

Dynamic Behavior of Carbocations on Zeolites: Time scale for Mobility and Rearrangement of the C₄H₇⁺ System.

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Introduction

Zeolites are crystalline aluminosilicates widely used as catalysts in the petrochemical industry. The true nature of the intermediates on the acid-catalyzed zeolite reactions is a matter of debate, in which covalent alkoxides and ionic carbocations can play a role. We have studied the nature of these intermediates adsorbing alkylhalides over metal-exchanged zeolites. 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 show the rearrangement and nucleophilic substitution of cyclopropylcarbanyl halides over NaY at room temperature.¹ The results were interpreted in terms of the formation of the bicyclobutonium cation (C₄H₇⁺), which may be nucleophilically attacked in three different positions, giving rise to cyclobutyl and allylcarbanyl halides, as well as the parent cyclopropylcarbanyl halide. In this work, we studied the dynamics of the C₄H₇⁺ system on Chabazite by *ab initio* molecular dynamic calculations at different temperatures (50, 150, 300 and 500 K) to elucidate the time scale and barriers for the interconversion among the possible species.

Results and Discussion

The theoretical MD results also revealed the fluxionality of the C₄H₇⁺ cation, indicating that the energy barrier for the interconversion between the bicyclobutonium and cyclopropylcarbanyl cations is relatively small on the zeolite surface, as observed in superacid solution. In fact, it was observed several times, along the trajectories calculated at 50, 150, 300 and 500 K, the back and forth interconversion between the bicyclobutonium and cyclopropylcarbanyl cations as depicted in the Figure 1.

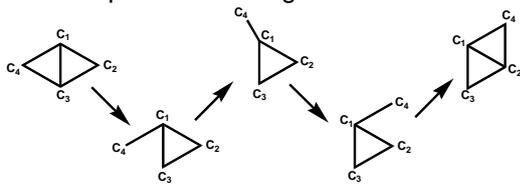


Figure 1. Bicyclobutonium and cyclopropylcarbanyl cations interconversion observed along the MD trajectories.

The C₂-C₄ bond length is an indicative of the bicyclobutonium-cyclopropylcarbanyl-bicyclobutonium cations interconversion along the MD trajectories. Figure 2 shows the probability density of the C₂-C₄ bond length along the MD trajectories. The C₂-C₄ bond length change between a minimum and maximum value corresponding to the two bicyclobutonium structures shown in the Figure 1 in the trajectories calculated at 150, 300 and 500 K. However, this process was not observed along the trajectories calculated at 50 K due to the low thermal energy available.

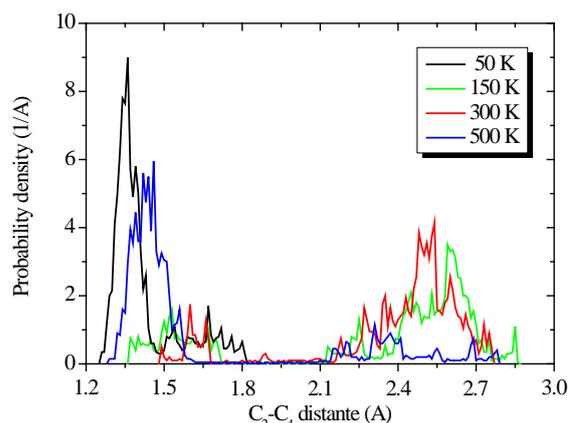


Figure 2. Probability density of the C₂-C₄ bond length along the MD trajectories calculated at 50, 150, 300 and 500 K.

Conclusions

MD calculations on the C₄H₇⁺ system adsorbed on chabazite surface reinforce the idea 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.

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¹ M. Franco, N. Rosenbach, G. B. Ferreira, A. C. O. Guerra, W. B. Kover, C. C. Turci, C. J. A. Mota, *J. Am. Chem. Soc.* **2008**, 130, 1592-1600.