

The Role of Carbocations and Alkoxides on Hydrocarbons Reactions Catalyzed by Zeolites

Nilton Rosenbach Jr.¹, Alex P. A. dos Santos¹ and Claudio J. A. Mota^{1*}

¹Universidade Federal do Rio de Janeiro, Instituto de Química, Av. Athos da Silveira Ramos 149, CT Bloco A, Cidade Universitária, 21941-909, Rio de Janeiro, (Brazil)

*cmota@iq.ufrj.br

Introduction

Acid zeolites are widely used in several petrochemical processes such as cracking, isomerization and alkylation [1]. 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 [2].

We have used metal-exchanged zeolite and alkylhalides to study carbocation/alkoxide on zeolites. In that procedure, the metal cation coordinates with the alkylhalide to form a metal-halide and an alkoxide bonded to the zeolite structure. Recently, we were able to show the rearrangement of cyclopropylcarbanyl chloride over NaY [3]. 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, allylcarbanyl chlorides and the parent cyclopropylcarbanyl. We also observed an unknown nucleophilic substitution process, named halogen switch reaction (HSR), which reinforce the hypothesis of formation of *tert*-butyl cation inside the zeolite cavity. In this study we use the ONIOM method to evaluate the interactions that affect the stability of carbocation and alkoxide on the zeolites surface.

Computational Methods

A cluster of the zeolite Y ($Si_{84}O_{132}H_{72}$), corresponding to two coupled supercavities, was used in the calculations. The free valences of the border silicon atoms were saturated with hydrogen atoms, located at 1.09 Å distance and in the same plane of the Si-O bond. The position of the hydrogen atoms was kept fixed during the optimization steps, to avoid distortion of the model. All calculations were done using the ONIOM method. 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)/6-31G(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 both, the bicyclobutonium and the *tert*-butyl cation (Figure 1), are minima on the potential energy surface. As shown in the table 1, the energy difference between the carbocations and the respective alkoxides is about 20 kcal.mol⁻¹ 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. Furthermore, the calculations show that inclusion of short-range dispersion effects increase the stability of the cationic species. Thus, formation of the bicyclobutonium and *tert*-butyl cation 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⁻¹.

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

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

$C_4H_7^+$		$C_4H_7^+ + NaCl$		$C_4H_9^+$	
BCB cation	17.4	BCB cation.	10.0	<i>tert</i> -butyl cation	19.8
CPC cation	21.4	CPC cation	-	<i>n</i> -butyl alkoxide	3.3
CB alkoxide	0.0	CB alkoxide	0.0	<i>iso</i> -butyl alkoxide	0.2
CPC alkoxide	1.9	CPC alkoxide	2.2	<i>sec</i> -butyl alkoxide	0.0
AC alkoxide	0.0	AC alkoxide	0.9	<i>tert</i> -butyl alkoxide	7.2

BCB = bicyclobutonium; CPC = cyclopropylcarbanyl; CB = cyclobutyl; AC = allylcarbanyl

Significance

Understanding the mechanism of hydrocarbon reactions over zeolites is crucial to develop better catalysts for oil refining and petrochemical. The results of this work may lead to new approaches to develop more active and selective zeolite catalysts, not only focused on acidity, but on improving the stabilization of the carbocation through interactions with the zeolite framework.

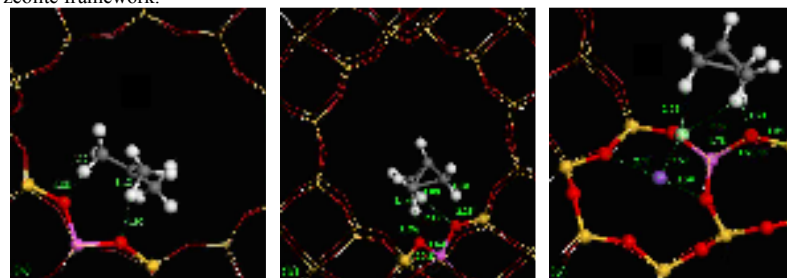


Figure 1. Structures for the (a) *tert*-butyl, (b) bicyclobutonium and (c) bicyclobutonium cation plus NaCl adsorbed on Y zeolite surface determined at ONIOM(MP2(FULL)/6-31G(d,p):MNDO) level.

References

1. A. Corma, Chem. Rev. 95 (1995) 559-614.
2. J.F. Haw, Phys. Chem. Chem. Phys. 4 (2002) 5431-5441.
3. M. Franco, N. Rosenbach, G.B. Ferreira, A.C.O. Guerra, W.B. Kover, C.C. Turci, and C.J.A. Mota, J. Am. Chem. Soc. 130 (2008) 1592-1600.