

Carbocations on Zeolites. *Quo Vadis?*

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A natureza dos carbocátions adsorvidos na superfície da zeólita é discutida neste artigo, destacando estudos experimentais e teóricos. A adsorção de halogenetos de alquila sobre zeólitas trocadas com metais tem sido usada para estudar o equilíbrio entre alcóxidos, que são espécies covalentes, e carbocátions, que têm natureza iônica. Cálculos teóricos indicam que os carbocátions são mínimos (intermediários) na superfície de energia potencial e estabilizados por ligações de hidrogênio com os átomos de oxigênio da estrutura zeolítica. Os resultados indicam que zeólitas se comportam como solventes sólidos, estabilizando a formação de espécies iônicas.

The nature of carbocations on the zeolite surface is discussed in this account, highlighting experimental and theoretical studies. The adsorption of alkylhalides over metal-exchanged zeolites has been used to study the equilibrium between covalent alkoxides and ionic carbocations. Theoretical calculations indicated that the carbocations are minima (intermediates) on the potential energy surface and stabilized by hydrogen bonds with the framework oxygen atoms. The results indicate that zeolites behave like solid solvents, stabilizing the formation of ionic species.

**Keywords:** zeolites, carbocations, alkoxides, catalysis, acidity

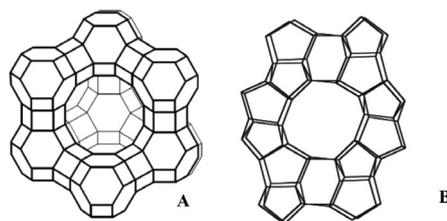
## 1. Introduction

Zeolites are crystalline aluminosilicates with pores of molecular dimensions. Their structure are constructed by the interconnection of tetrahedral  $\text{SiO}_4$  and  $\text{AlO}_4^-$  units, forming pores and cages of different geometries. Hence, zeolites have molecular sieve properties, allowing only specific molecules to diffuse inside their pores. For instance, zeolite Y or Faujasite (Figure 1), with pore diameter of 7.4 Å, permits the entrance of molecules with sizes similar to neopentane, whereas ZSM-5 (Figure 1), with channels in the range of 5.3 to 5.6 Å, is able to adsorb molecules up to the size of cyclohexane.<sup>1</sup>

The  $\text{AlO}_4^-$  units in the zeolite framework must be compensated by cations to keep the electronic neutrality of the material, but these cations are not part of the framework and can be easily exchanged. For instance, zeolite Y is usually synthesized in the sodium form ( $\text{NaY}$ ); meaning that each framework aluminum atom is compensated by a sodium cation. Nevertheless, the sodium ions can be exchanged by other mono, di and even trivalent cations.

Thus,  $\text{NH}_4\text{Y}$  can be prepared by exchange of the  $\text{NaY}$  with ammonium salt solutions. An acidic material can be obtained by calcination of the ammonium-exchanged zeolites, releasing  $\text{NH}_3$  as by-product. These protonic zeolites are widely used in catalysis, being important catalysts in oil refining and petrochemistry.<sup>2</sup>

Acidic zeolites are used in cracking, alkylation and isomerization of hydrocarbons. It is believed that they protonate hydrocarbon molecules to form carbocations as intermediates. However, there still exists controversy concerning the nature of the carbocations on the zeolite surface. The structure plays a significant role and some experimental and theoretical results pointed out that covalent alkoxides (Figure 2) are the real intermediates on zeolite-catalyzed reactions, whereas ionic carbocations



**Figure 1.** Representation of the structures of Faujasite or zeolite Y (A) and ZSM-5 (B).

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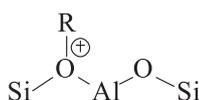
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would be just transition states. In this account, we will discuss experimental and theoretical results to address responses to the fundamental question about the nature of carbocations on zeolites.

## 2. *In Situ* Solid State NMR Spectroscopic Experiments with Olefins and Alcohols

The structure of carbocations could be studied in details with the use of superacid media<sup>3</sup> and nuclear magnetic resonance (NMR) spectroscopy. This approach<sup>4</sup> was developed by Olah in the 1960's and allowed the direct spectroscopic observation of many carbocations in solution. The planar geometry of the carbenium ions could be confirmed and the dynamics of carbocation rearrangement could be studied within the NMR time scale.<sup>5</sup> These studies made NMR spectroscopy a powerful tool for the *in situ* observation of carbocations in solutions.

