Supporting Information

A Universal Descriptor for the Entropy of Adsorbed Molecules in Confined Spaces

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Table S1-A. Gas phase entropy and adsorption entropy of hydrocarbons in FAU

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	300	5.7	32.5	Grav/cal	1
2	Butane	3	9.9	37.3	Grav/cal	2
3	Butane	300	8.1	37.3	Grav/cal	1
4	2-methylpropane	300	7.6	30.0	Grav/cal	1
5	Pentane	30	9.0	41.8	IGC	3
6	Pentane	13	8.1	41.8	IGC	3
7	Pentane	3	8.2	41.8	IGC	3
8	Pentane	3	10.5	41.8	Grav/cal	2
9	Pentane	300	10.8	41.8	Grav/cal	1
10	2-methylbutane	300	10.0	41.4	Grav/cal	1
11	Hexane	30	9.5	46.8	IGC	3
12	Hexane	13	8.8	46.8	IGC	3
13	Hexane	3	8.6	46.8	IGC	3
14	Hexane	3	11.1	46.8	Grav/cal	2
15	Hexane	300	11.5	46.8	Grav/cal	1
16	Heptane	30	10.4	51.5	IGC	3
17	Heptane	13	9.4	51.5	IGC	3
18	Heptane	3	9.0	51.5	Grav/cal	2
19	Octane	30	11.1	56.2	IGC	3
20	Octane	13	10.0	56.2	IGC	3
21	Octane	3	9.5	56.2	IGC	3
22	Octane	300	11.5	56.2	Grav/cal	1
23	Nonane	30	11.8	60.9	IGC	3
24	Nonane	13	10.4	60.9	IGC	3
25	Nonane	3	10.0	60.9	IGC	3

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-B. Gas phase entropy and adsorption entropy of hydrocarbons in TON

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	54	12.5	32.5	Grav/cal	4
2	Butane	54	14.9	37.3	Grav/cal	4
3	2-methylpropane	54	11.9	30.0	Grav/cal	4
4	Pentane	30	13.4	41.8	IGC	5
5	Pentane	54	16.8	41.8	Grav/cal	4
6	2-methylbutane	54	14.3	41.4	Grav/cal	4
7	Hexane	30	15.3	46.8	IGC	5
8	Hexane	54	18.7	46.8	Grav/cal	4
9	Heptane	30	17.3	51.5	IGC	5
10	Octane	30	19.1	56.2	IGC	5
11	Nonane	30	20.6	60.9	IGC	5

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-C. Gas phase entropy and adsorption entropy of hydrocarbons in MFI

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	20	10.7	32.5	FT-IR	6
2	Propane	29	10.9	32.5	FT-IR	6
3	Propane	75	11.4	32.5	FT-IR	6
4	Propane	35	12.3	32.5	Grav/Cal	7
5	Propane	35	11.3	32.5	Grav/Cal	3
6	Butane	29	12.6	37.3	FT-IR	6
7	Butane	35	14.3	37.3	Grav/cal	7
8	Butane	35	12.5	37.3	Grav/cal	3
9	Pentane	20	14.2	41.8	FT-IR	6
10	Pentane	29	14.3	41.8	FT-IR	6
11	Pentane	75	14.4	41.8	FT-IR	6
12	Pentane	35	16.2	41.8	Grav/Cal	7
13	Pentane	35	14.2	41.8	Grav/Cal	3
14	Pentane	137	13.1	41.8	IGC	3
15	2-methylbutane	137	14.4	41.3	IGC	8
16	Hexane	20	17.4	46.8	FT-IR	6
17	Hexane	29	16.6	46.8	FT-IR	6
18	Hexane	75	17.6	46.8	FT-IR	6
19	Hexane	35	18.3	46.8	Grav/Cal	7
20	Hexane	35	14.6	46.8	Grav/Cal	3
21	Hexane	137	14.7	46.8	IGC	3
22	Hexane	137	16.0	46.8	IGC	8
23	2-methylpentane	137	16.1	45.8	IGC	8
24	3-methylpentane	137	16.1	46.1	IGC	8
25	2,2-dimethlybutane	137	16.1	43.1	IGC	8
26	2,3-dimethlybutane	137	16.0	44.0	IGC	8
27	Heptane	20	19.4	51.5	FT-IR	6
28	Heptane	29	20.9	51.5	FT-IR	6
29	Heptane	75	20.3	51.5	FT-IR	6
30	Heptane	137	16.2	51.5	IGC	3
31	Heptane	137	17.6	51.5	IGC	8
32	2-methylhexane	137	17.9	50.5	IGC	8
33	3-methylhexane	137	17.9	51.2	IGC	8
34	2,3 dimethylpentane	137	18.0	49.8	IGC	8
35	Octane	137	17.8	56.2	IGC	3
36	Octane	137	19.3	56.2	IGC	8
37	2-methylheptane	137	19.4	55.3	IGC	8
38	3-methylheptane	137	19.5	56.0	IGC	8
39	4-methylheptane	137	19.5	55.0	IGC	8

