# A Theoretical Study of Carbocationics Species on Y Zeolite

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#### Introduction

Zeolites are the main catalyst of the petrochemical industries. The importance of these materials is due their capacity to promote many reactions. According to initial suggestions, carbocations should be key intermediates in these reactions. However, these species are seldom observed on the zeolite surface as persistent intermediates. In the experimental investigations, ones observe only covalent species (alkoxides). Therefore, many studies suggest that the alkoxides should be the key intermediates and the carbocations should be only transition states in these reactions. However, recent studies show halogen derivates can give carbocationics reactions on Y zeolite surface<sup>1</sup>. On the other hand. the bicyclobutonium/cyclopropylcarbinyl system plays a key role in solvolysis of cyclopropylcarbinyl and cyclobutyl derivates. In this case, there is equilibrium between the two cabocations (bicyclobutonium and cyclopropylcarbinyl). In order investigate in more detail the mechanism of halogen derivates reactions on zeolite surface: we carried out ONIOM calculations to determine the possible intermediates involved in reaction of cyclopropylcarbinyl and cyclobutyl derivates on Y zeolite surface.

In this study, we have used a molecular system with 161 atoms, which represents a supercavity of the Y zeolite. The calculations were performed using the ONIOM method available in GAUSSIAN 98 package. The molecular system was divided into layers. The atoms of the active site (high layer) were treated by the B3LYP functional with 631G(p, d) orbital basis set, whereas the other atoms (low layer) were treated by the semiempirical MNDO method.

### Results and Discussion

The calculations showed the bicyclobutonium carbocation as a minimum in the potential energy surface. The cyclopropylcarbinyl carbocation is higher energy by 1.96 kcal.mol<sup>-1</sup>. This order of stability is observed in solution and gas phase. The three alkoxides are the most stable than all carbocations. The relative energies for all species investigated are shown in table 1. Analysis of the geometries shows that all carbocations are located on the active site, near the aluminum atom. This preferential localization

is responsible by the neutralization of the negative charge results from of the tetracoodination of the aluminum atom. The alkoxides are linked to oxygen atom near the aluminum atom, forming a covalent carbon-oxygen bond. For this reason, the alkoxide are most stable than all cabocations.

Table 1 – Relative energies for all species investigated.

Specie	Relative Energy (kcal.mol <sup>-1</sup> )
homoallyl	0.00
cyclobutyl	4.49
clopropylcarbinyl	4.72
bicyclobutonium	36.27
metylcyclopropyl	38.23

## Conclusions

The theoretical results show a carbocation as stable specie on Y zeolite surface. Based on our calculations, the reactions of the hydrocarbons and their derivates on zeolite surface involve carbocationic species. In these reactions, the carbocations will be intermediates and not transition state as suggest some previous mechanistic proposals. Like in the solvolysis of cyclopropylcarbinyl and cyclobutyl derivates, on zeolite surface there are also equilibrium between the two carbocationics species: bicvclobutonium cvclopropvlcarbinvl. and Our calculations also showed alkoxides as the most stable species on zolite surface. In summary, based insights gained via guantum mechanical on calculations for the reactions of cyclopropylcarbinyl and cyclobutyl derivates on Y zeolite surface, we suggest equilibrium between alkoxides and carbocations, since both species are intermediates or minimum in the potential energy surface.

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