With the development of magic angle spinning (MAS) and related techniques,<sup>6</sup> solid state NMR became an important tool for the study of catalysts and catalytic reactions. In 1989, Gorte and co-workers<sup>7</sup> and Haw *et al.*<sup>8</sup> independently reported the observation of reactive intermediates on the zeolite surface with the use of <sup>13</sup>C solid state NMR. They developed specific devices<sup>9</sup> to allow adsorption of the reactants and spectroscopic measurements in the absence of water and other impurities. Gorte and co-workers<sup>7</sup> studied the adsorption and reaction of *tert*-butanol over HZSM-5 zeolite, whereas Haw *et al.*<sup>8</sup> focused on the propene/HY system. In both studies, the main conclusion was that no ionic carbocation was observed within the time scale of the NMR experiments. For instance, the <sup>13</sup>C NMR spectra of the isopropyl and *tert*-butyl cation in superacid solution present a peak relative to the cationic carbon around 320-330 ppm.<sup>4</sup> However, on zeolites the most deshielded peaks were observed in the range of 250 ppm, far below the region of simple carbocationic species. A peak at about 88 ppm in the <sup>13</sup>C NMR spectrum of propene over HY was ascribed to a covalent species, named alkoxide, in which the carbon atom is attached to the framework oxygen atom (Figure 2). The alkoxides were identified as long-living intermediates on the zeolite surfaces, and after these experiments many authors believed they are the real intermediates on zeolite-catalyzed reactions.



**Figure 2.** Pictorial representation of the alkoxide on the zeolite surface.

A point that stressed this belief was the fact that even indirect evidences for the formation of a short-lived ionic carbocation could not be obtained from the spectroscopic experiments. Haw published<sup>10</sup> an elegant study on the adsorption of different <sup>13</sup>C labeled propene over AlBr<sub>3</sub> and HZSM-5. Using either propene-1-<sup>13</sup>C or propene-3-<sup>13</sup>C they observed essentially the same NMR spectrum over HZSM-5, with intense peaks in the region of 30 ppm, ascribed to methyl groups. By contrast, when using propene-2-<sup>13</sup>C an intense peak at 88 ppm was observed near room temperature, which is consistent with the formation of the alkoxide. In the experiments over the zeolite, no significant scrambling of the <sup>13</sup>C atom was observed, differently of the results over AlBr<sub>3</sub>. Scrambling is a strong indication that a short-lived isopropyl cation was formed over AlBr<sub>3</sub> but not over HZSM-5, because <sup>13</sup>C scrambling is observed in the NMR spectrum of this carbocation in superacid solution.<sup>11</sup>

The peak at 250 ppm, observed in the early experiments of Haw and Gorte, was ascribed to conjugated cyclopropenyl cations. These type of carbocations are formed through complex condensation reactions and can be spectroscopically observed even in sulfuric acid solutions,<sup>12</sup> due to their charge delocalization, which stabilizes the carbocation.

In summary, solid state NMR experiments did not find evidences for the formation of simple alkyl carbocations, such as the *tert*-butyl and isopropyl cations over the zeolite surface at room temperature. Instead, covalent alkoxides were observed as long-lived intermediates and can undergo condensation reactions to more complex structures upon reaction with the excess of olefins present in the system.

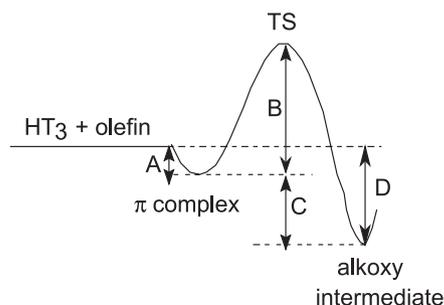
## 3. Early Theoretical Studies using Finite Clusters

The first theoretical studies of carbocations on zeolites appeared in the 1990's. The complexity of the zeolitic system, with many atoms to describe the unit cell, and the computational capabilities of that period limited the theoretical approach used in the early studies. Thus, most of the works were based on the finite cluster approach, where only a part of the zeolite structure was considered, notably the acid site. Hartree-Fock (HF) methods were firstly used, but they were soon supplanted by density functional theory (DFT) calculations, which provide description of electron correlation, at reasonably accepted computational costs.

