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The mobility and rearrangement of the $C_4H_7^+$ system over Chabazite were studied using *ab initio* molecular dynamics. The results indicated the high mobility of the cations, which can rearrange within picosecond time intervals. Experimental studies of nucleophilic substitution supported the theoretical findings.

Zeolites are crystalline aluminosilicates widely used as catalysts in the petrochemical industry due to their acidic and shape selective properties.¹ The true nature of the intermediates in the acidcatalyzed zeolite reactions is a matter of debate, in which covalent alkoxides and ionic carbocations can play a role.² We have studied the nature of these intermediates by adsorbing alkylhalides over metal-exchanged zeolites.³ In these systems, the metal cation coordinates with the alkylhalide to form a metal-halide species, leaving a carbocation or an alkoxide on the zeolite structure. Using this technique we were able to show⁴ the rearrangement and nucleophilic substitution of cyclopropylcarbinyl halides over NaY at room temperature. The results were interpreted in terms of the formation of the bicyclobutonium cation $(C_4H_7^+)$, which may be nucleophilically attacked at three different positions, giving rise to cyclobutyl and allylcarbinyl halides, as well as the parent cyclopropylcarbinyl halide (Scheme 1).

The nature of the $C_4H_7^+$ cation has been extensively discussed in the last 50 years. Roberts suggested the bicyclobutonium cation, which behaves as a set of charge-delocalized rapidly equilibrating carbonium ions, as the main intermediate in the rearrangement of the cyclopropylcarbinyl system.⁵ However, ¹³C NMR studies performed in superacid solution pointed to a set of rapidly equilibrating ions of lower symmetry.⁶ The temperature dependence of the ¹³C NMR chemical shifts indicated a rapid equilibrium between two cations with a low rearrangement barrier.



Dynamic behaviour of carbocations on zeolites:

mobility and rearrangement of the C₄H₇⁺ system

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Scheme 1 Product distribution of nucleophilic attack on the three centre bond of the bicyclobutonium ion.

Isotopic perturbation experiments have supported these conclusions.⁷ The cyclopropylcarbinyl and the bicyclobutonium cations were considered as the most likely species involved in this equilibrium. The interconversion between them involves a barrier of less than 16.7 kJ mol⁻¹ at 270 K in the gas phase. The structural equilibration occurs within a time interval of less than 10^{-10} s.⁸ Such results are also supported by theoretical methods used to elucidate the potential energy surface of $C_4H_7^+$ in the gas phase⁹ and in solution.¹⁰ Most of the calculations indicate that the cyclopropylcarbinyl cation is slightly less stable than the bicyclobutonium ion in the gas phase. In addition, the potential energy surface of $C_4H_7^+$ is nearly flat and might involve different carbocations as, for example, the allylcarbinyl cations.

There are few computational studies on the dynamics of carbocations in solution, most of them involving fluxional systems¹¹ or ion pairing.¹² The studies of molecular dynamics on zeolites mostly involve hydrocarbon interactions with the active site,¹³ without explicitly studying the dynamics of carbocation formation or reaction. We wish to show *ab initio* molecular dynamics results of the $C_4H_7^+$ system, which may help in understanding the time scale of carbocation rearrangement within the zeolite cavity and the role of alkoxides and ion pairing.

The simulations were carried out using a trigonal unit cell of Chabazite (a = b = c = 9.421 Å and $\alpha = \beta = \gamma = 94.2^{\circ}$) containing 36 atoms, in which a silicon atom of the structure was replaced by an aluminium atom (Si–Al ratio equal to 11). In such a molecular model, the shortest distance between atoms of the reactive domain and their repeated images is greater than 9 Å in all trajectories, minimizing the possibility of undesired interactions between the organic moieties. The bicyclobutonium cation was

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Fig. 1 Mean square displacement (MSD) of the $C_4H_7^+$ species adsorbed on the Chabazite zeolite at 50, 150, 300 and 500 K.

inserted into the main channel near the aluminium atom. Periodic potential was restricted to the second Brillouin zone. The calculations were performed using the Vienna *Ab initio* Simulation Package $(VASP)^{14}$ using generalized gradient approximation (GGA) formulated by Perdew and Wang for the exchange–correlation functional, the plane-wave basis with a cut-off energy of 300 eV for electron valence contributions and ultra soft pseudopotentials to describe the electron–core interactions. The molecular dynamics trajectories of 3.0 ps (after 1.0 ps of equilibration) were obtained using the Verlet algorithm with a time step of 0.5 fs within the NVT (canonical) ensemble at different temperatures (50, 150, 300 and 500 K) controlled by the Nosé–Hoover thermostat.

