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Theoretical study on reactions catalyzed by gallium-substituted zeolites

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Abstract. The dehydrogenation and cracking reactions of light alkanes in gallium-containing zeolites were studied using density functional theory. Gallium isomorphically substituted, generating Brønsted acid sites, was used in the computations. The following reactions were examined: dehydrogenation of methane, ethane, propane, isobutane and cracking of ethane, propane and isobutene, all catalyzed by the framework gallium species. The cracking reaction seems to be favored relative to the dehydrogenation when framework gallium species are used. This behavior is also observed in aluminum-containing zeolites (H-ZSM5). The geometries and energetics of the transition states found for the gallium zeolites were compared with theoretical data for the same transition states in aluminum zeolites. There seems to be no significant difference between framework gallium and framework aluminum species. Therefore the framework gallium should not be the species responsible for the catalytic enhancement observed in gallium-containing zeolites.

Keywords: Zeolite – Gallium – Catalysis by zeolites

Introduction

Zeolites are crystalline inorganic microporous solids, mostly aluminum silicates, containing channels and cavities of molecular dimensions (3–10 Å). These peculiar structural characteristics make them useful materials for a wide range of industrial processes, such as separation, purification and ion exchange. However, it is in

the field of heterogeneous catalysis that the most important applications of these materials can be found [1].

The micropores of the zeolites are very uniform and in the same size range as small molecules (4–12 Å). As a consequence, zeolites can exhibit specificity and selectivity in adsorbing or rejecting molecules based upon differences in molecular shape, size and polarity. The catalytic activity is related to the presence of Brønsted acid sites in the zeolite structure. Some modifications in this structure can be made, such as the inclusion of metallic species such as gallium and iron, which modify the catalytic behavior in terms of selectivity and activity.

Zeolites containing gallium constitute an extremely interesting class of compounds. The gallium-containing zeolite [Ga]ZSM-5, analogous to ZSM-5 (MFI), catalyses the transformation of linear alkanes (C3–C5) into aromatic hydrocarbons [2]. For instance, the conversion of propane, in the Cyclar process, produces by weight 63.1% of a mixture of benzene, toluene and xylene (BTX) and 5.9% of H₂ besides light alkanes, especially ethane and methane [3].

Different gallium species exhibiting catalytic behavior have been reported in the literature: gallium incorporated by direct synthesis [4, 5, 6, 7, 8, 9, 10, 11, 12, 13] with the formation of framework gallium (replacing an aluminum atom in the original framework) and non-framework gallium incorporated by impregnation [6, 10], ion exchange [6, 13, 14] or even a physical mixture of Ga₂O₃ and H-ZSM-5 [7, 10, 15]. In spite of that, the particular role of the framework and nonframework gallium is still very controversial. Some authors believe that only nonframework species are responsible for the catalytic activity [8, 15]. In particular, Price et al. [15] reported significant catalytic activity exhibited by a gallium-exchanged MFI sample with virtually no Brønsted sites, which implies no active framework gallium species. Others say that only the framework gallium responds for the catalytic activity [7, 16]. Yet, some authors state that the nonframework species are

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involved in the process but the catalytic activity also depends on the number of Brønsted acid sites, generated by the presence of framework gallium [9, 10]. Finally the latest reports on this matter indicate cooperation between the two species in a bifunctional mechanism. These latest studies suggest that the framework gallium is the catalytic site, while the nonframework species behaves as a promoter [11, 12, 13]. According to Iglesia et al. [14] the Brønsted acid sites are responsible for the C–H bond activation, which yields surface alkyl and hydrogen atom species, whereas the gallium sites promote recombination of surface hydrogen atoms to molecular hydrogen.

Besides the discussion on which species are really involved in the catalytic process (framework or non-framework), there is also the question about the structure of these species. The framework gallium species have been well characterized by several authors, using different techniques, as replacing an aluminum atom in the crystalline framework of the zeolite, giving rise to sites like the ones shown in Fig. 1, slightly less acidic than the analogous ones in ZSM-5 [5, 6, 11, 13].

The characterization of nonframework gallium is still a matter of debate. Some authors suggest that the gallium species is adsorbed in the dihydride form (Fig. 2) [17], while others suggest the gallilic ion form is involved (Fig. 3) [18].