In 1991, Kazansky and Senchenya<sup>13</sup> published a study of ethene protonation over an Al(OH)<sub>3</sub>H<sub>2</sub>O cluster representing the acid site of the zeolite. The results indicated a concerted mechanism, with the proton being transferred to the double bond simultaneously with the nucleophilic attack of the

oxygen atom into the other carbon atom of double bond. Although the cluster used to represent the acid site was oversimplified, there were important highlights from this study, such as the simultaneous participation of two oxygen atom in the protonation process. Later on, the minimum structure used to represent the zeolite acid site was the  $H_3Si-OH-Al(OH)_2-O-SiH_3$  finite cluster ( $HT_3$ ), where T stands for Si or Al atom. Although it better describes the acid site in terms of the electronic configuration, it did not include the effects of the zeolite cavity and, by this way, it did not represent any particular zeolitic system. Studies of the protonation of ethene, propene and isobutene, using  $HT_3$  clusters and HF level of theory, appeared in the literature.<sup>14,15</sup> The results pointed out for a concerted process, forming an alkoxide as the final product. The transition state however, resembles a carbenium ion and the activation energy was straightforward related with the structure of the hydrocarbon. Table 1 shows the calculated energy for the adsorption of the olefins to an  $HT_3$  cluster at different level of calculations, whereas Figure 3 shows the energy profile. One can see that, regardless of the level of theory used in the calculations, the activation energy decreases on going from ethene to isobutene, which reflects the stability of the respective carbocation in the transition state. The stability of the alkoxide follows an opposite trend, indicating steric repulsions between the methyl groups and the  $T_3$  cluster.

Calculation of the relative stability of butoxide isomers<sup>16</sup> afforded a comparison among the primary, secondary and tertiary alkoxides. Table 2 shows the energy difference indicating the lower stability of the *tert*-butoxide, which is due to the steric repulsion between the methyl groups and the framework atoms. The steric effects associated with the attachment of an alkyl group to the framework oxygen atom could be highlighted on a larger zeolite cluster, describing a real part of the zeolite Y structure. We carried out a study with a  $T_{30}$  cluster,<sup>17</sup> comprising the hexagonal prism and the sodalite cage of the zeolite. The results indicated that the flexibility of the zeolite framework is limited and bulky alkyl groups experience strong repulsions with the



**Figure 3.** Energy profile for the protonation of olefins over an  $HT_3$  cluster.

**Table 1.** Calculated energy (kcal mol<sup>-1</sup>) for the protonation of olefins over an  $HT_3$  cluster at different levels of calculations

Barrier	Reference	Ethene	Propene	Isobutene
A	14 <sup>a</sup>		-5.9	-8.2
	15 <sup>b</sup>	-5.1	-5.6	-7.0
	16 <sup>c</sup>	-	-	-6.8
B	14 <sup>a</sup>		35.7	34.4
	15 <sup>b</sup>	27.8	22.8	13.3
	16 <sup>c</sup>	-	-	22.7
C	14 <sup>a</sup>		-17.6	-15.5
	15 <sup>b</sup>	-16.1	-14.5	-9.3
	16 <sup>c</sup>	-	-	-1.5
D	14 <sup>a</sup>		-47.4	-41.7
	15 <sup>b</sup>	-21.2	-20.1	-16.3
	16 <sup>c</sup>			-8.3

<sup>a</sup>HF/3-21G; <sup>b</sup>MP2(fc)6-31G(d,p)//HF/6-31G(d,p); <sup>c</sup>B3LYP/6-31G(d,p).

framework. In addition, different adsorption sites on the zeolite structure could be investigated. Nevertheless, the use of semi-empirical methods at that time limited the scope of the results, providing only a qualitative trend.

**Table 2.** Calculated enthalpy difference between the butoxy isomers on a  $T_3$  finite cluster, at B3LYP/6-31G(d,p)

Alkoxy Intermediate	$\Delta H / (\text{kcal mol}^{-1})$
<i>n</i> -butoxy	+0.2
<i>sec</i> -butoxy	0.0
<i>iso</i> -butoxy	+0.7
<i>tert</i> -butoxy	+5.2

The spectroscopic studies that characterized the alkoxides as long-living intermediates over the zeolite surface, together with calculations of hydrocarbon protonation with finite clusters, which confirmed the spectroscopic findings, led many authors to believe that the alkoxides were the real intermediates on hydrocarbon reactions over zeolites. Therefore, theoretical studies of cracking,<sup>18</sup> isomerization<sup>19</sup> and hydride transfer,<sup>20</sup> considering the alkoxides as intermediates, appeared in the literature, although the calculations sometimes pointed out for highly energetic barriers. Simple alkyl carbocations were then considered only transition states over the zeolite surface.