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-D. Gas phase entropy and adsorption entropy of hydrocarbons in FER

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	30	12.3	32.5	Grav/cal	4
2	Butane	30	15.8	37.3	Grav/cal	4
3	Pentane	30	17.6	41.8	Grav/cal	4
4	Hexane	30	18.8	46.8	Grav/cal	4

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-E. Gas phase entropy and adsorption entropy of hydrocarbons in CHA

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Methane	14	7.6	22.4	Grav/cal	9
2	Ethane	14	9.2	27.6	Grav/cal	9
3	Propane	14	10.5	32.5	Grav/cal	9
4	Methane	3	7.8	22.4	Volumetric	10
5	Ethane	3	8.5	27.6	Volumetric	10
6	O_2	3	7.3	24.7	Volumetric	11
7	N_2	3	9.6	23.0	Volumetric	11
8	Ne	3	6.7	17.6	Volumetric	11
9	Ar	3	7.4	18.6	Volumetric	11
10	Kr	3	7.4	19.7	Volumetric	11
11	Xe	3	7.6	20.4	Volumetric	11

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-F. Gas phase entropy and adsorption entropy of hydrocarbons in MOR

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	10	10.2	32.5	Grav/cal	2
2	Butane	10	10.7	37.3	Grav/cal	2
3	Pentane	5	10.5	41.8	IGC	3
4	Pentane	10	11.5	41.8	Grav/cal	2
5	Hexane	5	11.2	46.8	IGC	3
6	Hexane	10	12.5	46.8	Grav/cal	2
7	Heptane	5	12.4	51.5	IGC	3
8	Octane	5	13.2	56.2	IGC	3
9	Nonane	5	14.0	60.9	IGC	3

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-G. Gas phase entropy and adsorption entropy of hydrocarbons in KFI

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Propane	4	10.2	32.5	Grav/cal	4
2	Butane	4	12.1	37.3	Grav/cal	4
3	Pentane	4	13.2	41.8	Grav/cal	4
4	Hexane	4	13.3	46.8	Grav/cal	4

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-H. Gas phase entropy and adsorption entropy of hydrocarbons in BEA

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Pentane	12	9.3	41.8	IGC	3
2	Hexane	12	10.2	46.8	IGC	3
3	Heptane	12	11.2	51.5	IGC	3
4	Octane	12	12.1	56.2	IGC	3
5	Nonane	12	13.2	60.9	IGC	3

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

Table S1-I. Gas phase entropy and adsorption entropy of hydrocarbons in LTL

Entry	Adsorbate	Si/Al	$-\Delta S_{ads}°/R$	$S_{gas}°/R$	method[a]	ref.
1	Methane	n.r.	8.5	22.4	Volumetric	10
2	Ethane	n.r.	9.9	27.6	Volumetric	10
3	Propane	n.r.	10.6	32.5	Volumetric	10
4	Butane	n.r.	11.2	37.3	Volumetric	10

a – adsorption entropies were measured using a combination of gravimetry and calorimetry (grav/cal), inverse gas chromatography (IGC), volumetric uptake and FT-IR.

