



DFT analysis of propane cyclization over binuclear Ga-clusters in mordenite[☆]

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ABSTRACT

Molecular and dissociative adsorption of propane on binuclear $(\text{Ga}_2\text{O}_2)^{2+}$ cluster located at the cation positions of Ga-exchanged mordenite zeolite are modeled using DFT calculations via the isolated cluster approach. Relative energies of the dissociative intermediates show the most stable bidentate complexes, i.e., via both primary C atoms of propane to both Ga atoms. This structure really is the suitable precursor of cyclo-propane formation. The hypothesis of cyclo-propane intermediate was proposed by Derouane et al. to explain the $^{13}\text{C}/^{12}\text{C}$ exchange migration within propane molecules in Ga-exchanged zeolites.

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1. Introduction

To our opinion, only several experimental studies on zeolites in which key questions on reactivity have been clearly formulated so far. The Ga-exchanged zeolites present a rare case with industrial applications, for example, in CYCLAR process of hydrocarbon dehydrogenation [1]. A number of experimental and theoretical studies of probable catalytic active sites and dehydrogenation reaction mechanisms were provided for these catalysts but, nevertheless, many aspects of the process remain questionable. In this field, the analysis of NMR data on the $^{13}\text{C}/^{12}\text{C}$ exchange migration within a hydrocarbon [2,3] has been proven very useful. To explain the quick $^{13}\text{C}/^{12}\text{C}$ exchange in propane molecule, Derouane et al. proposed the formation of cyclo-propane (c-propane) [2,3]. Such a scheme allows the back opening of a C–C bond of c-propane and the migration of the ^{13}C atoms between the primary and secondary positions. Among several objections as discussed in Ref. [4], the strain of the c-propane structures is the first and main objection to this proposition, because an additional process should compensate the energy

losses. It would thus be interesting to model the problem at theoretical level.

The first question here is the structure of the active site. Recent experimental and theoretical studies [5–8] show the strong tendency to form binuclear Ga-oxide clusters, stabilized at cation positions in Ga-exchange zeolites. Such form of active site allows us to consider binuclear GaC_3Ga and mononuclear GaC_3 dissociative adsorption which can be considered as precursors of the c-propane formation. The 4-membered ring (4R) windows are often considered regarding di-valent cations with various ligands in cyclopropane chemistry, for example, nickel NiL_n complex with phosphine L ligands [9], seleno SeRR' using alkyl ligands ($\text{R}, \text{R}' = \text{Me}, \text{Bu}$) [10], and chromium carbonyls $\text{Cr}(\text{CO})_4$ [11]. Upon dehydrogenation such a 4R structure approaches a stable c-butyl cation geometry. Together with methyl-c-propyl cation, they belong to a series of resonance structures generally named as bi-cyclobutonium [12]. Transformation of bi-cyclobutonium to c-propane derivatives is a well known synthetic reaction [13]. Bi-cyclobutonium is the simplest Hückel system with two π -electrons obeying to the $(4n+2)$ -rule, n being the number of π -electrons, which explains its stability [14]. Involving the 4R intermediates of the GaC_3 type could be productive for a dehydrogenation study.

In this paper, a series of intermediate complexes, including the GaC_3 type, was simulated at the DFT level via the isolated cluster approach. Several structures which compensate the energy losses in the course of the cyclization are obtained.

2. Computational details

First, we fully optimized the geometry of a supercell with two primitive cells of Zn-form of mordenite (MOR) using the GULP code [15] and Catlow force field (FF) [16,17] with Al in position T4 [18],

[☆] The activity of Prof. Eric G. Derouane expanded over numerous directions in zeolite chemistry, from the development of pioneering physical concepts to the optimization of chemical synthesis, including catalysis. His ideas were an inspiring basis of many modern experimental and theoretical studies for many researchers at MSU, BIC, and FUNDP. Particularly, at the later where Eric has been Full Professor for over 20 years, one of us (DPV) has benefited personally from Eric's friendship and highly stimulating and inspiring advices, which helped him for his tenure position and to tackle molecular simulations of zeolites in general. With this paper, we refer to the cyclization of propane over Ga-form zeolites, whose possibility has been first proposed by E.G. Derouane. A theoretical evidence of such a possibility is clearly proven for the first time.