#### 4. Alkylhalides as Source of Carbocations on Zeolites

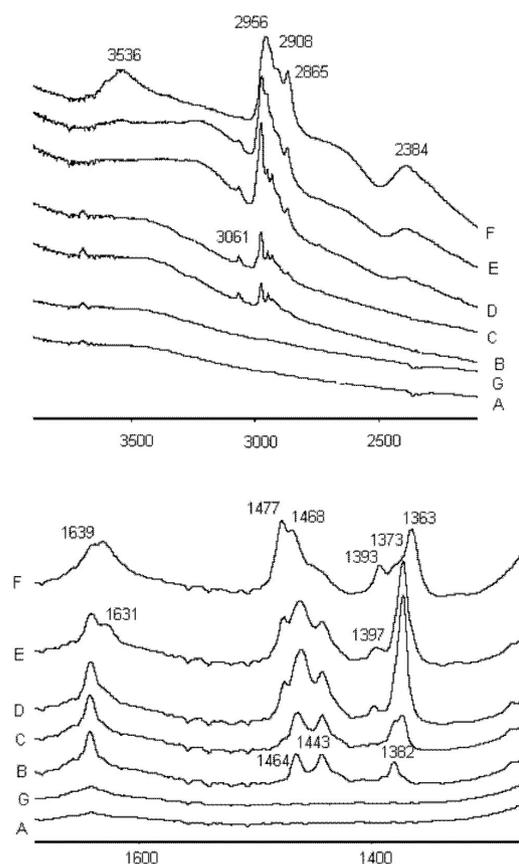
Most of the spectroscopic studies to characterize the nature of carbocations on zeolites were carried out with

olefins or alcohols over acidic zeolites. Although this system is closer to what would be found in oil refining processes, such as cracking or alkylation, the presence of secondary reactions sometimes mask the results. The high concentration of olefins and the presence of acidic sites favor complex condensation reactions. The peak around 250 ppm in the  $^{13}\text{C}$  NMR of solid state propene over HY<sup>8</sup> exemplifies this process. However, the most dramatic situation arises from the studies with the *tert*-butoxide. Although the formation of the *tert*-butoxide was considered in the first studies<sup>7</sup> of *tert*-butanol over HZSM-5, further investigation<sup>21</sup> with isobutene over acidic zeolites revealed that, in fact, the *tert*-butoxide is not a long-living species, yielding complex condensation reactions with the olefins in the medium to afford higher molecular weight intermediates. This trend was also confirmed by infrared studies<sup>22</sup> of *tert*-butanol and isobutene over acidic zeolites, which pointed out for a rapid dimerization process. Thus, the *tert*-butoxide was never spectroscopically characterized as a long-living intermediate over the zeolite surface.

To minimize the problems associated with the condensation process when using olefins or alcohols over acidic zeolites, we started working with alkylhalides over metal-exchanged zeolites. The main idea was that the metal cations on zeolites might behave as weak Lewis acid sites, complexing with the halide and giving rise to adsorbed carbocations, either covalent alkoxides or ionic carbocation species.

We initially applied the method for the study of different butoxides over NaY zeolite using *in situ* infrared spectroscopy at different temperatures.<sup>23</sup> Whereas *n*-butyl and *sec*-butyl chlorides afforded spectra consistent with the formation of the respective alkoxides, the *tert*-butyl chloride showed a complete different behavior. A sharp band at 1639  $\text{cm}^{-1}$ , relative to C=C stretching, was observed even at  $-125\text{ }^\circ\text{C}$  (Figure 4). The spectrum at this temperature is consistent with the formation of adsorbed isobutene, indicating a fast proton elimination as the *tert*-butyl chloride was admitted to the medium. As the temperature increases, the olefinic band broadens suggesting the presence of oligomers. Indeed, the spectrum at room temperature is similar to the infrared spectrum observed in the adsorption of *tert*-butanol or isobutene over acidic zeolites,<sup>22</sup> which pointed out for a dimerization reaction. Thus, the *tert*-butoxide was not spectroscopically characterized even with the use of *tert*-butyl chloride and NaY, indicating the high reactivity of the system.

DFT calculations using a  $\text{NaT}_3$  cluster supported the experimental results. For the *n*-butyl and *sec*-butyl chlorides, formation of the respective alkoxide was the lower energy barrier process, whereas elimination to afford 1-butene and 2-butene, respectively, was significantly more energetic. On the other hand, calculations with the

