Supplemental Information

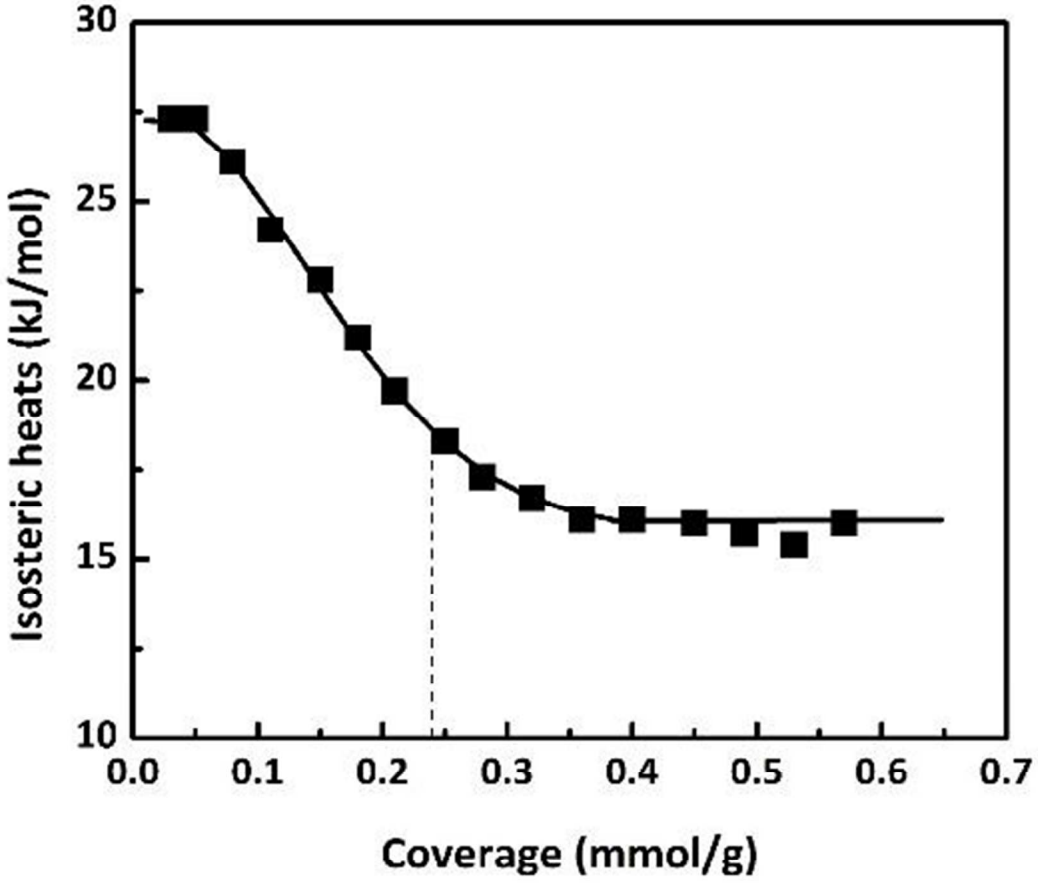

Figure S1. CO adsorption on the defect free H-ZSM-5(F,Al) at 195 K. The dashed line is shown at the Brønsted-site concentration.