Irrespective of the nature and structure of the active site, the catalytic process in the interior of a gallium-containing zeolite is complex, with several intermediates and different reaction channels. The difficulty to experimentally detect all intermediates and to determine the energy parameters for each elementary step involved in the catalytic process suggests the use of theoretical methods to bring new insights to the problem. Some efforts have already been made in this direction. Himei and coworkers [19, 20], for instance, have studied the chemical and physical adsorption of methane on gallium-exchanged ZSM5, as well as the effect of water poisoning, using the extra-framework gallium cluster in

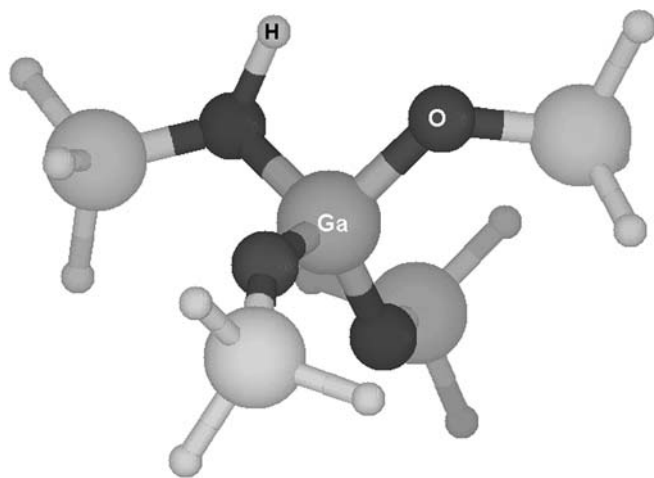


Fig. 1. T5-cluster model for the framework gallium species

the gallilic ion form. Stave and Nicholas [21] have studied how the size of the zeolite cluster model affects the calculated results for the gallium isomorphically substituted H-ZSM5, as well as the relative acidity of H-ZSM5 substituted by boron, aluminum, gallium and iron. Viruela-Martín [22] examined the protonation of

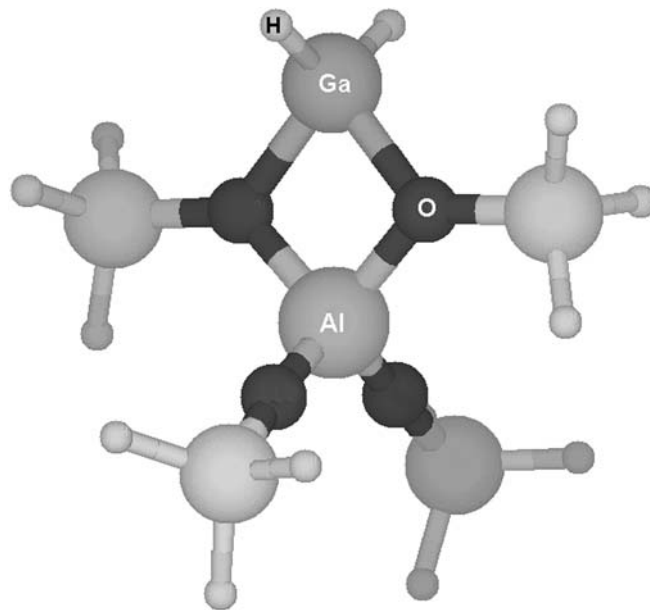


Fig. 2. T5-cluster model for the dihydride form of extra-framework gallium

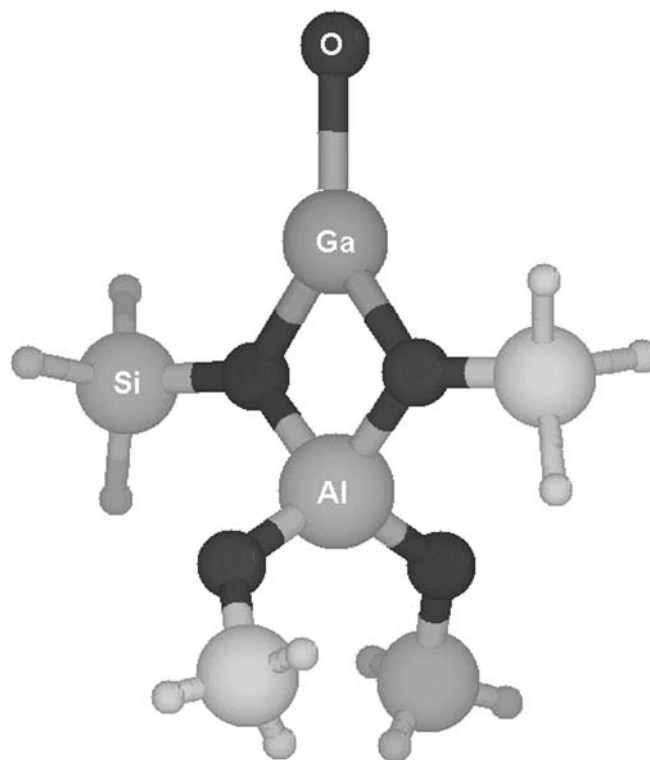


Fig. 3. T5-cluster model for the gallilic ion form of the extra-framework gallium