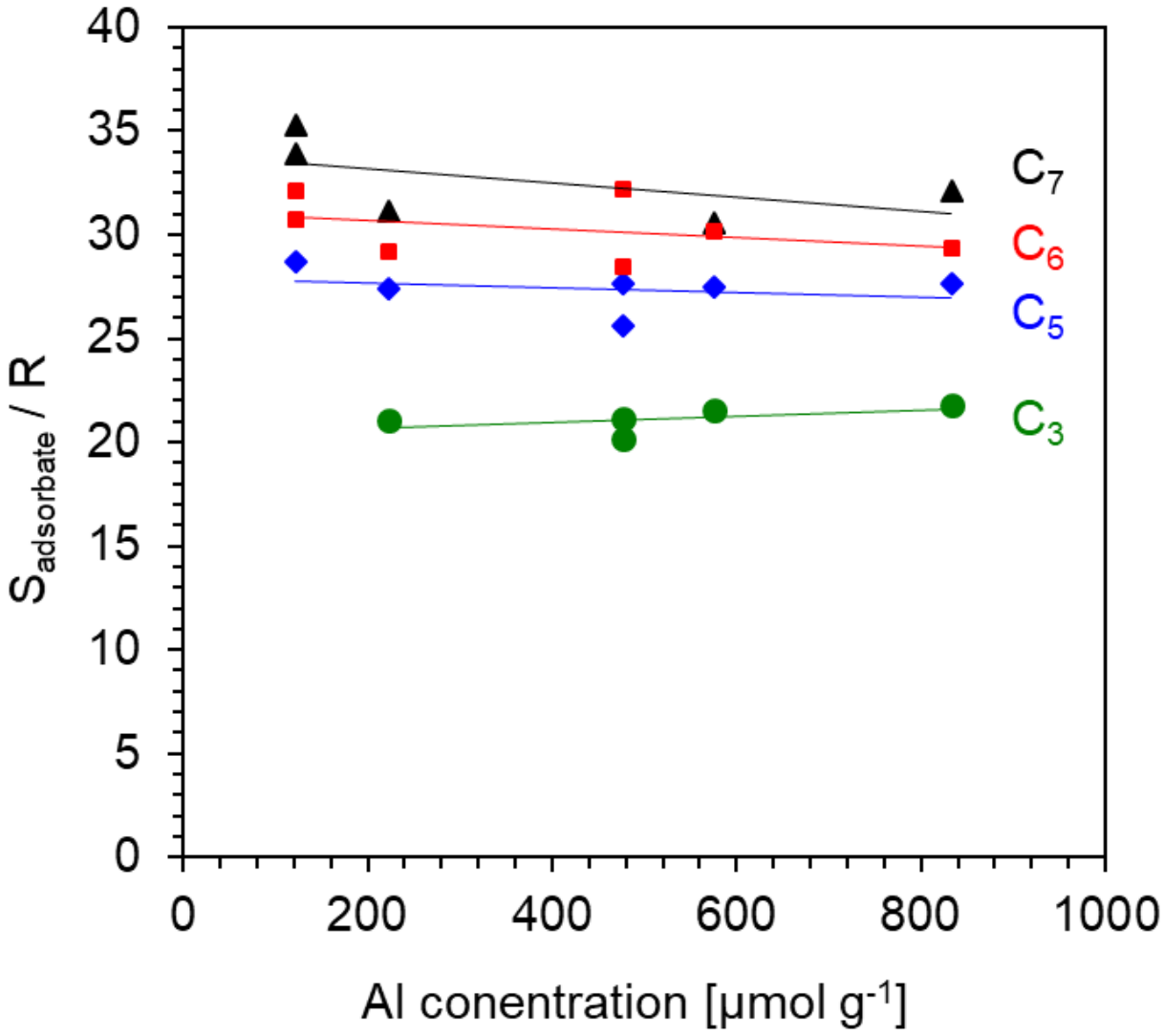

Figure S1. Adsorbate entropy for C3-C7 linear alkanes on MFI as a function of bulk Al concentration.

