Isobutene in Zeolites

Protonated Isobutene in Zeolites: *tert*-Butyl Cation or Alkoxide?**

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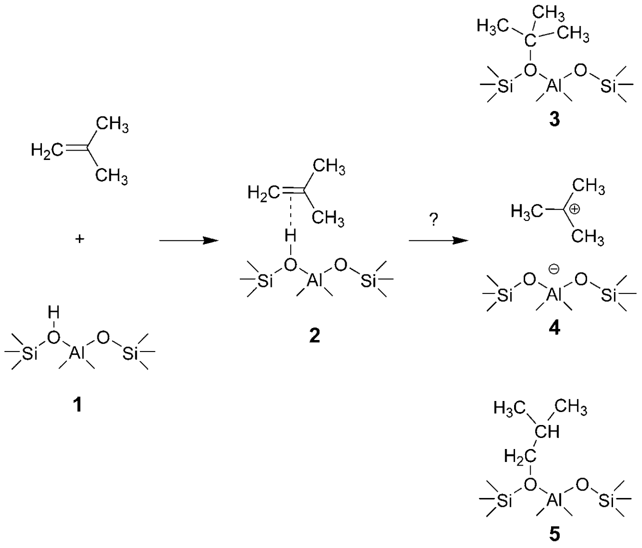
Acid zeolite catalysts are industrially used for a variety of hydrocarbon transformation processes. Initially it was assumed that these reactions follow mechanisms known from chemistry in superacidic media, and involve carbocations as intermediates formed upon protonation of hydrocarbons by Brønsted acid sites.[1] However, NMR spectroscopic studies failed to find simple carbenium ions as intermediates, and instead produced evidence for surface alkoxides.[2,3] Around the same time, quantum chemical calculations employing small cluster models showed that alkoxides are minima on the potential energy surface (PES) and, hence, intermediates, while carbenium ions represent saddle points on the PES and are only present as extremely short-lived transition states.[4] So far, evidence for persistent carbenium ions has only been produced for cyclic alkenyl or aromatic carbenium ions by NMR,[5] UV/Vis,[6] and IR spectroscopy[7] or computational techniques.[8]

Among the carbenium ions derived from small alkenes, the *tert*-butyl cation has attracted much interest because it is more stable than primary or secondary carbenium ions; the competing formation of *tert*-butoxide may be sterically hindered. Previous computational studies have shown that, depending on the framework and the position at the zeolite wall to which they are bound, *tert*-butoxides may be as unstable as the *tert*-butyl cation.[9–12] Only the embedded cluster study by Boronat et al.[12] reports a local minimum on the PES for the *tert*-butyl cation in mordenite. It is, however, about 26 kJ mol^{-1} less stable than the adsorption π complex of isobutene with the Brønsted site. Nevertheless, all experimental attempts[13,14] to produce evidence for either the *tert*-butyl cation or an alkoxide have been unsuccessful so far, and the existence of *tert*-butyl cations in zeolites remains controversial.

Herein we report density functional theory (DFT) calculations for the reaction of isobutene with H-ferrierite (H-FER, **1**) with formation of the π complex **2** (Scheme 1). We applied periodic boundary conditions to a large simulation cell of dimensions 1870 × 1417 × 1496 pm^3.[15] We show that the complex with the *tert*-butyl cation (**4**)—one possible structure formed upon proton transfer to isobutene in **2**—is a local minimum on the potential energy surface. For the first time we have evaluated entropy contributions to assess the stability of **4** relative to the adsorption π complex **2** and other possible proton transfer products, that is, surface alkoxides (**3**, **5**), at finite temperatures.



Scheme 1. Reactions considered for the protonation of isobutene in H-FER (**1**).

Our simulation cell of H-FER (**1**) has the composition $HAlSi_{71}O_{144}$. After aluminum substitution at the crystallographic position T2,[16] the proton is most stable at O7.[15] We used the Perdew–Burke–Ernzerhof (PBE) density functional[17] with a plane wave basis set.[18] Stationary points obtained by relaxation of the positions of all atoms in the cell are characterized by harmonic frequencies, from which zero-point vibrational energies, finite temperature energy, and entropy contributions are obtained.[19] All calculations employed the CPMD code.[20]

