven ( $\theta = 5.5$ ), and (d) twelve ( $\theta = 6.0$ ) total methanol molecules adsorbed. Differential binding enthalpies ( $\Delta H_{diff}$ ) and free energies ( $\Delta G_{diff}$ ) are shown in kJ mol<sup>-1</sup> and differential binding entropies ( $\Delta S_{diff}$ ) are shown in J mol<sup>-1</sup> K<sup>-1</sup>.

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