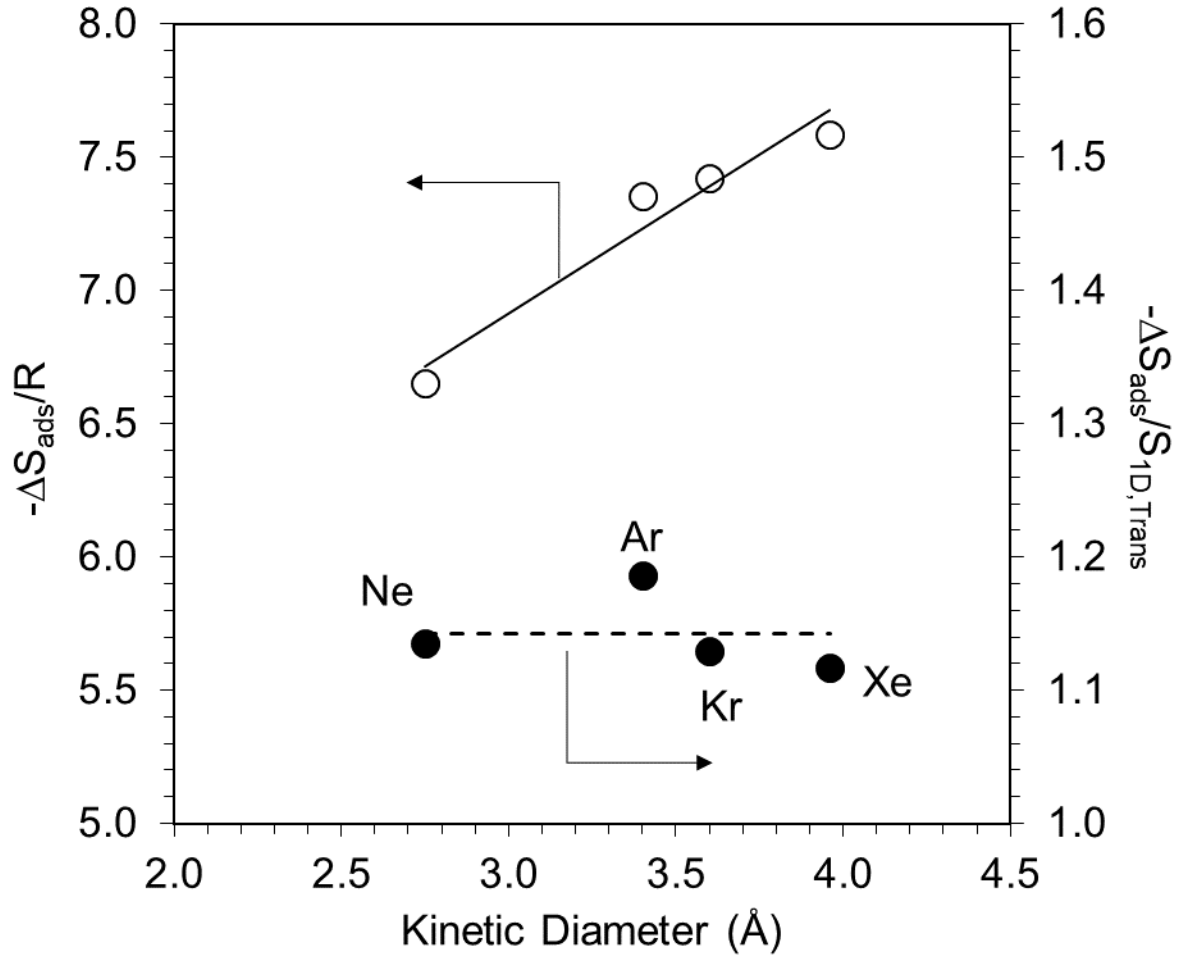

Figure S2. Experimentally measured entropy of adsorption (open symbols) for Ne, Ar, Kr and Xe on CHA (Si/Al = 3, Table S1-E), filled symbols indicate entropies of adsorption normalized by the entropy associated with one degree of translational freedom.

Table S2. Translational, rotational and molecular gas phase entropy of alkanes and permanent gases.

Entry	Molecule	S_{Trans}^0/R	S_{Rot}^0/R	S_{gas}^0/R[a]
1	H_2	14.1	1.5	15.7
2	O_2	18.3	5.3	24.7
3	N_2	18.1	5.0	23.0
4	Ne	17.6	0.0	17.6
5	Ar	18.6	0.0	18.6
6	Kr	19.7	0.0	19.7
7	Xe	20.4	0.0	20.4
8	Methane	17.2	4.9	22.4
9	Ethane	18.2	9.0	27.6
10	Propane	18.7	12.6	32.5
11	Butane	19.2	16.5	37.3
12	Pentane	19.5	19.9	41.8
13	Hexane	19.8	23.3	46.8
14	Heptane	20.0	26.8	51.5
15	Octane	20.2	30.4	56.2
16	Nonane	20.3	33.9	60.9
17	2-methylpropane	19.2	14.6	35.4
18	2-methylbutane	19.5	19.1	41.3
19	2-methylpentane	19.8	22.3	45.8
20	3-methylpentane	19.8	22.5	46.1
21	2,2-dimethlybutane	19.8	20.1	43.1
22	2,3-dimethlybutane	19.8	20.8	44.0
23	2-methylhexane	20.0	25.8	50.5
24	3-methylhexane	20.0	26.4	51.2
25	2,3 dimethylpentane	20.0	25.2	49.8
26	2-methylheptane	20.2	29.7	55.3
27	3-methylheptane	20.2	30.3	56.0
28	4-methylheptane	20.2	29.4	55.0