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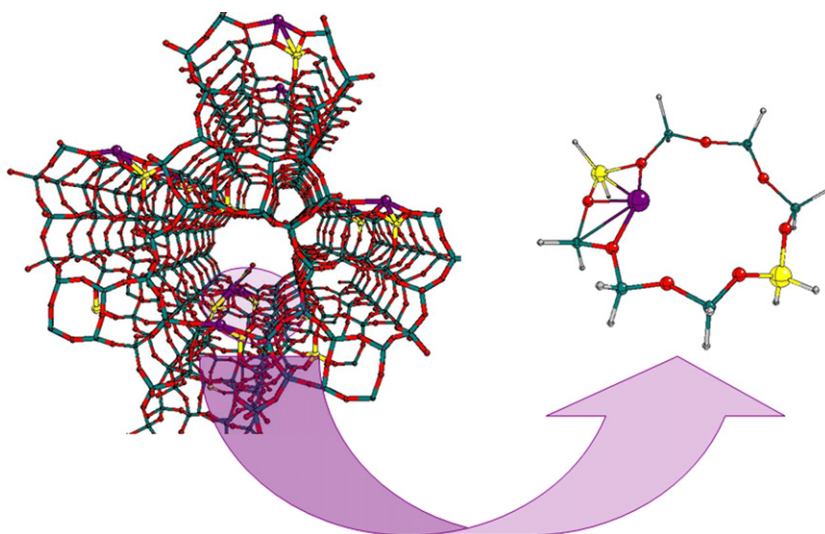


Fig. 1. Selection of the chosen fragments from ZnMOR. The color code is: Zn in purple, O in red, Si in green, Al in yellow, H in grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

on the opposite sides of the large channel in ZnMOR. One of the 8R windows which open the side pockets in ZnMOR was isolated from the 3D structure and the second Si atom was replaced by Al at T4. Keeping the Zn cation near the 8R window and capping the ruptured T–O bonds of all T atoms (T = Si, Al) by hydrogen atoms, one reached a neutral fragment $\text{ZnAl}_2\text{Si}_6\text{O}_8\text{H}_{16}$, in which one replaced Zn by Ga (Fig. 1). The T–H bond lengths were initially fixed at 1.4 Å, close to the optimal value as estimated at the B3LYP/6-31G* level. The T–H lengths were further optimized using GAUSSIAN03 [19] with fixed O–T–H, T'–O–T–H angles, and fixed positions of the other atoms. Then, H atoms only were fixed and the coordinates of the other atoms were varied also at the B3LYP/6-31G* level. The geometry optimization was then repeated considering different Al-sequences in the 8R window and the most stable –Al–O–Si–O–Si–O–Si–Al–ring was used for further analysis. Possible products of hydration and hydrogenation of Ga_2O_2 were studied as well for different Al-sequences.

Propane and c-propane molecules were initially positioned near the cluster at van der Waals distances. To look for the products of dissociative adsorption, two H atoms of primary or secondary carbons of propane were transferred to the Ga_2O_2 (8R) cluster whose geometry was optimized together with the dehydrogenation product. Optimized physisorbed propane is shown in Fig. 2a. The propane and c-propane complexes with Ga_2O_2 were named according to the 6R, 5R, and 4R cycles including the Ga, C, and O atoms, i.e., 6-(–C₁–C₂–C₃–Ga–O–Ga–) ring in Fig. 2b and c, 5-(–C₂–C₃–Ga–O–Ga–) ring in Fig. 2d, 4-(–C₁–C₂–C₃–Ga–) ring in Fig. 2e and f, with the exception of the case named as “chain” in Fig. 2g in which the 6R cycle is ruptured via the Ga–O bond (shown by arrow in Fig. 2c). The optimized geometry of physisorbed c-propane is shown in Fig. 2h.

