

Supporting Information

Isobutene protonation in H-FAU, H-MOR, H-ZSM-5 and H-ZSM-22

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PW91+D//PW91 versus PBE-D//PBE-D energies. Table S1 summarizes optimized unit cell parameters of H-FAU, H-MOR, H-ZSM-5 and H-ZSM-5 using the PW91 method. Tables S2 and S3 show the physisorption, activation and chemisorption electronic energies of isobutene in H-FAU, H-MOR, H-ZSM-5 and H-ZSM-22, obtained using PW91+D//PW91 and PBE-D//PBE-D. The DFT contributions are denoted as PW91//PW91 and PBE//PBE-D, while the dispersion contributions are denoted as D//PW91 and D//PBE-D.

The DFT contributions, i.e. PW91//PW91 and PBE//PBE-D, in all physisorption, activation and chemisorption energies are very similar in the PW91 and PBE-D calculations, as maximum differences of only 7 kJ mol⁻¹ are noticed. Also the dispersion (D) contributions, i.e. D//PW91 and D//PBE-D, are nearly identical for the PW91 and PBE-D calculations. This results in total energies, respectively PW91+D//PW91 and PBE-D//PBE-D, that differ no more than 8 kJ mol⁻¹.

Based on this, it is concluded that the add on dispersion correction of PW91 energies with a dispersion term proposed by Grimme¹ for the PBE functional (PW91+D//PW91), yields practically the same physisorption, activation and chemisorption energies as PBE-D//PBE-D does.

Table S4 shows the criteria used to calculate the full or partial Hessian. In case the standard optimization settings led to a bad conditioned Hessian due to the presence of spurious frequencies, a re-optimization and subsequent frequency calculation was performed with

tighter settings for plane wave energy cutoff E_{cutoff} , the SCF loop convergence criterion ΔE_{SCF} or the maximum force.

Table S5 shows estimates for physisorption enthalpies of isobutene ($\Delta H_{\text{phys, isobutene}}^0$) in H-FAU and H-MOR.

$$\Delta H_{\text{phys, isobutene}}^0 = \Delta H_{\text{phys, isobutane}}^0 + E_{\pi-H} \quad (1)$$

in which $\Delta H_{\text{phys, isobutane}}^0$ is the physisorption enthalpy of isobutane taken from early work by Eder et al.² and $E_{\pi-H}$, the interaction energy between the alkene double bond and the Brønsted acid site, was estimated to amount to 25 kJ mol⁻¹.^{3,4}

Table S6 shows the energy to enthalpy correction, which comprises ZPVE and thermal contributions (see text).

Table S7 shows the standard physisorption, chemisorption, activation and protonation enthalpies.

Figure S1 shows $\ln(K_{\text{phys}})$ and $\ln(K_{\text{chem}})$ as function of the reciprocal of temperature; data are grouped per isobutene complex and on every plot the results for the different zeolites are presented. This allows to evaluate in which zeolite the formation of a given physisorption or chemisorption complex is thermodynamically most favored. The values for $\ln(K_{\text{phys}})$ and $\ln(K_{\text{chem}})$ are calculated according to:

$$\ln(K_{\text{ads}}) = -\frac{\Delta H_{\text{ads}}^0 - T\Delta S_{\text{ads}}^0}{RT} \quad (2)$$

in which “ads” may be “phys” or “chem”. Based on this equation, it is clear that the contribution of ΔS_{ads}^0 to the value for the equilibrium coefficient becomes more important with increasing temperature. A higher value for K_{phys} or K_{chem} implies a higher stability of the physisorption or chemisorption complex.

For the physisorption of isobutene, $\ln(K_{\text{phys}})$ is calculated based on the values for ΔH_{phys}^0 and ΔS_{phys}^0 for respectively **I-p**, **I-t** and the average of both. The latter case is here discussed: at low temperatures the physisorption preference increases in the order: H-FAU < H-MOR < H-ZSM-5 < H-ZSM-22. This order results from the stronger adsorption in the zeolites with smaller pores, due to the higher van der Waals stabilization; in other words, the enthalpic

contribution is decisive at low temperatures. At higher temperatures, entropic contributions become more important, resulting in an inverse order: due to the lower entropy losses in H-FAU compared to H-MOR, H-ZSM-5 and H-ZSM-22, physisorption becomes most preferred in this zeolite.