propylene and isobutene by isomorphically substituted zeolites. Intermediates and transition states for those reactions with boron-, aluminum- and gallium-substituted zeolites were found. Frash and van Santen [23, reported the dehydrogenation of ethane to ethene with the nonframework species. However, none of these authors have computed the reaction with the framework gallium in order to compare the two species. This comparison would be of major importance in the discussion of the role played by each of the gallium species.

In this paper we examine the catalytic behavior of framework gallium species with respect to the dehydrogenation and cracking reactions of several light alkanes in order to gain some understanding of the role played by the different gallium species. These reactions are competitive and are also elementary steps for more complex processes such as aromatization. The investigation of nonframework gallium species and the possible cooperative effects (framework and nonframework gallium) will be the subject of another publication.

Models and computational details

For the reactions with the framework gallium a T5 model (Fig. 1) was used. This same model was employed in previous studies with H-ZSM5 [24, 25, 26], the only difference being the replacement of the aluminum with the gallium atom.

All the calculations were performed with the density functional theory (DFT) method using the hybrid exchange–correlation functional B3LYP [27, 28], along with the LACVP basis set (6-31G** and effective core potential, ECP for gallium) with the program JAGUAR 3.5 [29]. A DFT-based method was chosen because very reasonable results can be obtained at relatively low computational cost. B3LYP was chosen because it has been widely used in other calculations [24, 25, 26], including some with gallium atoms [19, 20, 23], providing, among the presently available functionals, the best description of these reactions. The activation energy for the dehydrogenation of methane was calculated at the same level (DFT B3LYP/6-31G**) but without using the ECP for gallium, with the program GAUSSIAN [30] and little difference in the energy owing to the ECP was observed (1.7 kcal/mol). No restrictions were imposed during geometry optimizations and saddle point searches. No attempts were made at calculating adsorption energies since in the present case they could be dominated by weak interactions, such as dispersion forces, which are poorly described by the presently available DFT functionals. Therefore, the calculated activation energies should be compared to the experimental apparent activation energies.

Results and discussion

The dehydrogenation reaction of methane, ethane, propane and isobutene, as well as the cracking of ethane, propane and isobutene, was investigated with the framework species. The total energies for the structures involved in each reaction are shown in Table 1.

The transition-state energies are compared with theoretical transition-state energies [24, 25] for H-ZSM5 and are displayed in Table 2. The transition states for both the dehydrogenation and the cracking reactions with the framework gallium are very similar to those found for H-ZSM5 [24, 25, 26]. The activation energies are almost the same as the analogous ones with H-ZSM5

Table 1. Internal energies (B3LYP/6-31G** with zero-point-energy correction) of the framework gallium structures of the transition states

| | | <i>E</i> (hartrees) |
|-----------------|--------------|---------------------|
| Dehydrogenation | Methane | −1,509.243662 |
| | Ethane | −1,548.538017 |
| | Propane | −1,587.827050 |
| | Propane sec. | −1,587.844836 |
| | Isobutane | −1,627.145041 |
| Cracking | Ethane | −1,548.545253 |
| | Propane | −1,587.848939 |
| | Isobutane | −1,627.143228 |
| | T5cluster | −1,468.891176 |
| Substrates | Methane | −40.478994 |
| | Ethane | −79.763808 |
| | Propane | −119.051649 |
| | Isobutane | −158.340855 |

Table 2. Apparent activation energies (kilocalories per mole) of the reactions with H-ZSM5 and framework gallium (H-[Ga]ZSM5)

| | | H-ZSM5 | H-[Ga]ZSM5 |
|-----------------|--------------|-------------------|------------|
| Dehydrogenation | Methane | | 79.4 |
| | Ethane | 72.7 ^a | 73.4 |
| | Propane | 69.7 ^a | 72.6 |
| | Propane sec. | 59.9 | 61.5 |
| | Isobutane | 52.7 ^a | 54.6 |
| Cracking | Ethane | 67.1 ^b | 68.9 |
| | Propane | 56.8 ^b | 58.9 |
| | Isobutane | 53.5 ^b | 55.7 |

^aRef. [24] ^bRef. [25]

(Table 2), since the slight difference (1–3 kcal/mol) can be attributed partly to the use of the ECP. It should be noted that the activation barrier for the dehydrogenation of propane at the primary carbon atom is higher than the activation barrier for the reaction at the secondary carbon atom, as expected, since in the later case a stabler secondary carbocation is formed.