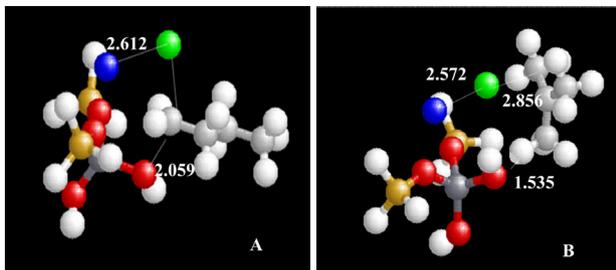


**Figure 4.** Infrared spectra of *tert*-butyl chloride over NaY: (A) NaY prior adsorption; (B) adsorption at  $-125\text{ }^\circ\text{C}$ ; (C) adsorption at  $-105\text{ }^\circ\text{C}$ ; (D) adsorption at  $-90\text{ }^\circ\text{C}$ ; (E) adsorption at  $-60\text{ }^\circ\text{C}$ ; (F) adsorption at  $25\text{ }^\circ\text{C}$ ; (G) NaY after heating to  $400\text{ }^\circ\text{C}$  and evacuating to  $10^{-4}$  Torr. Reprinted from reference 23 with copyright permission from Royal Society of Chemistry.

*tert*-butyl chloride afforded only isobutene as product and all attempts to characterize the *tert*-butoxide were unsuccessful. These results were in close agreement with the experimental findings.

Figure 5 A shows the transition state for alkoxide formation from the *n*-butyl chloride, showing a resemblance with an  $\text{S}_{\text{N}}2$  mechanism. The departure of the chloride ion takes place at the opposite side of the nucleophilic attack. On the other hand, the transition state of proton elimination from *tert*-butyl chloride resembles an E2 mechanism (Figure 5 B), with departure of the chloride simultaneous to proton transfer to the zeolite.

Although the use of alkylhalides did not prevent oligomerization in tertiary systems, it proved to be useful to study the formation and reactivity of alkoxides on zeolites. The metal cation also plays a role in the reactivity of the system.<sup>24</sup> The use of alkylhalides and metal-exchanged zeolite in alkylation,<sup>25</sup> and natural gas conversion to olefins<sup>26</sup> or methanol,<sup>27</sup> are practical applications of the concepts developed in the more fundamental spectroscopic and theoretical studies.



**Figure 5.** Calculated transition state for alkoxide formation from the adsorption of *n*-butyl chloride (A) and proton elimination from the adsorption of *tert*-butyl chloride (B) over NaY, at B3LYP/6-31G(d,p). Reprinted from reference 23 with copyright permission from Royal Society of Chemistry.

## 5. Theoretical Studies Considering the Zeolite Cavity

The finite cluster approach used in the first studies of carbocations on zeolites does not describe the electronic and steric effects associated with the entire zeolite cavity, which might favor ionic carbocations. The covalent C-O bond in the alkoxides imposes some steric repulsion with the zeolite framework, and it is possible that these species would be high in energy on zeolites of constrained pore environment.

The advances in theoretical methods and computers permitted a more precise description of the zeolitic system in recent years, especially with the inclusion of the whole cavity. It is of special importance the development of methods based on periodic boundary conditions (PBC) calculations,<sup>28</sup> where a box containing the system is replicated by translation throughout space to form an infinite lattice, and the ONIOM scheme,<sup>29</sup> where different parts of the system are treated at different levels of theory.

With the inclusion of the zeolite cavity it became clear the importance of steric constraints on the relative stability of the alkoxides, especially on zeolites in which the pore walls are significantly curved, such as Chabazite.<sup>30</sup> Calculations<sup>31</sup> indicated that the *tert*-butyl cation could be characterized as minimum on the potential energy surface on certain zeolite structures, but the energy difference between the carbocation and the *tert*-butoxide depends, mainly, on short-range effects and local steric constraints.<sup>32</sup>

Most of the theoretical studies using periodical and ONIOM methods relied on less complex zeolite structures, like Chabazite and Ferrierite, or curved structures, such as Mordenite. Nevertheless, the industrial most important zeolite catalyst is Faujasite or zeolite Y. This material is the main ingredient of cracking catalysts, responsible for the production of high-octane gasoline and liquefied petroleum gas (LPG). Thus, it is important to study the

carbocation/alkoxide system on this particular zeolite structure. We have carried out an ONIOM study<sup>33</sup> on the protonation of isobutene over a large cluster model of zeolite Y, comprising 288 atoms ( $\text{Si}_{84}\text{O}_{132}\text{H}_{72}$ ), which corresponds to two coupled supercavities. The coordinates were obtained from the crystallographic data available in the literature.<sup>34</sup> The acid site and the organic moiety were treated by *ab initio* methods, whereas the rest of the zeolite structure was treated by the semiempirical MNDO method. Table 3 shows the enthalpy difference between the isobutene  $\pi$ -complex, the *tert*-butoxide and the *tert*-butyl cation, at different levels of theory. In all cases, the  $\pi$ -complex was found to be the most stable species, but we were able to characterize the *tert*-butyl cation as a discrete intermediate on the zeolite surface. The energy difference between the carbocation and the alkoxide depends on the level of theory. The stabilization of the *tert*-butyl cation is mostly due to short-range interactions, such as hydrogen bonding and electrostatic effects, whereas the alkoxide is more sensitive to dispersion interactions. It is interesting to note that the *tert*-butoxide is higher in energy compared with the isobutene  $\pi$ -complex, in agreement with our spectroscopic observation<sup>23</sup> of the adsorption of *tert*-butyl chloride over NaY.