For isobutoxy **III-p**, $\ln(K_{\text{chem}})$ increases in the order: H-FAU < H-MOR < H-ZSM-22 \leq H-ZSM-5 in the whole temperature range; as variations of ΔS_{chem}^0 are relatively small in the various zeolites, this order accords to the variations in ΔH_{chem}^0 among the different zeolites.

For t-butoxy **III-t**, $\ln(K_{\text{chem}})$ increases in the order: H-ZSM-22 < H-FAU \approx H-MOR < H-ZSM-5. The lower stability of t-butoxy in H-ZSM-22 results from the presence of strong steric repulsion and is reflected in the value for ΔH_{chem}^0 . Also, the highest entropy loss is calculated for t-butoxy formation in H-ZSM-22.

The stability of the t-butyl carbenium ions **IV-t** is mainly determined by the variations for ΔH_{chem}^0 among the different zeolites. As such the stability increases in the order: H-MOR < H-ZSM-5 < H-ZSM-22 in the whole temperature range.

Figure S2 shows ΔG^0 versus T plots accounting for an ad hoc SIC error of 40 kJ mol⁻¹ for the t-butyl carbenium ion; this is discussed in the text.

Composite protonation rate coefficient account for the influence of the physisorption of gas phase isobutene:

$$\begin{aligned} k_{\text{prot}/\text{comp}} &= k_{\text{prot}} \cdot K_{\text{phys}} \\ &= \frac{k_B T}{h} \exp\left(\frac{\Delta S_{\text{act}}^0}{R}\right) \exp\left(-\frac{\Delta H_{\text{act}}^0}{RT}\right) \left[\exp\left(\frac{\Delta S_{\text{phys}}^0}{R}\right) \exp\left(-\frac{\Delta H_{\text{phys}}^0}{RT}\right) \right] \\ &= A_{\text{prot}/\text{comp}} \exp\left(-\frac{E_{\text{prot}/\text{comp}}^\#}{R}\right) \end{aligned} \quad (3)$$

in which composite pre-exponential factor and composite activation energy are:

$$E_{\text{prot}/\text{comp}}^\# = E_{\text{prot}}^\# + \Delta H_{\text{phys}}^0 \quad (4)$$

$$\ln(A_{\text{prot}/\text{comp}}) = \ln(A_{\text{prot}}) + \frac{\Delta S_{\text{phys}}^0}{R} \quad (5)$$

The reverse deprotonation rate coefficient of chemisorbed **III-t/IW-t** can be expressed as:

$$\begin{aligned}
 k_{dep} &= \frac{k_B T}{h} \exp\left(\frac{\Delta S_{act/dep}^0}{R}\right) \exp\left(-\frac{\Delta H_{act/dep}^0}{RT}\right) \\
 &= A_{dep} \exp\left(-\frac{E_{dep}^\ddagger}{R}\right)
 \end{aligned}
 \tag{6}$$

Activation entropy (X=S) and activation enthalpy (X=H) for the deprotonation of **III-t/IV-t** are calculated as:

$$\Delta X_{act/dep}^0 = X_{II-t} - X_{III-t/IV-t}
 \tag{7}$$

Hence, the composite protonation equilibrium coefficient is defined as:

$$K_{prot/comp} = \frac{k_{prot,comp}}{k_{dep}}
 \tag{8}$$

Table S1. Optimized unit cell parameters for H-FAU, H-MOR, H-ZSM-5 AND H-ZSM-22 from periodic DFT calculations using the pw91 functional. Also, deprotonation energies (ΔE_{DP} , kJ mol⁻¹) and entropies (ΔS_{DP} , J mol⁻¹ K⁻¹) obtained using the QM-POT program (MP2//B3LYP:GULP) are presented.

| | H-FAU | H-MOR | H-ZSM-5 | H-ZSM-22 |
|-------------------------------------|---------|---------|---------|----------|
| a / pm | 1740.05 | 1834.55 | 2047.22 | 1132.93 |
| b / pm | 1736.21 | 2041.26 | 2010.87 | 1130.77 |
| c / pm | 1742.39 | 1506.58 | 1357.58 | 1542.76 |
| α / ° | 59.88 | 89.99 | 89.97 | 90.14 |
| β / ° | 59.82 | 89.90 | 89.88 | 90.07 |
| γ / ° | 59.87 | 90.03 | 89.99 | 77.04 |
| FD ^a / Tnm ⁻³ | 13.3 | 17.0 | 18.4 | 18.1 |
| density | | | | |
| ΔE_{DP} | 1181 | 1211 | 1210 | 1210 |
| ΔS_{DP} | 95 | 93 | 85 | 84 |

^aFD: framework density values of zeolites taken from ref 1.