Three basis sets were utilized for the analysis of the relative B3LYP energies, i.e., D95(T, H_t)/6-311G**(O, C, H)/6-31G*(Ga) (basis set 1), D95(T, H_t)/6-311G**(O)/6-31G*(Ga, C, H) (basis set 2), and 6-31G*(basis set 3), where T = Si, Al, and H_t are the terminal hydrogens of the framework.

3. Results

For the propane and c-propane molecules over Ga_2O_2 , we observed a crucial influence of the basis set on the relative stabilities. The 6Ra complex (Fig. 2b) is the most stable one with the best balanced basis set 1 for the Ga and O atoms responsible for bond-

Table 1

Relative energies (kcal/mol) of optimized physisorbed propane (C_3H_8), 6R complexes with C_3H_6 connected to both Ga atoms through two primary carbons (6Ra, 6Rb), 5R complex connected to both Ga atoms through primary and secondary carbons (5R), 4R complexes Ga1– C_3H_6 (4Ra, 4Rb), chain or ruptured 6R complex (chain), c-propane (c- C_3H_6) with basis sets 1–3.

Models	Basis set 1		Basis set 2		Basis set 3	
	U	ΔU	U	ΔU	U	ΔU
C_3H_8	–6949.153165	0.0	–6949.110394	0.0	–6949.565992	0.0
6Ra	–6949.162632	–5.9	–6949.111963	–1.0	–6949.564021	1.2
6Rb	–	–	–6949.084587	16.2	–6949.536313	18.5
5R	–6949.131086	13.8	–6949.088000	14.0	–6949.541845	15.2
4Ra	–6949.132178	13.2	–6949.080101	19.0	–6949.526179	25.1
4Rb	–6949.101071	32.7	–6949.051976	36.7	–	–
Chain	–6949.157551	–2.8	–6949.104627	3.6	–6949.549842	10.1
c- C_3H_6	–6949.129749	14.7	–6949.084888	16.0	–6949.524035	26.3

ing even if the absolute energies are more stable with basis set 3 (Table 1). Hence, below we will mainly address to the results with basis set 1.

Two landmark geometries of adsorbed propane and c-propane are presented in Fig. 2a and h. They correspond to weak heats of physical adsorption, i.e., 6.3 and 5.0 kcal/mol, respectively. The relative energies of adsorbed propane and c-propane together with the products of their interactions with the zeolite are shown in Table 1, the energy of physisorbed propane being taken as zero. The type of Al–(Si)₃–Al alternation, i.e., Al–O–Si–O–Si–O–Si–O–Al, in the 6R complex (Fig. 2b) is the most favored for the Ga_2O_2 cluster (Table 2) as compared for example to the known Al_2O_2 cluster

Table 2

Relative energies ΔU (kcal/mol) of the 8R(Ga_2O_2) clusters, of the products of hydrogenation and of hydration at the B3LYP/6-31G* level (for Ga_2O_2 after slash, ΔU values at the B3LYP/D95(T, H_t)/6-311G**(O, C, H)/6-31G*(Ga) level). For Ga_2O_2 , relative energies are given relative to the most favored Al-alternation case $n=3$, for which $\Delta U=0$. Heats of adsorption are given for the $\text{Ga}_2\text{O}_2 + \text{H}_2$ and $\text{Ga}_2\text{O}_2 + \text{H}_2\text{O}$ pairs.

Cluster type	ΔU		
	$n=3$	$n=2$	$n=1$
Ga_2O_2	0.0/0.0	7.7/3.4	28.5/40.9
$\text{Ga}_2\text{O}_2 + \text{H}_2$	–2.6	–2.4	–2.5
Ga–O(H)–GaOH	–18.0	–31.7	–27.3
HGa–O–GaOH	–26.4	–17.2	–24.6
$\text{Ga}_2\text{O}_2 + \text{H}_2\text{O}$	–11.6	–25.3	–13.9
HOGa–O–GaOH	–41.8	–29.6	–5.5