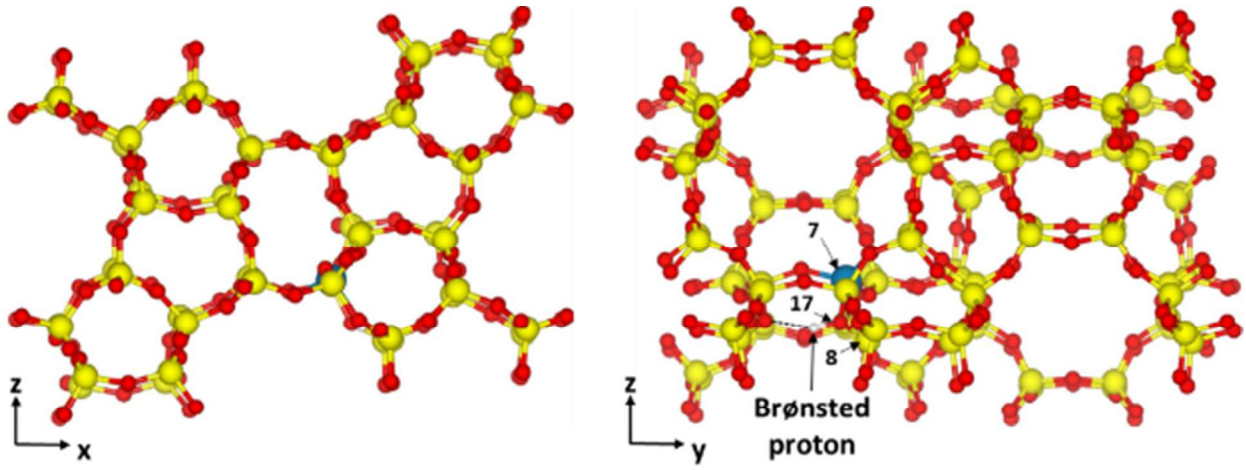

Figure S2: Zeolite ZSM-5 with the most stable location of Brønsted site (Al7-O17-Si8). The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. The dashed line indicates a hydrogen bond between the Brønsted proton and a nearby oxygen atom. Key: Oxygen (●), silicon (●), aluminum (●), and hydrogen (○).

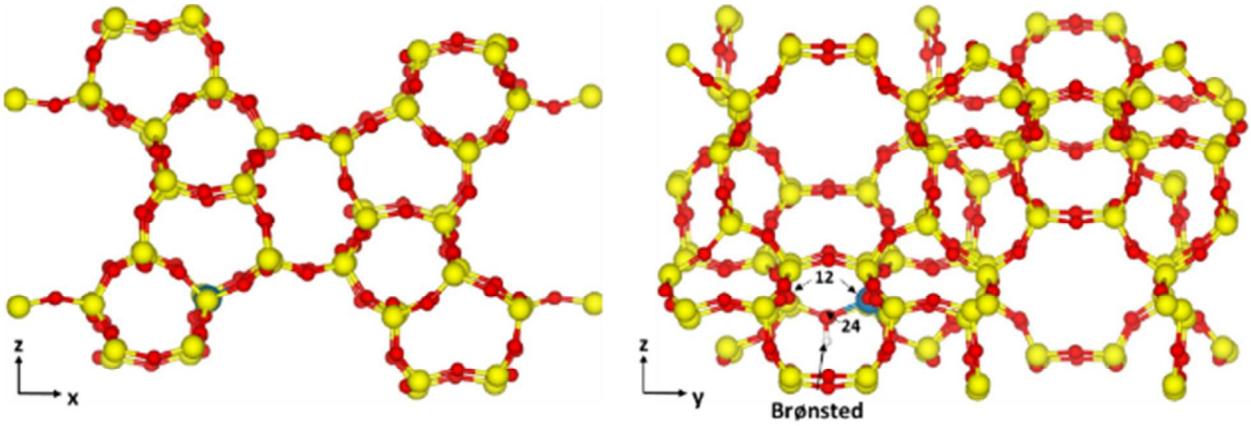

Figure S3: Zeolite ZSM-5 with a Brønsted site (Al12-O26-Si12) at the intersection of straight and sinusoidal channels. The left hand side shows the view perpendicular to the axis of the straight channel. The right hand side explicitly shows the structure along the axis of the straight channel. Key: Oxygen (●), silicon (●), aluminum (●), and hydrogen (○).