Table S2. PW91+D//PW91 physisorption, activation and chemisorption electronic energies for isobutene in H-FAU, H-MOR, H-ZSM-5 and H-ZSM-22. The separate contributions (x//PW91) to the total energy, i.e. the DFT and the dispersion contributions are also indicated.

| [kJ mol ⁻¹] x//PW91 ⁽¹⁾ | H-FAU | | | H-MOR | | | H-ZSM-5 | | | H-ZSM-22 | | |
|---|-------|-----|--------|-------|-----|--------|---------|-----|--------|----------|-----|--------|
| | PW91 | D | PW91+D | PW91 | D | PW91+D | PW91 | D | PW91+D | PW91 | D | PW91+D |
| $\Delta E_{\text{phys,I-p}}$ | -34 | -40 | -75 | -37 | -53 | -89 | -34 | -54 | -88 | -17 | -76 | -94 |
| $\Delta E_{\text{phys,I-t}}$ | -40 | -36 | -76 | -30 | -50 | -80 | -31 | -60 | -91 | -27 | -72 | -100 |
| $\Delta E_{\text{act,II-p}}$ | 104 | -3 | 101 | 119 | -9 | 110 | 111 | -6 | 105 | 88 | 0 | 88 |
| $\Delta E_{\text{act,II-t}}$ | 40 | -9 | 31 | 23 | 2 | 24 | 35 | -5 | 30 | 15 | 1 | 15 |
| $\Delta E_{\text{chem,III-p}}$ | -28 | -44 | -72 | -26 | -54 | -80 | -43 | -60 | -103 | -22 | -78 | -101 |
| $\Delta E_{\text{chem,III-t}}$ | -16 | -60 | -76 | -11 | -69 | -80 | -19 | -76 | -95 | 15 | -91 | -77 |
| $\Delta E_{\text{chem,IV-p}}$ | (2) | (2) | (2) | -11 | -48 | -59 | -15 | -57 | -72 | -20 | -72 | -92 |

(1) x is equal to “PW91”, “D” or “PW91+D”

(2) not stable

Table S3. PBE-D//PBE-D physisorption, activation and chemisorption electronic energies for isobutene in H-FAU, H-MOR, H-ZSM-5 and H-ZSM-22. The separate contributions (x//PBE-D) to the total energy, i.e. the DFT and the dispersion contributions are indicated.

| [kJ mol ⁻¹] x//PBE-D ⁽¹⁾ | H-FAU | | | H-MOR | | | H-ZSM-5 | | | H-ZSM-22 | | |
|--|-------|-----|-------|-------|-----|-------|---------|-----|-------|----------|-----|-------|
| | PBE | D | PBE-D | PBE | D | PBE-D | PBE | D | PBE-D | PBE | D | PBE-D |
| $\Delta E_{\text{phys,I-p}}$ | -27 | -47 | -73 | -32 | -57 | -88 | -29 | -57 | -87 | -12 | -79 | -91 |
| $\Delta E_{\text{phys,I-t}}$ | -36 | -41 | -77 | -24 | -53 | -77 | -24 | -64 | -88 | -24 | -73 | -97 |
| $\Delta E_{\text{act,II-p}}$ | 104 | 1 | 105 | 118 | -4 | 114 | 111 | -2 | 110 | 93 | 3 | 96 |
| $\Delta E_{\text{act,II-t}}$ | 41 | -3 | 38 | 26 | 5 | 30 | 32 | 3 | 34 | 16 | 3 | 19 |
| $\Delta E_{\text{chem,III-p}}$ | -24 | -47 | -70 | -23 | -57 | -80 | -43 | -63 | -106 | -17 | -81 | -98 |
| $\Delta E_{\text{chem,III-t}}$ | -12 | -62 | -74 | -6 | -71 | -78 | -13 | -76 | -89 | 20 | -93 | -73 |
| $\Delta E_{\text{chem,IV-p}}$ | (2) | (2) | (2) | -5 | -55 | -60 | -9 | -63 | -72 | -15 | -75 | -90 |

(1) x is equal to “PBE”, “D” or “PBE-D”

(2) not stable

Table S4. Criteria used for the frequency calculations on investigated isobutene complexes in H-FAU, H-MOR, H-ZSM-5 and H-ZSM-22. The plane wave energy cutoff E_{cutoff} , the SCF loop convergence criterion ΔE_{SCF} , and the maximum force on the atoms are mentioned.