The calculated structures and the corresponding reaction energies are shown in Figure 1 and Table 1. Formation of the π complex of isobutene with the Brønsted acidic site is exothermic (**2**, $\Delta E_0 = -6.6$ kJ mol^{-1}). In contrast, chemisorption of isobutene is an endothermic process. Of the two different alkoxides, the isobutoxide (**5**) is more stable than the *tert*-butoxide (**3**). The longer C–O bond in *tert*-butoxide (161 pm) compared to isobutoxide (151 pm) indicates increased steric constraints due to the three methyl groups at the C–O carbon atom. Both the adsorbed isobutene and the *tert*-butyl cation are connected by hydrogen bonds to the zeolite framework. The corresponding bond lengths are 190.2 and 242.5 pm for $r(\mathrm{AlOH}\cdots\mathrm{C}^1)$ and $r(\mathrm{AlOH}\cdots\mathrm{C}^2)$ in the π complex and 174.0 pm for $r(\mathrm{AlO}\cdots\mathrm{HC})$ in the carbenium ion structure. The carbenium ion complex **4** is electronically least favored. It is 46 kJ mol^{-1} less stable than the adsorption π complex, while isobutoxide is 14 kJ mol^{-1} and *tert*-butoxide is 27 kJ mol^{-1} less stable.

Similar relative energies have been found in a previous DFT (PW91) study for chabasite, ZSM-22, and mordenite[11]

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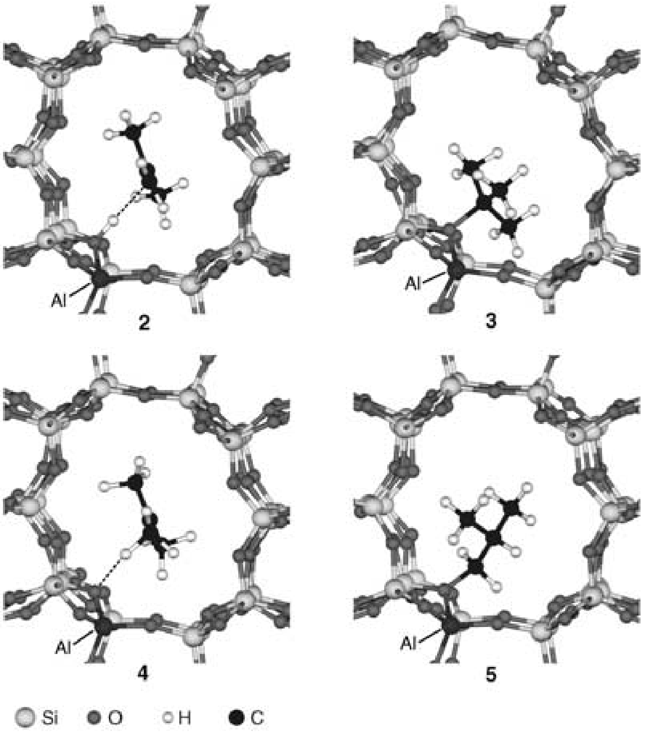

Figure 1. Portions of the structures calculated for the π complex of isobutene in ferrierite (**2**), for the *tert*-butyl cation in ferrierite (**4**), and for the *tert*-butoxide (**3**) and isobutoxide (**5**) of ferrierite.

Table 1: Electronic (ΔE) and ZPVE-corrected (ΔE_0) reaction energies, enthalpies (ΔH_{298}), and Gibbs energies (ΔG_{298}; pressure 1 atm) in kJ mol^{-1} for the formation of structures **2**–**5** from isobutene and H-FER (**1**).

Compound	ΔE	ΔE_0	ΔH_{298}	ΔG_{298}
2	−9.4	−6.6[a]	−4.9	40.4
3	17.2	35.0	27.5	119.0
4	36.2	32.2	34.9	76.0
5	4.8	24.4	18.8	96.8

[a] For comparison, ΔE_0 for isobutene in mordenite is −6.4 kJ mol^{-1} (B3PW91).[12]

as well as in a B3PW91 study on mordenite.[12] The density functionals that are currently used do not properly account for dispersion interactions (see, e.g., references [21,22]). This results in too low energies of adsorption, but may also change the relative energies of chemisorbed species compared to adsorption π complexes and carbenium ions.[15] Future refinements of the present results by explicit inclusion of dispersion interactions may be obtained by an MP2/DFT hybrid technique[23] or by adding a damped dispersion term.[22] The results obtained with the PBE/PW91 family of functionals require less correction than those with functionals including Becke exchange.[21,22,24]

Inclusion of zero-point vibrations and finite temperature effects stabilizes the *tert*-butyl carbenium ion relative to the chemisorbed species (see ΔE_0 and ΔH_{298} in Table 1). An important new finding of the present study is the effect of entropy on the Gibbs energy: At temperatures higher than about 120 K, the *tert*-butyl cation complex **4** becomes favored over the alkoxides (**3**, **5**, Figure 2). The different slopes for the change in Gibbs energy for the alkoxides compared to the π complex and the carbenium ion reflect different entropy contributions. The existence of an additional covalent bond in the alkoxides (C−O) limits the mobility of the hydrocarbon species, and suggests a lower entropy compared to the other two structures.