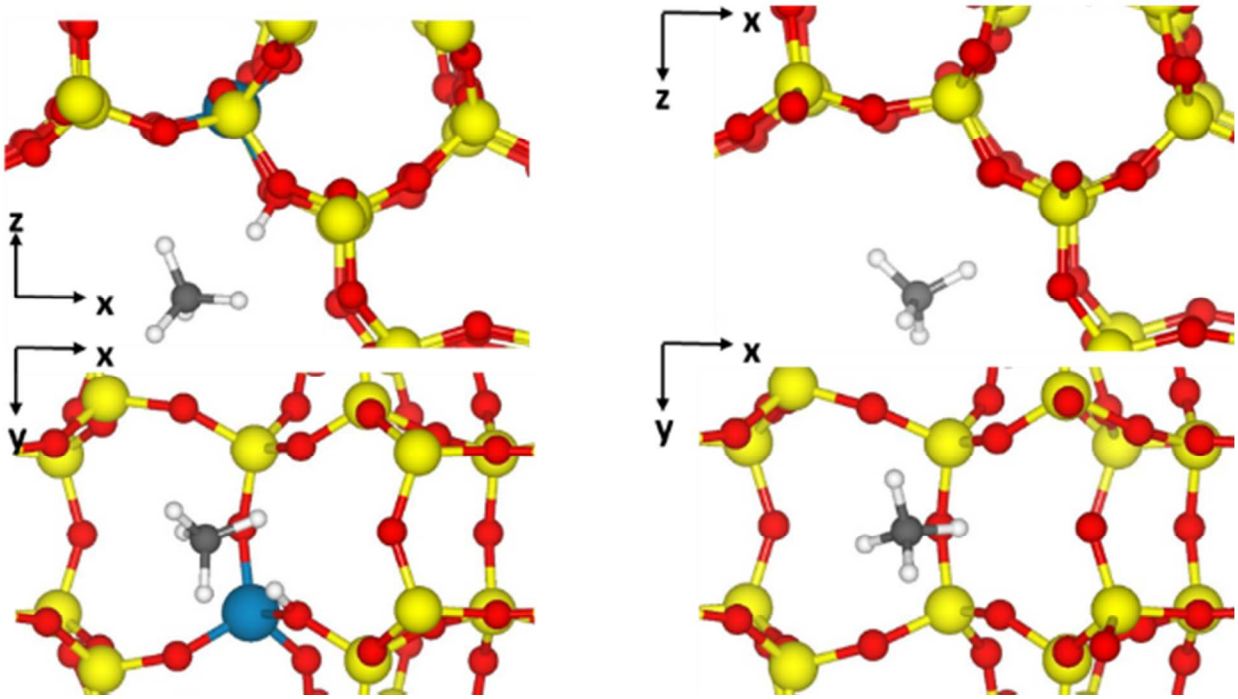

Figure S4: Preferred CH_4 adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Two views (top and bottom) are shown for comparison on the CH_4 location in the presence and absence of Brønsted proton. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