The dehydrogenation reactions (Fig. 4) follow the same trends as observed when H-ZSM5 is used [24, 25, 26]. For the linear alkanes the reaction coordinate clearly indicates the formation of molecular hydrogen and the respective alkoxides; however, for isobutane, the *t*-butyl cation eliminates isobutene and a proton, which restores the acid site on the zeolite [24, 25, 26].

It is also worth noticing that, for the isobutane transition state, the distance between the cluster and the substrate is nearly 1.2 Å greater than for the propane transition state (Table 3). This can be attributed to the steric hindrance of the methyl groups as the isobutane approaches the acid site. Again this is in perfect agreement with the results obtained for the reactions with H-ZSM5 [24, 25, 26].

The transition states for the cracking reactions of ethane, propane and isobutane are shown in Fig. 5. Once more the transition states are very similar to those found with H-ZSM5 [24, 25, 26]. The zeolite proton attacks the carbon atom of the alkane substrate, giving

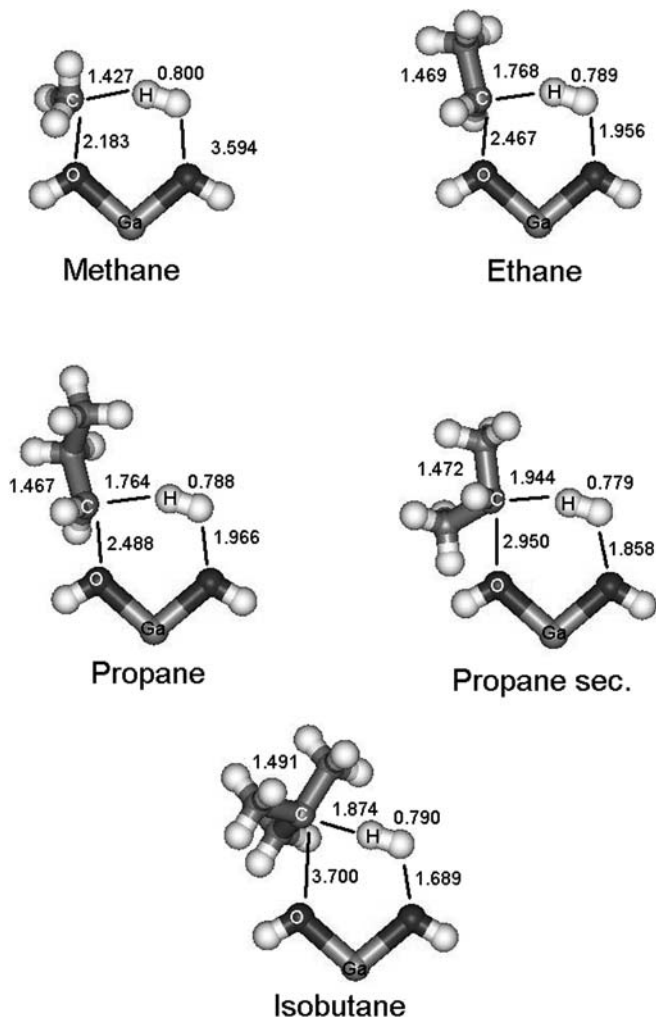


Fig. 4. Transition states of the dehydrogenation reaction of methane, ethane, propane and isobutane with the framework gallium species

rise to a carbocation and a neutral alkane of smaller chain length (Table 4).

Irrespective of the zeolite being used (H-[Ga]ZSM5 or H-ZSM5), the cracking of ethane and propane is favored over the dehydrogenation reaction, while for the isobutane molecule these reactions are practically competitive.

From the results presented here, it is clear that the H-[Ga]ZSM5 and H-ZSM5 zeolites exhibit very similar

Table 3. Relevant parameter for the transition states of the dehydrogenation reactions with the framework gallium. Distances in angstroms

| | Methane | Ethane | Propane | Propane sec. | Isobutane |
|-------|---------|--------|---------|--------------|-----------|
| H1-H2 | 0.800 | 0.789 | 0.788 | 0.779 | 0.790 |
| O1-H2 | 3.594 | 1.956 | 1.966 | 1.858 | 1.689 |
| C1-H1 | 1.427 | 1.768 | 1.764 | 1.944 | 1.874 |
| C1-O1 | 2.980 | 2.786 | 2.787 | 3.230 | 3.676 |
| C1-O3 | 2.183 | 2.467 | 2.488 | 2.950 | 3.700 |
| C1-C2 | - | 1.469 | 1.467 | 3.700 | 1.491 |