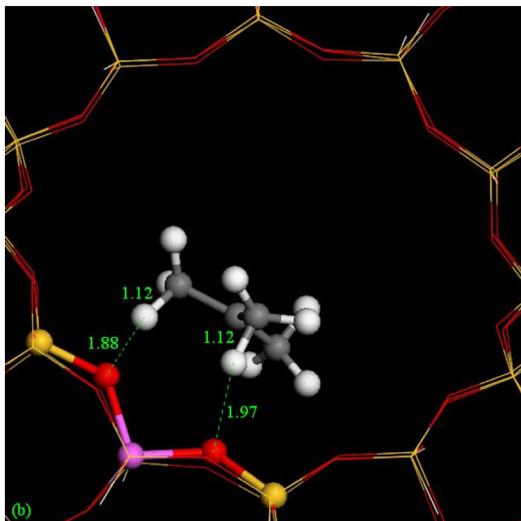
**Table 3.** Calculated enthalpy difference for the  $i\text{-C}_4\text{H}_9^+$   $\pi$ -complex, alkoxide and carbocation adsorbed on the zeolite Y pore cavity, at different levels of theory

Species	$\Delta H / (\text{kcal mol}^{-1})$		
	ONIOM (MP2:MNDO)	ONIOM (MP2:PBE1PBE)	PBE1PBE
$\pi$ -complex	0	0	0
<i>tert</i> -butoxide	9.0	2.4	4.3
<i>tert</i> -butyl cation	18.6	25.8	14.8

Figure 6 shows the calculated structure of the *tert*-butyl cation inside the zeolite Y cavity. One can see the hydrogen bond interactions between the *tert*-butyl cation and the framework oxygen atoms, which is an important source of stabilization of carbocations on the zeolite surface.

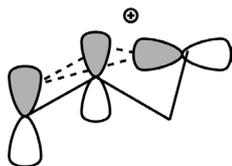
## 6. Rearrangement and Nucleophilic Substitution on Alkylhalides: the Bicyclobutonium Cation

Although the theoretical studies considering the entire zeolite cavity have demonstrated that the *tert*-butyl cation can be an intermediate on zeolite-catalyzed reactions, they pointed out to a significant energy difference with respect to the alkoxide. Thus, it was not clear if carbocations were really involved in the reaction mechanism, or if they are formed only at high temperatures, typically of oil refining



**Figure 6.** Structure of the *tert*-butyl cation adsorbed on Y zeolite surface determined at ONIOM(MP2(FULL)/6-31G(d,p):MND0) level. Reprinted from reference 33, with permission from Elsevier.

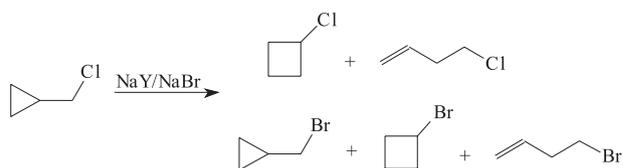
(*e.g.* 400-500 °C) or on particular zeolite structures, where steric constraints play a decisive role. To show that equilibrium between covalent alkoxides and ionic carbocations can occur, even at room temperature, we decided to carry out a study with a small cyclic system. The cyclopropylcarbinyl chloride undergoes a rearrangement when solvolyzed in polar solvents to yield three isomeric compounds.<sup>35</sup> This chemistry was extensively studied in solution by J. D. Roberts, who proposed the involvement of the bicyclobutonium cation (Figure 7). This ion has a three-center two electron bond, permitting the nucleophilic attack at three different positions. Therefore, if the same kind of rearrangement occurs on zeolites, it would be a strong evidence for the formation of the bicyclobutonium cation.