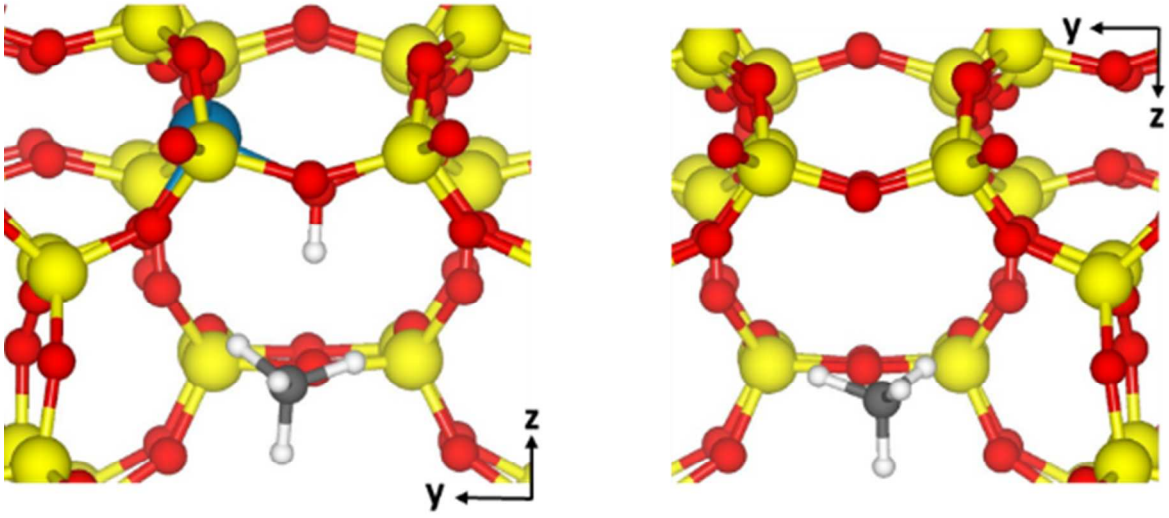

Figure S5: Preferred CH_4 adsorbed state on T12-O26-T12 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

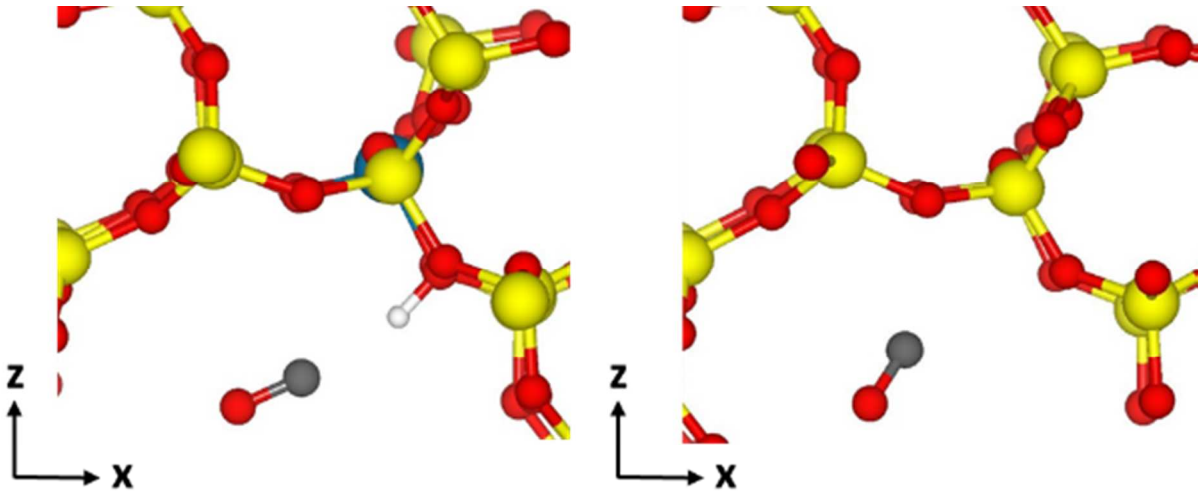

Figure S6: Preferred CO adsorbed state on T7-O17-T8 location with a Brønsted site (left) and in purely siliceous form (right) in zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