To more deeply understand the mobility of the $C_4H_7^+$ cation within the zeolite cavity, molecular dynamics (MD) simulations were performed at different temperatures. According to the analysis of the NVT trajectories, the $C_4H_7^+$ cation is mobile inside the Chabazite cavity over all trajectories calculated at 50, 150, 300 and 500 K. However, such behaviour is more pronounced above room temperature, as shown using the mean square displacement (MSD)[†] of the $C_4H_7^+$ cation at different temperatures evaluated by means of the classical equation (Fig. 1).

The theoretical results of the mobility of $C_4H_7^+$ inside the zeolite cavity can be supported by experiments of nucleophilic substitution of the cyclopropylcarbinyl chloride in the presence of alcohols. We have previously observed that the product distribution of nucleophilic substitution of the cyclopropylcarbinyl chloride over NaBr impregnated on NaY does not follow the kinetic distribution observed in solution, which favours the cyclic cyclobutyl and cyclopropylcarbinyl products.⁴ However, this result could be either due to successive ionization of the formed bromides, yielding the thermodynamically more stable allycarbinyl halide, or due to a preferential attack on the bicyclobutonium cation due to ion pairing with the zeolite framework, which may result in preferential orientation of the cation toward the nucleophile. To answer this question we performed the rearrangement of cyclopropylcarbinyl chloride on NaY in the presence of methanol, ethanol and n-propanol as external nucleophiles. The procedure was basically the same as reported elsewhere,⁴ just introducing two-fold molar excess of the alcohol in relation to the halide at room temperature. Control experiments showed that in the absence of the zeolite, no reaction takes place between the chloride and the alcohols at room temperature. The rearrangement of cyclopropylcarbinyl chloride on NaY at room temperature is slower in the presence of alcohols, with pseudo first order kinetic constants of 4 \times 10⁻⁴ min⁻¹ for

methanol, 10^{-4} min⁻¹ for ethanol and 5 \times 10^{-5} min⁻¹ for n-propanol. These values are at least 100 orders of magnitude slower than the kinetic constant observed in the absence of alcohols. The explanation may be related to the competition between the alcohol and the cyclopropylcarbinyl chloride for coordinating with the sodium cations on the zeolite. Besides the rearranged chlorides, formed upon internal return of the halide, we were able to observe the respective ethers, formed upon the nucleophilic attack of the alcohols on the carbocation. The distribution of the ethers is similar to the distribution found in solution, favouring the cyclopropylcarbinyl and cyclobutyl isomers, which were formed in approximately 48% and 47% selectivity, over the allycarbinyl ether, which was produced in about 5% selectivity at room temperature. This distribution can be explained by the activation energy¹⁰ for nucleophilic attack at the bicyclobutonium cation and expresses the kinetic control. Since the distribution observed on zeolites is similar to the distribution found in solution,⁵ the results support the mobility of the $C_4H_7^+$ cation inside the zeolite cavity, allowing the carbocation to be attacked at the most favourable positions. These results are in agreement with MD calculations that indicated the high mobility of the $C_4H_7^+$ cation within the zeolite cavity at room temperature, thus reinforcing the lower significance of ion pairing processes in zeolite-catalyzed reactions at higher temperatures.

The theoretical MD results also revealed the fluxionality of the $C_4H_7^+$ cation, indicating that the energy barrier for the interconversion between the bicyclobutonium and cyclopropylcarbinyl cations is relatively small on the zeolite surface, as observed in superacid solution. In fact, it was frequently observed along the trajectories calculated at 50, 150, 300 and 500 K, the back and forth interconversion between the bicyclobutonium and cyclopropylcarbinyl cations, as depicted in Scheme 2.

The C_2 - C_4 distance is indicative of the bicyclobutonium-cyclopropylcarbinyl interconversion along the MD trajectories. Fig. 2 shows



Scheme 2 Bicyclobutonium–cyclopropylcarbinyl cation interconversion (the positive charge was not shown).