| | H-FAU | | | H-MOR | | | H-ZSM-5 | | | H-ZSM-22 | | |
|-------------------|-----------------------------|---------------------------------|---------------------|-----------------------------|---------------------------------|---------------------|-----------------------------|---------------------------------|---------------------|-----------------------------|---------------------------------|---------------------|
| | E_{cutoff} [eV] | ΔE_{SCF} [eV] | Max force [eV/Å] |
| zeolite | 400 | 10^{-8} | 0.010 | 400 | 10^{-8} | 0.010 | 400 | 10^{-8} | 0.010 | 400 | 10^{-8} | 0.010 |
| Phys I-p | 400 | 10^{-8} | 0.015 | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.020 | 600 | 10^{-10} | 0.015 |
| Phys I-t | 600 | 10^{-8} | 0.015 | 400 | 10^{-8} | 0.015 | 400 | 10^{-8} | 0.020 | 600 | 10^{-8} | 0.020 |
| TS II-p | 400 | 10^{-10} | 0.040 | 400 | 10^{-8} | 0.040 | 400 | 10^{-8} | 0.040 | 400 | 10^{-8} | 0.040 |
| TS II-t | 400 | 10^{-8} | 0.040 | 400 | 10^{-8} | 0.040 | 400 | 10^{-8} | 0.040 | 400 | 10^{-8} | 0.040 |
| Chem III-p | 400 | 10^{-10} | 0.010 | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.020 |
| Chem III-t | 400 | 10^{-8} | 0.015 | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.020 |
| Chem IV-t | - | - | - | 400 | 10^{-8} | 0.020 | 400 | 10^{-8} | 0.015 | 400 | 10^{-8} | 0.015 |

Table S5. Estimates of physisorption enthalpies are compared with PW91//PW91-D physisorption energies of isobutene in H-FAU and H-MOR.

| | type | Si/Al | $\Delta H_{\text{phys / isobutane}}^0$ kJ mol ⁻¹ | $\Delta H_{\text{phys / isobutene}}^0$ kJ mol ⁻¹ |
|--------------|------|-------|--|--|
| H-FAU | | | | |
| PW91//PW91-D | sim | 95 | | -76 |
| Ref. 2 | exp | 3 | -40 | -65 |
| H-MOR | | | | |
| PW91//PW91-D | sim | 95 | | -80 |
| Ref. 2 | exp | 10 | -52 | -77 |

Table S6. Sum of the ZPVE and thermal contributions to the enthalpy ($\Delta(E \rightarrow H)$), at 300 K.

| [kJ mol ⁻¹] | H-FAU | H-MOR | H-ZSM-5 | H-ZSM-22 |
|---|-------|-------|---------|----------|
| $\Delta(E \rightarrow H)_{\text{phys,I-p}}$ | 0 | 1 | 0 | 1 |
| $\Delta(E \rightarrow H)_{\text{phys,I-t}}$ | 1 | 1 | 0 | -1 |
| $\Delta(E \rightarrow H)_{\text{act,II-p}}$ | -2 | -2 | -3 | -4 |
| $\Delta(E \rightarrow H)_{\text{act,II-t}}$ | -3 | -8 | -2 | -9 |
| $\Delta(E \rightarrow H)_{\text{chem,III-p}}$ | 13 | 13 | 12 | 12 |
| $\Delta(E \rightarrow H)_{\text{chem,III-t}}$ | 9 | 9 | 8 | 8 |
| $\Delta(E \rightarrow H)_{\text{chem,IV-p}}$ | (1) | -6 | -6 | -7 |

(1) not stable

Table S7. Physisorption (I-p and I-t), activation (II-p and II-t), chemisorption (III-p, III-t and IV-t) and protonation enthalpies at 300 K.

| [kJ mol ⁻¹] | $\Delta H_{\text{chem,III-p}}^0$ | $\Delta H_{\text{act,II-p}}^0$ | $\Delta H_{\text{phys,I-p}}^0$ | $\Delta H_{\text{phys,I-t}}^0$ | $\Delta H_{\text{act,II-t}}^0$ | $\Delta H_{\text{chem,III-t}}^0$ | $\Delta H_{\text{chem,IV-t}}^0$ | $\Delta H_{\text{prot,III-t}}^0$ | $\Delta H_{\text{prot,IV-t}}^0$ |
|-------------------------|----------------------------------|--------------------------------|--------------------------------|--------------------------------|--------------------------------|----------------------------------|---------------------------------|----------------------------------|---------------------------------|
| H-FAU | -60 | 99 | -74 | -76 | 28 | -67 | (1) | 9 | (1) |
| H-MOR | -67 | 108 | -89 | -79 | 16 | -71 | -65 | 8 | 14 |
| H-ZSM-5 | -90 | 101 | -88 | -90 | 27 | -87 | -78 | 3 | 12 |
| H-ZSM-22 | -89 | 84 | -93 | -101 | 6 | -69 | -99 | 32 | 2 |