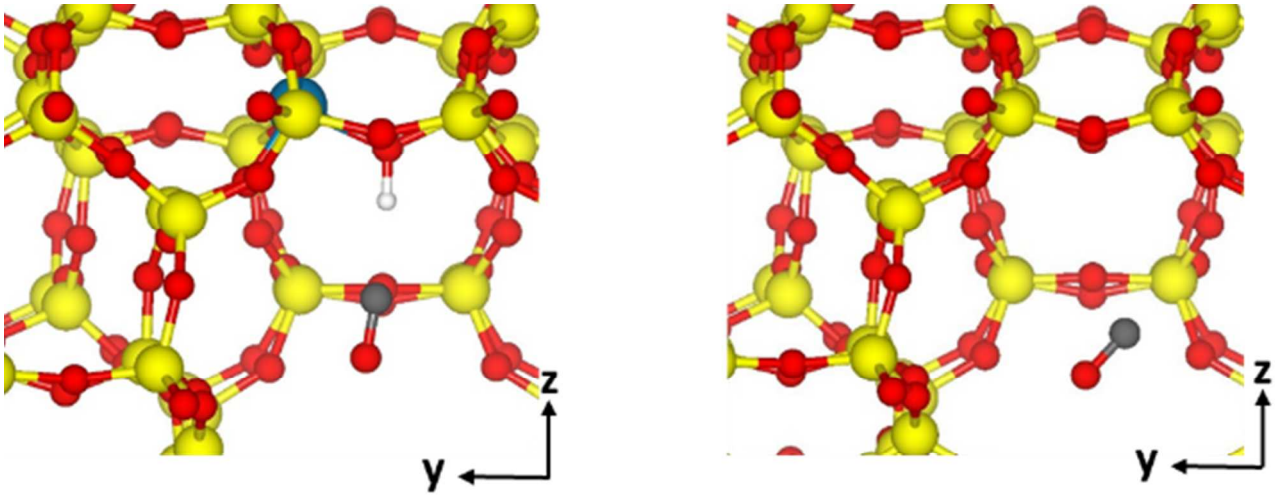

Figure S7: Preferred CO adsorbed state on T12-O26-T12 location a with Brønsted site (left) and in purely siliceous (right) form of zeolite ZSM-5. Key: Oxygen (●), silicon (●), aluminum (●), carbon (●), and hydrogen (○).