Fig. 2 Probability density of the C2-C4 distance as a function of temperature.

 $\mbox{Table 1}\ \mbox{Relative stability of the C_4H_7$^+ species adsorbed on Chabazite (values in kJ mol^{-1})$

Species	$\Delta U \left(\text{kJ mol}^{-1} \right)$
Allylcarbinyl cation	75.3
Cyclopropylcarbinyl cation	69.1
Bicyclobutonium cation	66.6
Allylcarbinyl alkoxide	0.0

the probability density of the C_2-C_4 distance along the MD trajectories. As the interconversion takes place, with formation of the cyclopropylcarbinyl cation, this distance may stretch up to 2.8 Å. At 50 K, due to the low thermal energy available, the bicyclobutonium ion prevails, as observed in the C_2-C_4 distance within 1.2 and 1.8 Å. At higher temperatures, there is significant probability of the C_2-C_4 distance to be within 2.1 and 2.8 Å, indicative of the interconversion into the cyclopropylcarbinyl cation.

In addition to the bicyclobutonium and the cyclopropylcarbinyl cations, the allylcarbinyl isomer was also observed in some of the trajectories calculated at 300 K and in all trajectories calculated at 500 K. This result is consistent with previous calculations¹⁰ that point out the higher energy of the allylcarbinyl cation relative to the bicyclobutonium and cyclopropylcarbinyl isomers. In one of the trajectories calculated at 500 K, the allylcarbinyl cation interacted with the framework oxygen atom near the aluminium atom to yield the respective alkoxide, which persisted till the end of the path.

Geometry optimizations of selected structures along the MD trajectory calculated at 500 K were performed in order to check if they correspond to minima on the potential energy surface (PES). Most of the optimizations systematically yielded the bicyclobutonium cation as the local minimum, being the most stable $C_4H_7^+$ ion. However, some of the structures corresponded to the cyclopropylcarbinyl and allylcarbinyl cations.

Table 1 shows the relative stability of the C₄H₇⁺ species on Chabazite calculated from the electron energy differences without considering thermal and vibrational contributions. The bicyclobutonium cation is more stable than the cyclopropylcarbinyl isomer by 2.5 kJ mol⁻¹ and by 8.7 kJ mol⁻¹ in relation to the allylcarbinyl cation. On the other hand, the allylcarbinyl alkoxide is the calculated most stable species, lying 66.6 kJ mol⁻¹ below the bicyclobutonium cation. Nevertheless, we were able to observe a trajectory for the formation of the alkoxide of the carbocation only at 500 K, when the allycarbinyl cation was formed. This result suggests that, although the alkoxides are thermodynamically more stable than the carbocations, their formation from their ionic counterparts is not straightforward. From the calculated trajectories, it is found that formation of the alkoxide can occur only when the carbocation is favourably orientated near the framework oxygen atom. With the increase in temperature and the consequent mobility of the cation toward the centre of the cavity, the formation of the alkoxide is less favourable, but when it occurs it persists for a long period, explaining the spectroscopic results,¹⁵ which normally point out the alkoxides as the longliving species on the zeolite surface.

Based on the relative stability it is possible to explain the dominance of certain C₄H₇⁺ isomers in the MD trajectories. The bicyclobutonium cation is the most stable $C_4H_7^+$ ion, which justifies its predominance in the trajectories calculated at 50 K. In addition, the small difference in stability between the bicyclobutonium and cyclopropylcarbinyl cations explains the fast interconversion between them in the trajectories calculated at room temperature and above. This result indicates that rearrangement of carbocations on zeolites is fast near room temperature and occurs within the picosecond time scale. The allylcarbinyl cation is rarely observed in the trajectories calculated at 300 K, but is more frequently observed in the trajectories calculated at 500 K. These data indicate that less stable carbocations can be formed inside the zeolite surface at higher temperatures, having enough time to be converted into products, before going to alkoxides. This may explain several hydrocarbon processes on zeolites, such as cracking, which occur at high temperatures.

Notes and references

 $\dagger \text{ MSD}(t) = \left\langle \Delta r_j^2(t) \right\rangle = \frac{1}{N} \sum_{j=1}^N \Delta r_j^2 = \frac{1}{N} \sum_{j=1}^N \left[r_j(t) - r_j(0) \right]^2$

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