(1) not stable

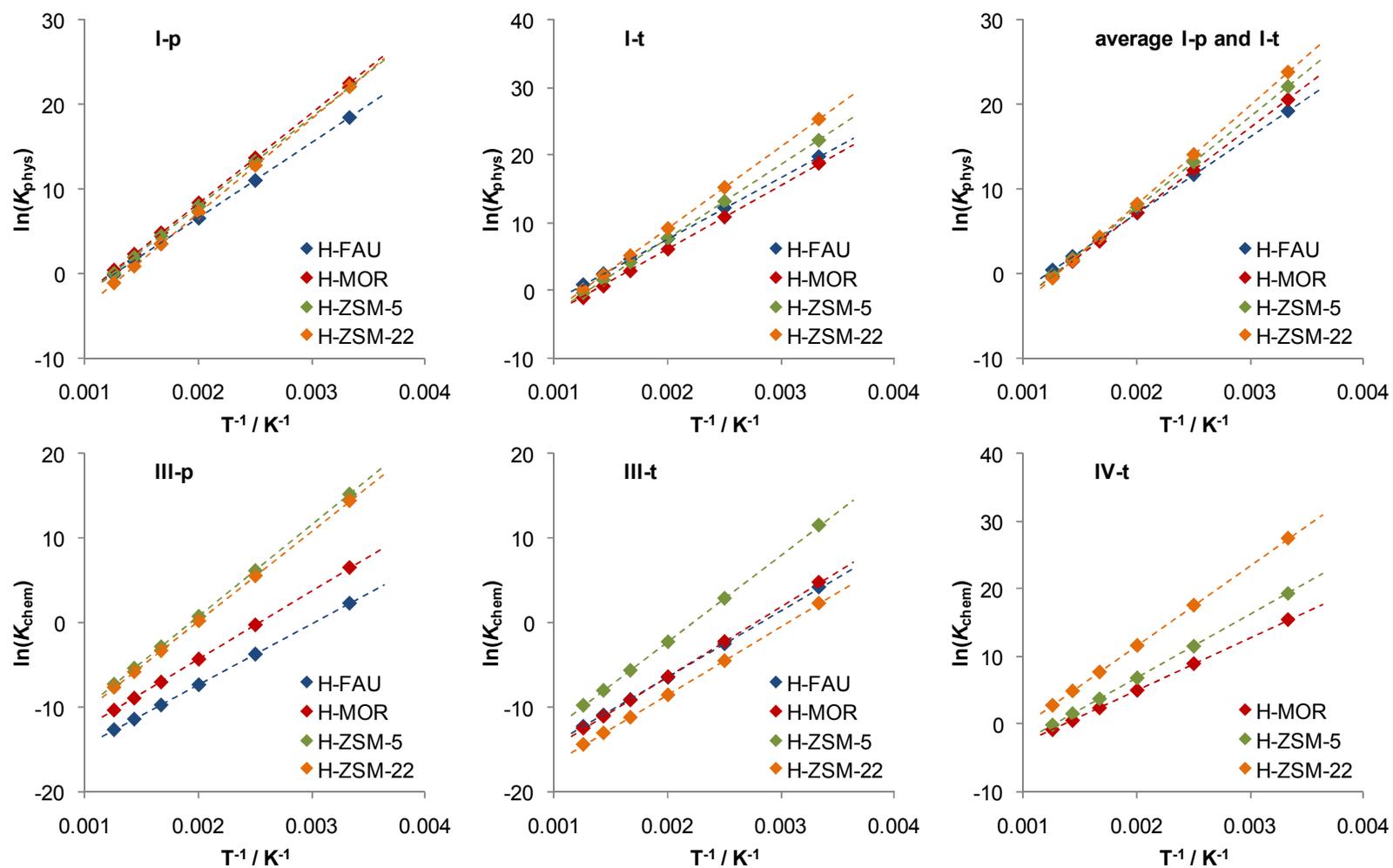


Figure S1. $\ln(K)$ vs. T^{-1} grouped per isobutene complex, i.e. I-p, I-t, the average of I-p and I-t, III-p, III-t and IV-t. This allows the evaluation of the zeolite topology influence on the stability of the studied isobutene complexes.