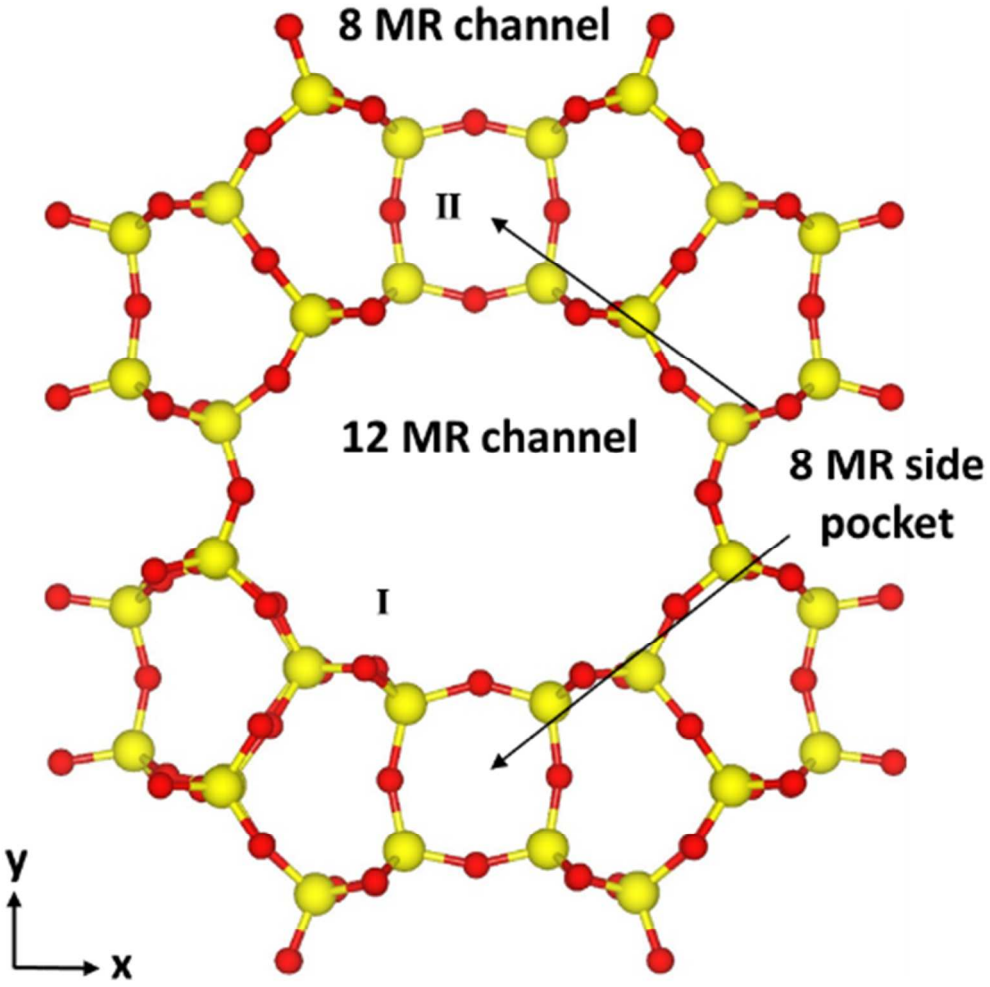

Figure S8: Siliceous mordenite (MOR) showing the channels along z axis. Two channels with eight (8 MR) and twelve (12 MR) membered-ring openings and a side pocket with eight membered ring opening (8 MR side pocket). Two regions of adsorption have been marked – 12 MR channel near the walls (I) and 8 MR side pocket (II). Key: Oxygen (●) and silicon (●).

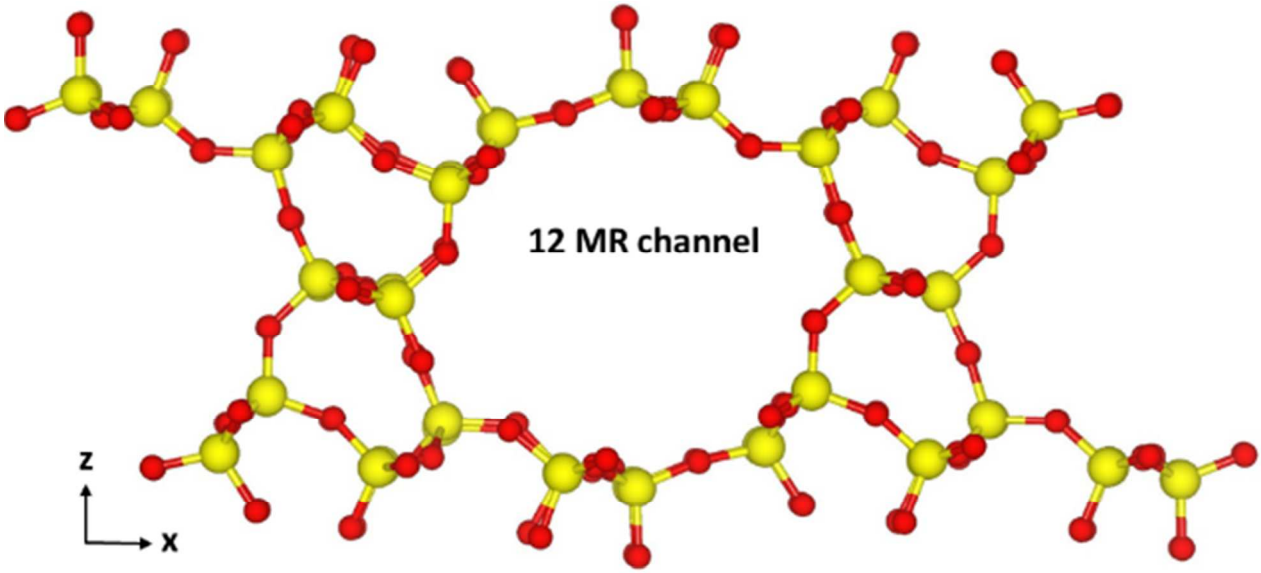

Figure S9: Siliceous ZSM-12 showing the channel along z axis. Adsorption is in the channel with 12 membered ring opening (12 MR channel). Key: Oxygen (●) and silicon (●).