**Figure 7.** Pictorial representation of the structure of the bicyclobutonium cation showing the three-center bond.

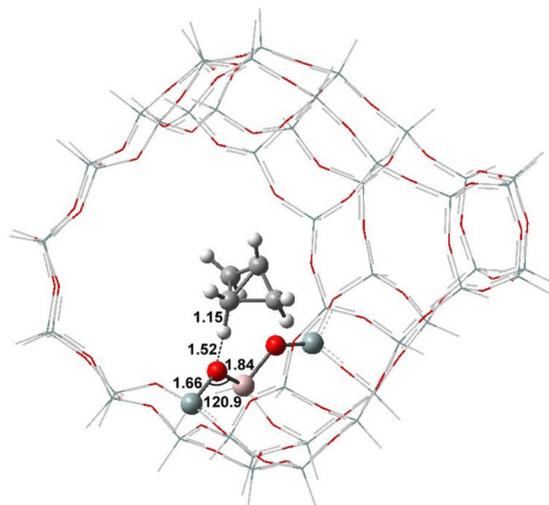
Upon exposing the cyclopropylcarbinyl halide (chloride or bromide) to NaY at room temperature, we were able to observe cyclobutyl and allylcarbinyl halides, together with the unreacted cyclopropylcarbinyl halide.<sup>36</sup> The characterization of rearranged products is consistent with formation of the bicyclobutonium cation and internal return of the halide ion. We also carried out the reaction of cyclopropylcarbinyl chloride with NaY impregnated with NaBr. Besides the rearranged chlorides, we were able to

observe cyclopropyl, cyclobutyl and allylcarbinyl bromides among the products. They were formed upon the nucleophilic attack of the bromide ion to the bicyclobutonium cation. The nucleophilic substitution and rearrangement were first-order in relation to the cyclopropylcarbinyl chloride, being independent of the concentration of the impregnated bromide. All these findings are unequivocal evidences for a mechanism involving ionization of the cyclopropylcarbinyl chloride to the bicyclobutonium cation. Internal return of the chloride anion affords the rearranged alkylchlorides and nucleophilic attack by the bromide anion impregnated inside the zeolite cavity gives rise to the alkylbromides (Scheme 1).



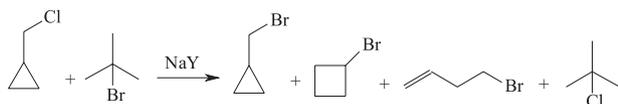
**Scheme 1.** Rearrangement and nucleophilic substitution of the cyclopropylcarbinyl chloride over NaY impregnated with NaBr. Adapted from reference 36.

The experimental results were supported by theoretical calculations, which indicated that the bicyclobutonium cation is an intermediate inside the zeolite Y cavity. The calculations, at PBE1PBE/6-31G(d,p):MND0 level of theory, identified, at least, three possible  $C_4H_7^+$  cations on zeolite Y. The relative stability of the carbocations is directly related with the strength of the hydrogen bond with the zeolite structure (Figure 8), stressing the short range stabilization of these species.



**Figure 8.** Most stable  $C_4H_7^+$  species, the bicyclobutonium cation, on the zeolite Y surface, calculated at PBE1PBE/6-31G(d,p):MND0 level. Reprinted from reference 36, with permission from American Chemical Society.

An interesting discovery that came with this study was the halogen switch reaction. When we concomitantly adsorbed *tert*-butyl bromide and cyclopropylcarbinyll chloride over NaY zeolite, we were able to observe among the products *tert*-butyl chloride, cyclopropylcarbinyll, cyclobutyl and allylcarbinyll bromides (Scheme 2). The same type of result occurs with *tert*-butyl chloride and cyclopropylcarbinyll bromide on NaY. The reaction was interpreted in terms of nucleophilic substitution, with attack of the chloride or bromide leaving group to the formed carbocations. This occurs inside the zeolite cage due to the pore confinement effect,<sup>37</sup> which permits the close proximity among the different species inside the pores. In liquid solutions, the substrate is completely surrounded by the solvents molecules, impairing the proximity between two different ionogen molecules. Thus, upon ionization either the solvent or the leaving group (internal return) attacks the formed carbocation. However, on zeolites, the pore structure permits the concentration of two different alkylhalide molecules inside the cavities, allowing the formed carbocations to interact with two different leaving groups (nucleophiles).