a – ref. S12

Table S3. Rotational and Translational degrees of freedom lost upon adsorption in different zeolite frameworks.

Framework	Rotational Degrees of Freedom Lost[a]	Translational Degrees of Freedom Lost[a]	Cavity Diameter (Å)
MFI	1.34	0.92	5.5
CHA	0.72	1.15	7.4
TON	0.99	1.35	5.0
FER	1.71	0.91	4.3
MOR	0.46	1.27	7.0
FAU	0.35	1.05	12.6
BEA	0.8	0.6	7.5
LTL	0.48	1.37	9.0
KFI	0.77	1.17	10.7

a - Degrees of freedom lost were obtained through non-linear least squares regression of Eq. 7 using experimental adsorption entropy data (Table S1) and calculated rotational/translational gas phase entropies (Table S2)

Table S4. Enthalpies and entropies of alkane adsorption in FER, TON, FAU, KFI, MFI, MOR and CHA frameworks.

Entry	Framework	Si/Al	Molecule	$-\Delta H_{ads}$ (kJ mol^{-1})	$-\Delta S_{ads}$ (J mol^{-1} K^{-1})	ref.
1	FER	30	Propane	49.0	102.6	4
2	FER	30	Butane	59.0	131.2	4
3	FER	30	Pentane	69.0	146.6	4
4	FER	30	Hexane	79.0	156.2	4
5	TON	52	Propane	49.0	103.8	4
6	TON	52	Butane	60.0	124.2	4
7	TON	52	Pentane	71.0	140.1	4
8	TON	52	Hexane	81.5	155.4	4
9	TON	52	Isobutane	47.5	99.0	4
10	TON	52	Isopentane	59.0	118.9	4
11	FAU	300	Propane	27.0	47.7	1
12	FAU	300	Butane	34.0	67.6	1
13	FAU	300	Pentane	41.0	89.4	1
14	FAU	300	hexane	47.0	95.6	1
15	FAU	300	Octane	61.0	95.9	1
16	FAU	300	Isobutane	33.0	63.5	1
17	FAU	300	Isopentane	39.0	83.5	1
18	FAU	3	Butane	39.0	82.0	2
19	FAU	3	Pentane	46.0	87.0	2
20	FAU	3	Hexane	53.0	92.0	2
21	KFI	4	Propane	47.0	85.0	4
22	KFI	4	Butane	52.0	100.5	4
23	KFI	4	Pentane	57.0	109.5	4
24	KFI	4	Hexane	60.0	110.9	4
25	MFI	35	Propane	41.0	94.0	3
26	MFI	35	Butane	52.0	104.0	3
27	MFI	35	Pentane	62.5	118.0	3
28	MFI	35	Hexane	72.0	121.0	3
29	MFI	35	Propane	46.0	102.0	2
30	MFI	35	Butane	58.0	119.0	2
31	MFI	35	Pentane	70.0	135.0	2
32	MFI	35	Hexane	82.0	152.0	2
33	MOR	10	Propane	41.0	85.0	2
34	MOR	10	Butane	50.0	89.0	2
35	MOR	10	Pentane	59.0	96.0	2
36	MOR	10	Hexane	69.0	104.0	2
37	CHA	14	Methane	17.0	63.5	9
38	CHA	14	Ethane	27.5	76.1	9
39	CHA	14	Propane	37.6	87.7	9