Method S1 Calculating temperature-dependent thermochemistry of adsorption in zeolites.

Shomate equations were derived for the thermochemistry of adsorbed and gas phase species. These equations are defined as:

$$t = \frac{T[K]}{1000}$$

$$C_P\left[\frac{J}{mol}.K\right] = A + Bt + Ct^2 + Dt^3 + {}^{E}/_{t}$$

$$H\left[\frac{kJ}{mol}\right] = At + B\,{}^{t^2}/_{2} + C\,{}^{t^3}/_{3} + D\,{}^{t^4}/_{4} - {}^{E}/_{t} + F$$

$$S\left[\frac{J}{mol}.K\right] = Aln(t) + Bt + C\,{}^{t^2}/_{2} + D\,{}^{t^3}/_{3} - {}^{E}/_{2t^2} + G$$

The procedure for the calculation of these parameters is as follows:

I. Calculate entropy of species at different temperatures
II. Fit the Shomate expression for entropy to this data set
III. Extract parameters A, B, C, D, and E from the fit, and fix F to H at a reference temperature. Here, we choose the reference temperature to be 10 K and H = E + ZPE where E is the total energy of the species calculated using DFT and ZPE is the zero point energy.

The entropy of the species is calculated by summing together translational, rotational, and vibrational components.

$$S = S_{trans} + S_{rot} + S_{vib}$$

For gas phase, the translational entropy is calculated assuming 3D translational freedom while rotational entropy is calculated based on the moments of inertia and symmetry. The vibrational term is calculated using the harmonic approximation (Gokhale et al. Chem Eng. Sci 2004, 59, 4679). For the adsorbed species, a 2D translational freedom is assumed (given in Equation 3 in the manuscript). The Hessian matrix is transformed to remove the modes corresponding to translation before diagonalization. All rotations are assumed to be frustrated vibrations. The translational surface area was assumed based on the estimates given by De Moor et al. (J Phys Chem C. 2011, 115, 1204); values for MTW were taken to be the same as FAU.

For the calculation of vibrational entropy values, we assumed a minimum cutoff of 100 cm^{-1}. All values lower than this were re-set to this cutoff value and all spurious imaginary frequencies were set to 100. A careful analysis of the sensitivity of this minimum value on the thermochemistry revealed that the entropy values vary within 10 J/mol-K and enthalpy by 2-4 kJ/mol.

Table S1. Calculated binding energy (ZPE corrected) values for CO and CH_4 (in eV) on Brønsted and non-Brønsted forms of two sites in ZSM-5 (1eV ~ 96.5 kJ/mol).

Adsorbate	T7-O17-T8[a]		T12-O26-T12[a]	
	Brønsted[b]	Non-Brønsted[b]	Brønsted[b]	Non-Brønsted[b]
CO	-0.27	-0.17	-0.39	-0.19
Methane	-0.27	-0.24	-0.38	-0.23

[a] "T" refers to the tetrahedral atom that is either Si or Al atom; [b] "Brønsted" refers to adsorption on a Brønsted site formed by replacing a Si atom of Tx-Oy-Tz site by Al atoms and adding a hydrogen to the oxygen atom "y". For T7-O17-T8, Al replaces a Si atom in the tetrahedral position 7 and for T12-O24-T12 Al replaces Si atom in the tetrahedral position 12.

Table S2. Calculated enthalpy of adsorption for CH_4 (in kJ/mol) on the T12-O8-T3 Brønsted and non-Brønsted forms of ZSM-5

Adsorbate	T12-O8-T3	
	Brønsted	Non-Brønsted
Methane	-24.8	-21.2

Note: T12-O8-T3 site is topologically equivalent to T12-O20 site of Tuma and Sauer (Journal of Chemical Physics (2010), 143, 102810). "Brønsted" refers to adsorption on a Brønsted site formed by replacing a Si atom of Tx-Oy-Tz site by Al atoms and adding a hydrogen to the oxygen atom "y". For T12-O8-T3, Al replaces Si atom in the position 12.

