

## The role of carbocations and alkoxides on hydrocarbon reactions.

Nilton Rosenbach Jr.<sup>1</sup> (PQ), Alex P. A. dos Santos<sup>1</sup> (PG), Valter L. C. Gonçalves<sup>1</sup> (PG), Clayton M. Rosman<sup>1</sup> (IC), Rodolfo Lorençato<sup>1</sup> (IC), Marcelo Franco<sup>2</sup> (PQ) & Claudio J. A. Mota<sup>1</sup> (PQ)\*  
[cmota@iq.ufri.br](mailto:cmota@iq.ufri.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).

2 - Universidade Estadual do Sudoeste da Bahia - Departamento de Estudos Básicos e Instrumentais, Praça Primavera, 40, 45700-000, Itapetinga, Bahia, Brasil.

Keywords: zeolites, carbocations, ONIOM calculations.

### Introduction

Acid zeolites are widely used in several petrochemical processes such as cracking, isomerization and alkylation. The key step in these reactions is the formation of the reactive carbocations. Although many efforts have been made to elucidate the nature of these species on the zeolite surface, there is no definite experimental evidence that simple alkyl carbocations are intermediate in zeolite-catalyzed reactions. Instead, most of the studies indicated that covalent species, named alkoxides, are thermodynamically more stable than simple alkyl carbocation and observed as persistent intermediates on the zeolite surface.

We have used metal-exchanged zeolite and alkylhalides to study carbocation/alkoxide on zeolites. Recently, we were able to show the rearrangement of cyclopropylcarbiny chloride over NaY. The results were interpreted in terms of formation of a bicyclobutonium cation ( $C_4H_7^+$ ), which may be nucleophilic attacked in three different positions, giving rise to cyclobutyl, allylcarbiny chlorides and the parent cyclopropylcarbiny. We also observe an unknown nucleophilic substitution process, named halogen switch reaction (HSR), which reinforce the hypothesis of formation of carbocation inside zeolite cavity.

In this study we use ONIOM method to evaluate the interactions that affect the stability of carbocation/alkoxide on zeolites surface. The cluster was divided in two layers (high and low layers) and the atoms of the cluster model and the organic moiety (high layer) were treated at the MP2(FULL)/6-31(d,p) or PBE1PBE/6-31G(d,p) level, whereas the rest of the zeolite cavity (low layer) was treated by the semiempirical MNDO method

### Results and Discussion

The results show that the bicyclobutonium (1), cyclopropylcarbiny (2) and the tert-butyl (3) cations are minima on the potential energy surface. As shown in the table 1, the energy difference between the carbocations and the respective cyclobutyl (3) cyclopropylcarbiny (4) allylcarbiny (5) *n*-butyl (7)

iso-butyl (8) sec-butyl (9) and *tert*-butyl (10) alkoxides is about 20 kcal.mol<sup>-1</sup> and depend on the level of calculation and size of the high layer. This gap is small enough to believe that both species, carbocations and alkoxides, might be in equilibrium during hydrocarbon reactions over zeolites. Both species are stabilized through hydrogen bonding interactions with the framework oxygen atoms. Further more, the calculations show that inclusion of short-range dispersion effects increase the stability of the cationic species. Thus, formation of carbocation on zeolite surface might become energetically favorable compared with the isolated reagents. In addition, short-range electrostatic effects, caused by the presence of monomeric species such as NaCl, significantly increase the stability of the bicyclobutonium cation, reducing the energy gap between the carbocation and the alkoxides in 10 kcal.mol<sup>-1</sup>.

**Table 1.** Enthalpy difference among carbocations and alkoxides at ONIOM(MP2(FULL)/6-31G(d,p):MNDO) level of calculations (values in kcal.mol<sup>-1</sup>).

$C_4H_7^+$		$C_4H_7^+ + NaCl$		$C_4H_9^+$	
1	17.4	1	10.0	6	19.8
2	21.4	2	-	7	3.3
3	0.0	3	0.0	8	0.2
4	1.9	4	2.2	9	0.0
5	0.0	5	0.9	10	7.2

### Conclusions

Our calculations reinforce the idea that carbocations are intermediate in zeolite-catalyzed reactions and might be in equilibrium with the alkoxides under reaction conditions, especially at the temperatures conditions employed in hydrocarbon transformations.

### Acknowledgments

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

<sup>1</sup> Franco, M.; Rosenbach, Jr. N.; Ferreira G. B.; Guerra, A. C. O.; Kover, W. B.; Turci, C. C.; Mota, C. A. J. *J. Am. Chem. Soc.*, **2008**, 130, 1600.