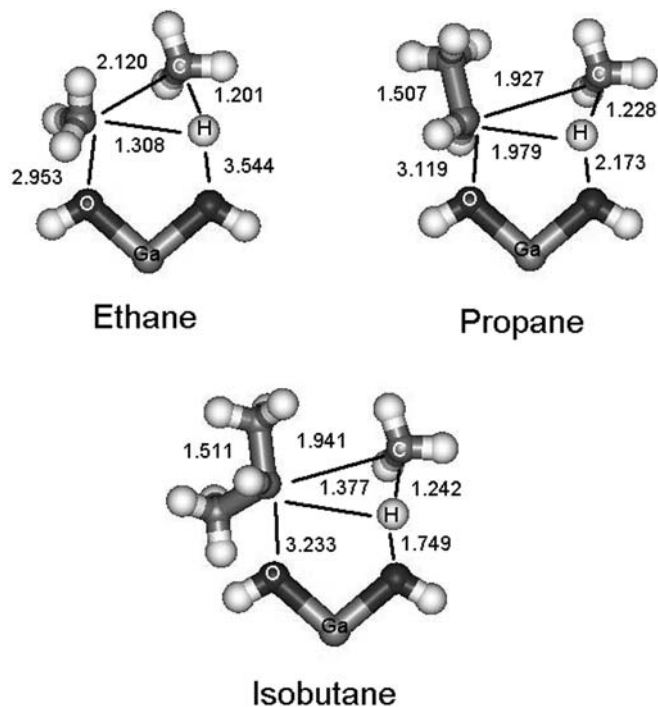


Fig. 5. Transition states of the cracking reaction of ethane, propane and isobutane with the framework gallium species

behavior as far as the activation of alkanes is concerned. Although this similarity in behavior could be anticipated, quantitative results are required for a comparative study on the catalytic activity of the framework and nonframework gallium zeolites. The mechanisms for the dehydrogenation and cracking reactions catalyzed by H-ZSM5 apply equally to those catalyzed by the framework gallium zeolite, with almost equal energetics. Thus, it seems unlikely that the isomorphically substituted gallium alone could be responsible for the enhancement in activity and selectivity exhibited by the gallium-exchanged zeolites [1, 2, 3, 31].

Before concluding, it is important to mention that, for H-ZSM5, we have recently investigated the effect of basis set and cluster sizes [32] on the mechanisms and energetics of all the reactions considered in the present paper. These calculations indicated that the mechanism of the reactions studied can be well established at the 6-31G**/5T-cluster level, although larger clusters are

Table 4. Relevant parameters for the transition states of the cracking reactions with the framework gallium. Distances in angstroms

| | Ethane | Propane | Isobutane |
|-------|--------|---------|-----------|
| C1-C2 | 2.120 | 1.927 | 1.941 |
| C1-H1 | 1.201 | 1.228 | 1.242 |
| C2-H1 | 1.308 | 1.279 | 1.377 |
| C2-O1 | 3.064 | 3.057 | 2.899 |
| C2-O2 | 2.953 | 3.119 | 3.233 |
| O1-H1 | 3.544 | 2.173 | 1.749 |
| C2-C3 | - | 1.507 | 1.511 |

required for more accurate activation energies. The results obtained with the 20T cluster [32] showed that the activation energies are lower by around 10 kcal/mol, relative to the results obtained with the 5T cluster. Also, preliminary estimates using the 96T cluster, indicate a correction of around 14 kcal/mol in the activation energies, relative to the 5T-cluster results, owing to the electrostatic potential of the infinite-sized crystal. Considering that H-ZSM5 and H-[Ga]ZSM5 exhibit very similar behavior towards the activation of alkanes at the 5T-cluster level of calculation, there is no reason to believe that this similarity will not be exhibited as the size of the cluster is increased.

Conclusion

The dehydrogenation and cracking reactions of methane, ethane, propane and isobutane were performed with a framework gallium model. The framework gallium species and the analogous species with aluminum (H-ZSM5) have extremely similar behavior in both dehydrogenation and cracking reactions. Ethane and propane are more likely to be cracked than to be dehydrogenated in the presence of framework gallium. This is not the case for isobutane, probably because of the higher steric hindrance in the cracking transition state.

Since the geometries and the energetics of the transition states for H-[Ga]ZSM5 are very similar, the framework gallium alone should not be the species responsible for the catalytic enhancement exhibit by gallium-containing zeolites.

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