**Scheme 2.** Halogens switch reaction over zeolite Y. Adapted from reference 36.

## 7. Concluding Remarks. Where Are We Going?

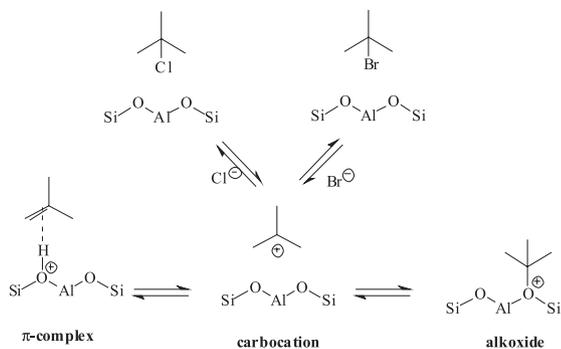
There are unequivocal evidences, both from theoretical calculations and experimental studies with alkylhalides, that simple alkyl carbocations can be intermediates on the zeolite surface. Although the relative stability among the ionic carbocation, the covalent alkoxide and the olefin  $\pi$ -complex is still a matter of debate and might be dependent on the zeolite structure, there is no doubt that the three species might be in equilibrium during zeolite-catalyzed reactions. Stabilization of the carbocations is mostly due to short-range interactions, such as hydrogen bonding and electrostatic forces. This picture may change the way people develop better zeolite catalysts, because instead of increasing the acid strength, the focus may be the modification of the structure or the pore environment towards the better stabilization of the carbocation. The acid strength is one of the factors, but certainly not the only one. In recent calculations, we observed that the bicyclobutonium cation becomes more stable than the respective alkoxides when a monomeric LiCl is considered inside the cavity. This indicates that the carbocations can

interact with other species inside the cavity, besides the framework oxygen atoms. It is known that ultrastable Y zeolites (USY), produced upon partial steam dealumination of the framework that also leads to formation of extra-framework aluminum (EFAL), present a high catalytic activity for hydrocarbon cracking.<sup>38</sup> Many authors explain<sup>39</sup> this behaviour to a synergistic effect between Bronsted and Lewis acid sites, the later being associated to the EFAL species. Nevertheless, the synergy between both acid sites has been questioned in some theoretical studies,<sup>40</sup> which indicated that hydrogen bonding stabilization of the deprotonated zeolite plays a major role. It is possible that the EFAL species may stabilize the formation of the carbocation through hydrogen bonding, as well as providing additional electrostatic stabilization. In fact, some acidity measurements<sup>41</sup> indicated a same acid strength distribution in Y zeolites, regardless of the presence of EFAL. Therefore, the focus must be on the intermediate species, such as carbocations, rather than on the initial state of the zeolite (acidity).

We believe that zeolites may act as solid solvents. An important property of solvents<sup>42</sup> is the ionizing ability, with the presence of electron-pair donor (EPD) and electron-pair acceptor (EPA) sites in the structure. We may consider the oxygen atoms of the framework structure of zeolites as EPD centers, whereas the metal cations act as EPA centers. In this sense, zeolites may be explored in other fields, rather than catalysis and adsorption. They provide a good environment for carrying out ionic reactions, especially for less polar substrates that are insoluble in water or other polar media.

Scheme 3 shows a general picture for ionic reactions on zeolites, highlighting the equilibrium among the isobutene  $\pi$ -complex, the *tert*-butoxide and the *tert*-butyl cation on the surface. Whereas the alkoxides and the  $\pi$ -complexes should be thermodynamically more stable than the ionic carbocations, many reactions, including cracking, isomerization, alkylation and nucleophilic substitution (shown in the scheme), occur through the involvement of carbocationic intermediates. The future experimental studies will be focused on the relation between the zeolite structure, and its acidity, with regard to the stabilization of carbocations. On the other hand, the theoretical studies will have to advance on the understanding of the short-range stabilization of carbocations, as well as giving inputs of the lifetime of such intermediates within the zeolite pore environment.

One may finally argue if the study of cyclopropylcarbinyll chloride rearrangement on NaY may be extended to acidic zeolites, which are the most important for industrial purposes. Table 4 show the kinetics of the cyclopropylcarbinyll chloride rearrangement on sodium,



**Scheme 3.** Equilibrium among the  $\pi$ -complex, alkoxide and the carbocation over the zeolite surface. It is also highlighted nucleophilic substitution reactions occurring from the carbocation. Adapted from reference 33.

ammonium and protonic Beta zeolite at 28 °C. One can see that the rearrangement occurs over ammonium and protonic zeolite Beta, although the reactions are significantly slower than over NaBeta. We are still investigating this system, but it will certainly shed more light into the mechanism of carbocation formation over protonic zeolites.

**Table 4.** Kinetics of the cyclopropylcarbinyl chloride rearrangement over zeolite Beta at 28 °C

Zeolite	$k / 10^{-3} \text{ min}^{-1}$
NaBETA	1.8
$\text{NH}_4\text{BETA}$	0.5
HBETA	0.5

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