A QTAIM study of the $C_4H_7^+$ system on Y zeolite.

Alex P. A. dos Santos[1] (PG), Nilton Rosenbach Jr.[1] (PQ), Valter L. C. Gonçalves[1] (PG), Clayton M. Rosman[1] (IC), Rodolfo Lorençato[1] (IC), Daniella R. Fernandes[1] (PG) & Claudio J. A. Mota[1] (PQ)* cmota@iq.ufrj.br

1 - Universidade Federal do Rio de Janeiro - Instituto de Química - Cidade Universitária CT Bloco A, 21949-900, Rio de Janeiro, Brasil, Laboratório de Reatividade de Hidrocarbonetos e Catálise Orgânica (LARHCO).

Keywords: *zeolites, carbocations, AIM.*

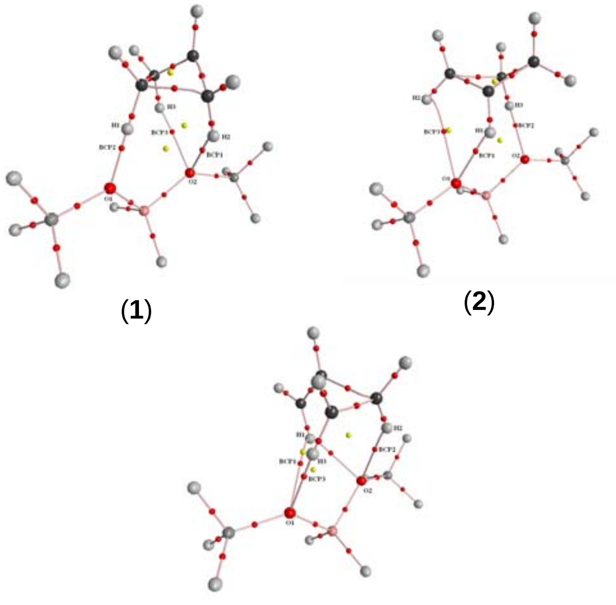
Introduction

The rearrangement of ciclopropylcarbinyl chloride in solution is well known in the literature. In a classical work published by Roberts and Mazur, the product distributions were explained by the formation of the byciclobutonium cation ($C_4H_7^+$). Recently, we were able to show the rearrangement of cyclopropylcarbinyl chloride over NaY. As in solution, we explained the results in terms of formation of the bicyclobutonium cation, which may be nucleophilic attacked in three different positions, giving rise to cyclobutyl, allylcarbinyl chlorides and the parent cyclopropylcarbinyl. In addition, our results reinforce the hypothesis of formation of simple carbocation species inside zeolite cavity. However, the most of the studies available in the literature indicated that covalent species, named alkoxides, are thermodynamically more stable than simple alkyl carbocation and observed as persistent intermediates on the zeolite surface.

In this study we use QTAIM to evaluate the interactions that affect the stability of carbocation/alkoxide on zeolites surface. The electronic density was derived from the Kohn-Sham orbitals obtained at the PBE1PBE/6-311++G** level and used to calculate the critical points, the Laplacian of charge density and the delocalization indexes.

Results and Discussion

Based on the Laplacian of the density function (L_b) and the relation $|\lambda_1|/\lambda_3$ at a bond critical point (BCP), it is possible to classify the bond type between each atomic pair. Closed-shell interactions such as hydrogen bond are characterized by $L_b < 0$ and $|\lambda_1|/\lambda_3$ smaller than 1. The values of L_b and BCPs at the bonds between each hydrogen of the bicyclobutonium (**1** and **2**) and cyclopropylcarbinyl (**3**) cations and the oxygen atom of the zeolite structure pair are negative and value of the relation $|\lambda_1|/\lambda_3$ from these BCPs is smaller than 1, which means that the interactions between each O-H atomic pair is hydrogen bond. All carbocations also present three ring critical points (RCP) that present similar charge density (ρ). The magnitude of the delocalization indexes (DI) between each O-H atomic pair can be used to predicted the interaction degree between both the carbocation and the zeolite structure. This results is in agreement with the relative stability of this species at PBE1PBE/6-311++G** level. All alkoxides are topologically different indicating steric repulsion between the organic moiety and zeolite structure.



(**1**) (**2**)

(**3**)

Figure 1. Molecular graphs of the bicyclobutonium (**1** and **2**) and cyclopropylcarbinyl (**3**) cations andsorbed on T_3 cluster.

Conclusions

QTAIM calculations reinforce the idea that carbocations on zeolite surface are stabilized mainly by short-range interactions such as hydrogen bond. Steric effects are predominant in the alkoxide stability.

Acknowledgments

The authors thank CAPES, CNPq and ANP for the financial support.

---

[1] Bader, R., *Atoms in Molecules: A Quantum Theory*, Oxford University Press, USA, **1994**.