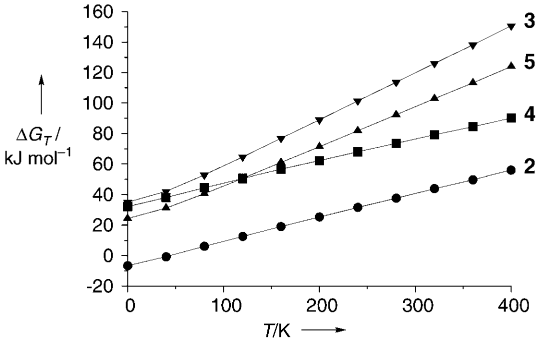

Figure 2. Plot of the Gibbs energy ΔG_T as a function of temperature T (at 1 atm) for the formation of **2**–**5** from isobutene and H-FER (**1**).

The vibrational states obtained from our frequency calculations are shown in Figure 3 (the vibrational frequencies can be found in the Supporting Information). A nearly continuous vibrational region from 1250 cm^{-1} down to far infrared with a window between about 1000 and 800 cm^{-1} is seen for unloaded H-FER (**1**) as well as for the hydrocarbon-containing structures. This is characteristic of zeolite lattice vibrations. The calculated frequencies for the zeolitic O−H and O−D stretching modes in unloaded H-FER (3643 and 2652 cm^{-1}, respectively) compare well with experimental data (3609 and 2663 cm^{-1}, respectively).[25] Quantitative agreement is not expected because of the limited accuracy of DFT and neglected anharmonicities. The vibrational spectra of structures **2**–**5** approximately resemble superpositions of those of the unloaded zeolite and the gas-phase species. In the isobutene π complex **2**, hydrogen bond formation shifts the zeolitic O−H and O−D stretching mode by −819 and

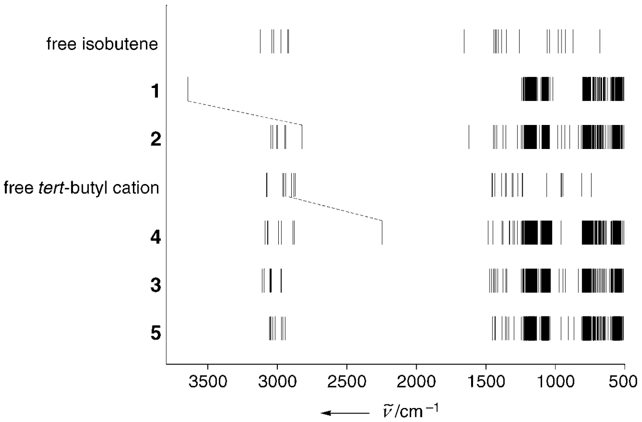

Figure 3. Vibrational spectra calculated for isobutene and the *tert*-butyl cation (both in the gas phase) as well as for structures **1**–**5**.

$-585\ \mathrm{cm^{-1}}$, respectively. Corresponding measurements on deuterated forms of different zeolites yield somewhat smaller O–D shifts: $-416\ \mathrm{cm^{-1}}$ (mordenite)[14] and $-388\ \mathrm{cm^{-1}}$ (faujasite).[26] It is known[27] that the PBE functional overestimates O–H frequency shifts upon hydrogen bond formation.

A significant change is predicted for the IR spectrum of the carbenium ion complex **4**: Only 8 instead of 9 vibrational modes are seen in the C–H stretching region around $3000\ \mathrm{cm^{-1}}$; the remaining mode corresponding to the O⋯HC hydrogen bond is found at $2245\ \mathrm{cm^{-1}}$, that is, well separated from the others. This is a new prediction which may help to identify the *tert*-butyl cation as a transient species in future laser-spectroscopic experiments.[28]

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[19] All atom positions were fully relaxed until the maximum component of cartesian atomic forces was smaller than $1.0\times 10^{-5}\ E_h/a_0$. Force constants were calculated by numerical differentiation of forces, stepsize 0.01 a_0. Vibrational modes were projected.

[20] CPMD 3.7.2: Copyright MPI für Festkörperforschung, Stuttgart, **1997–2001**, and IBM Research Division, Zürich, **1990–2003**.

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