Table S3. Difference in methane binding energies between Brønsted and non-Brønsted T12-O26-T12 site of ZSM-5 using different functionals and dispersion treatments.

Method	Dispersion-corrected	Difference [eV (kJ/mol)]
Reference (PBE+D2)	Yes	0.17 (16.3)
PBE	No	0.16 (15.1)
PW9	No	0.16 (15.3)
RPBE	No	0.13 (11.8)
PBE + D3	Yes	0.16 (15.1)
PBEsol	No	0.20 (19.2)

Table S4: ZPE corrected binding energy of CH_4, O_2, and Ar in the two adsorption regions of MOR. All binding energy values are in eV (1eV ~ 96.5 kJ/mol).

Adsorbate	12 MR channel	8 MR side pocket
CH_4	-0.20	-0.31
O_2	-0.13	-0.19
Ar	-0.14	-0.21

Table S5: ZPE corrected binding energy of CH_4, O_2, and Ar in ZSM-12. All binding energy values are in eV (1eV ~ 96.5 kJ/mol).

Adsorbate	Binding energy (eV)
CH_4	-0.23
O_2	-0.13
Ar	-0.17

Table S6: Vibrational frequencies (cm^{-1}) of methane adsorbed on HZSM-5.

Vibrational frequencies were calculated by diagonalizing a numerically derived Hessian obtained using finite differences. Atom displacement of 0.015 Angstrom with an SCF convergence of 10^{-8} eV was used to calculate the Hessian. The energy cutoff was taken to be 400 eV.

In some cases, spurious imaginary frequencies were observed, identified by their small magnitude (<100 cm-1). These spurious values arise as a result of approximation errors in energy calculations and are expected to vanish with more accurate calculations. In such cases, different atom displacements, SCF convergence values and higher energy cutoffs were tried to ensure that these frequencies indeed vanish. However, since all calculations were to be carried out at the same level of theory, these are replaced by a cutoff value of 100 cm^{-1} in thermochemistry calculations.

Adsorbate	T7-O17	T12-O26	T12-O8
Methane (HZSM-5)	*29.0i*, 94.7, 166.0, 194.9, 356.6, 1040.8, 1279.5, 1289.0, 1293.9, 1509.8, 1515.6, 2930.3, 3054.6, 3060.0, 3070.5, 3357.4	*41.5i*, 75.2, 126.9, 182.1, 411.0, 1013.7, 1274.4, 1283.4, 1298.5, 1504.3, 1513.2, 2930.7, 3047.5, 3060.4, 3077.5, 3427.0	94.6, 107.2, 173.5, 196.4, 419.9, 1041.1, 1283.8, 1291.4, 1294.8, 1516.6, 1517.8, 2924.1, 3046.6, 3055.9, 3066.2, 3357.6
Methane (ZSM-5)	20.0, 48.5, 54.5, 98.7, 1279.5, 1280.9, 1282.5, 1498.6, 1500.1, 2948.8, 3064.7, 3074.6, 3088.1	21.2, 39.3, 52.5, 63.7, 1278.4, 1280.8, 1281.7, 1497.0, 1499.6, 2948.9, 3072.4, 3073.7, 3076.8	

Note: Italicized and underlined numbers are spurious imaginary frequencies (identified by those that are imaginary with a magnitude < 100) resulting from numerical errors in the finite difference method used to calculate the Hessian. While these numbers vanished when higher cutoffs were tried, we report these numbers because they were used in the calculation of

thermochemical quantities. -The largest frequency value in HZSM-5 refers to the stretching frequency of the OH bond of the Bronsted site (in the presence of the adsorbate).