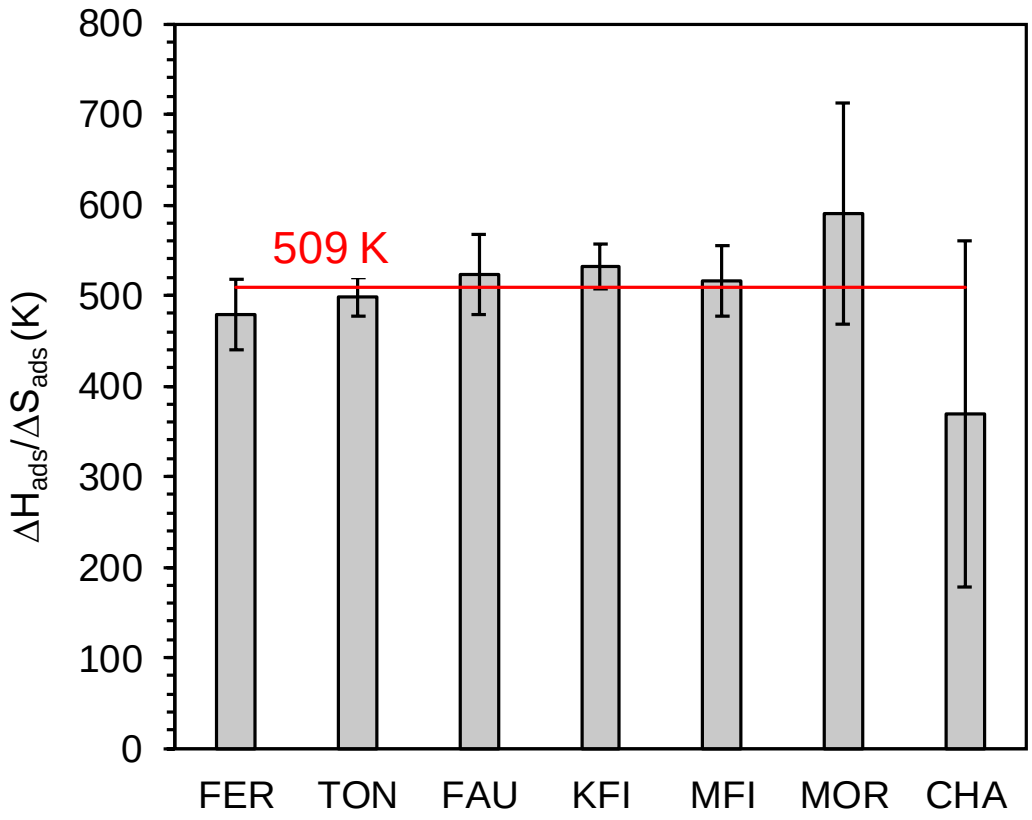

Figure S3. Ratio of the enthalpy-to-entropy of adsorption of the seven frameworks depicted in Figure 6A. Error bars represent a 95% confidence interval.

As per transition state theory, the desorption pre-exponential factor can be defined based on the ratio of the partition function of the transition and adsorbed state,

$$\nu_{des} = \frac{k_b T}{h} \frac{Q_{TS}}{Q_{ads}} \tag{S1}$$

Recasting this in terms of entropy, the desorption pre-exponential factor can be defined as,

$$\nu_{des} = \frac{k_b T}{h} e^{\frac{\Delta S_{TS,des}}{R}} \tag{S2}$$

The change in entropy associated with approaching the transition state of desorption starting from the adsorbed state is,

$$\Delta S_{TS,des} = S_{TS,des} - S_{ads} \tag{S3}$$

Each of the entropies of the transition state for desorption and the adsorbed state can be related to known quantities.

$$S_{TS,des} = S_{gas} - S_{1D,Trans} \tag{S4}$$

$$S_{ads} = S_{gas} + \Delta S_{ads} \tag{S5}$$

Combining Eq. S5 and Eq. 8 of the main text,

$$S_{ads} = S_{gas} - S_{1D,Trans} - F_{rot} S_{rot} \tag{S6}$$

Combining Eq. S3-S6, the change in entropy associated with approaching the transition state of desorption starting from the adsorbed state is,

$$\Delta S_{TS,des} = (S_{gas} - S_{1D,Trans}) - (S_{gas} - S_{1D,Trans} - F_{rot} S_{rot}) \tag{S7}$$