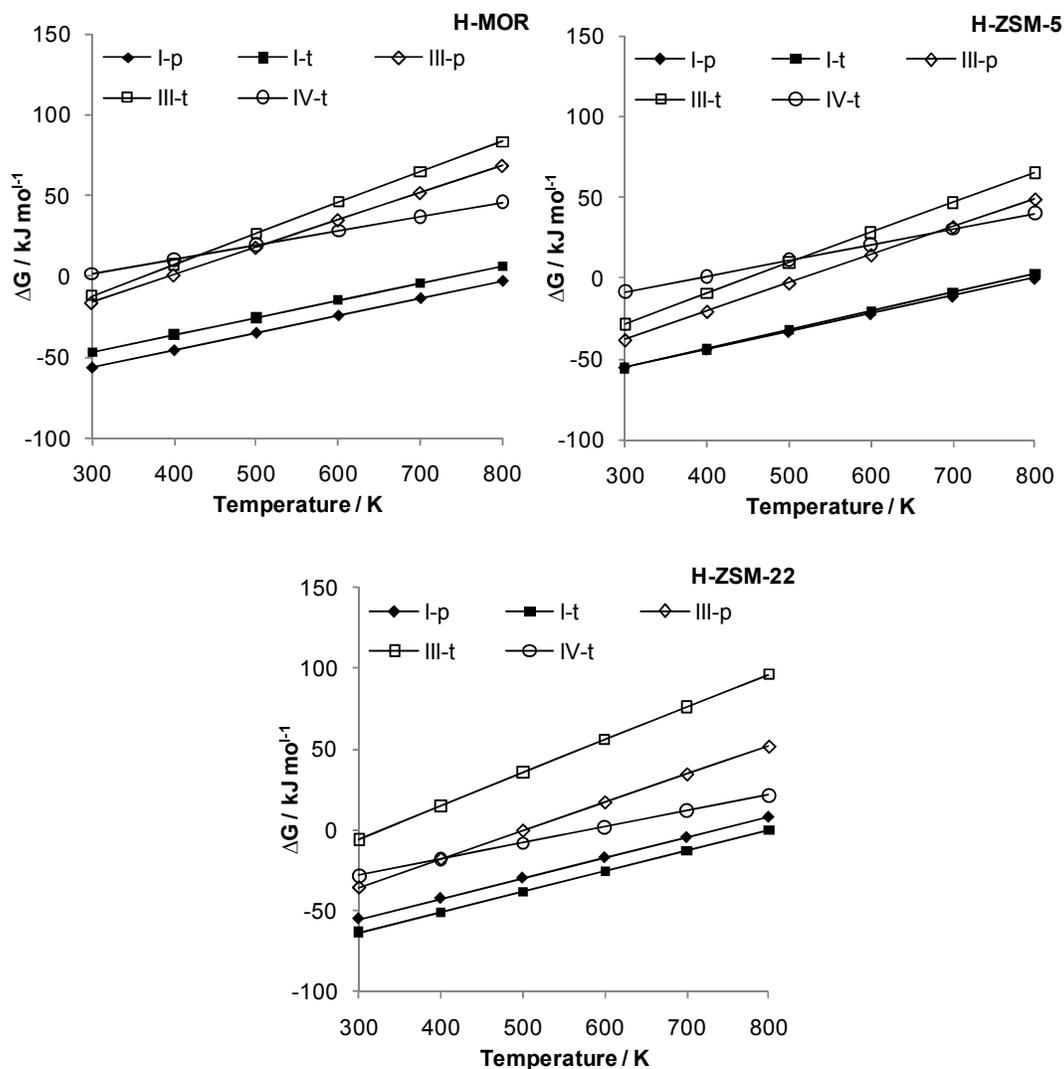


Figure S2. Gibbs free energy corresponding to physisorbed isobutene (I-p and I-t), isobutoxy (III-p), t-butoxy (III-t) and t-butyl carbenium ion (IV-t) in H-MOR, H-ZSM-5 and H-ZSM-22. The Gibbs free chemisorption energy of the t-butyl carbenium ion, $\Delta G_{\text{chem,IV-t}}$ has been corrected for an a posteriori assumed SIC error of 40 kJ mol^{-1} .

References

- (1) International Zeolite Association: Structural Databases. <http://www.iza-structure.org/databases> (accessed April 19, 2012).
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