$$\Delta S_{TS,des} = F_{rot} S_{rot} \tag{S8}$$

Inserting Eq. S8 into S2, the desorption pre-exponential factor is defined in terms of the losses in rotational entropy due to confinement,

$$\nu_{des} = \frac{k_b T}{h} e^{\frac{F_{rot} S_{rot}}{R}} \tag{S9}$$

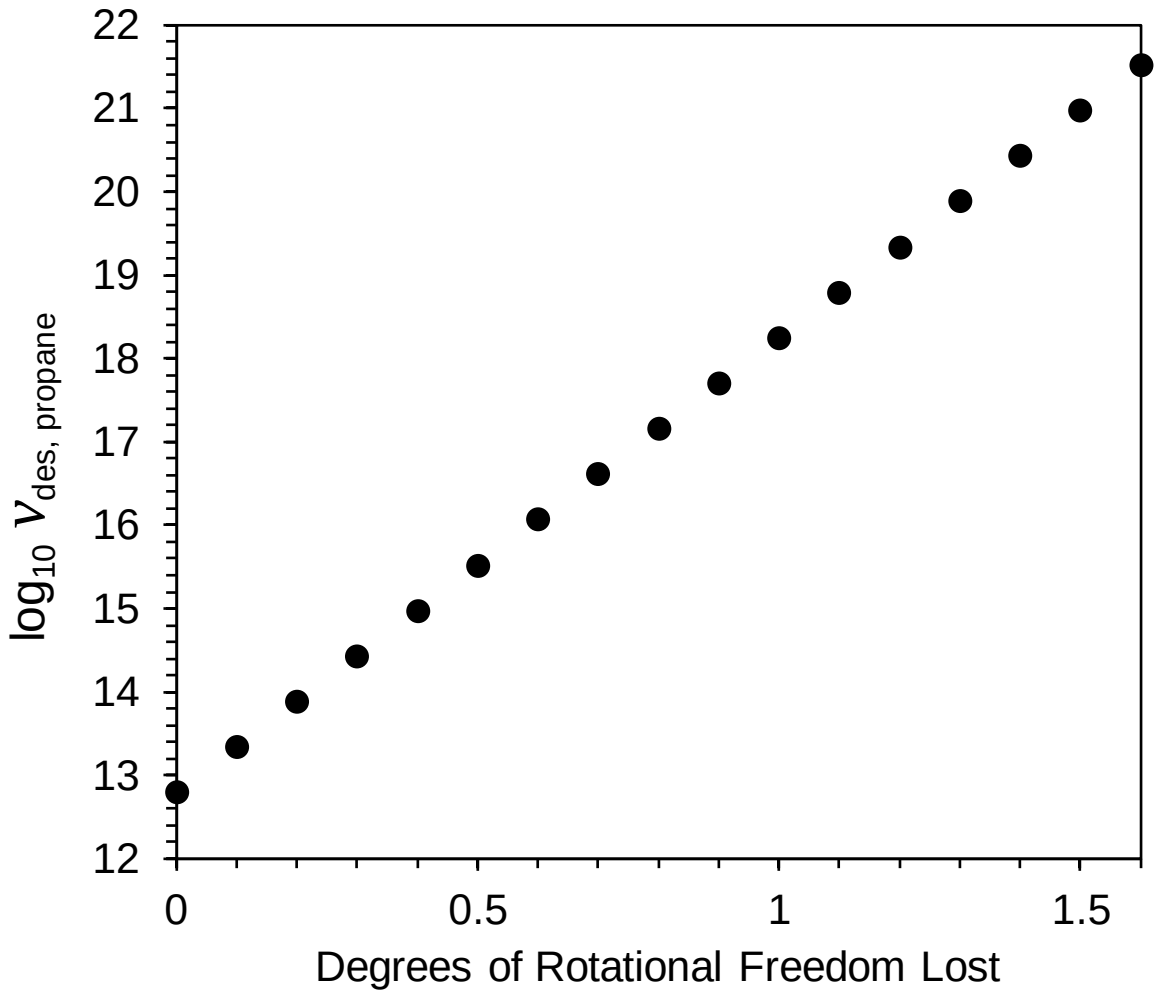

Figure S4. Relationship between the desorption pre-exponential factor of propane ($\nu_{des,propane}$) and the degrees of rotational freedom lost upon adsorption as per Eq. (S9).

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