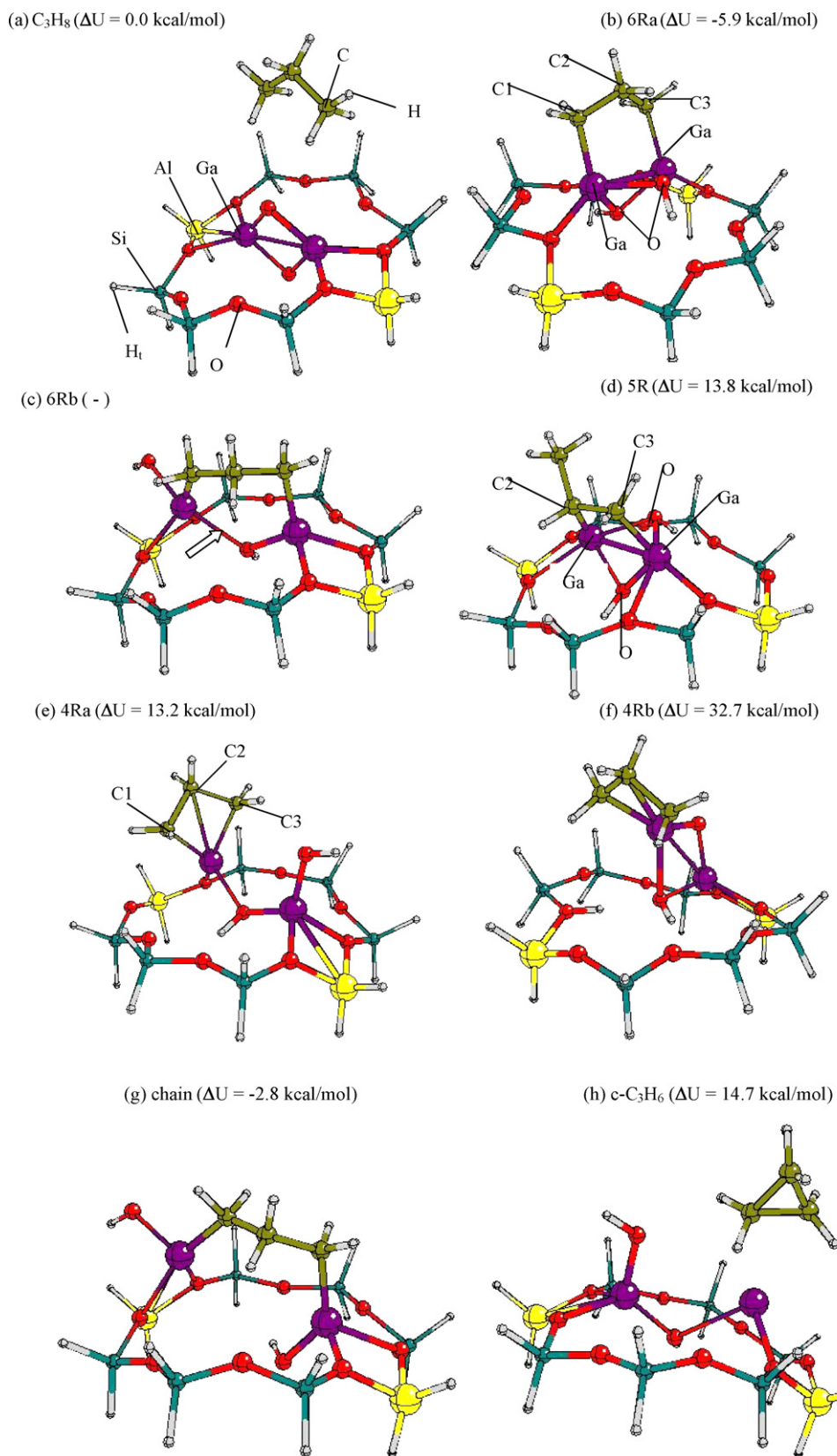


Fig. 2. Optimized structures of physisorbed propane (a), 6R complexes with C_3H_6 connected to both Ga atoms through two primary carbons (b and c), 5R complex connected to both Ga atoms via primary and secondary carbons (d), 4R Ga- C_3H_6 complexes (e and f), chain or ruptured 6R complex (g, ruptured bond is shown by white arrow in c), and physisorbed *c*-propane (h). The color code corresponds to the one in Fig. 1; carbon is in brown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

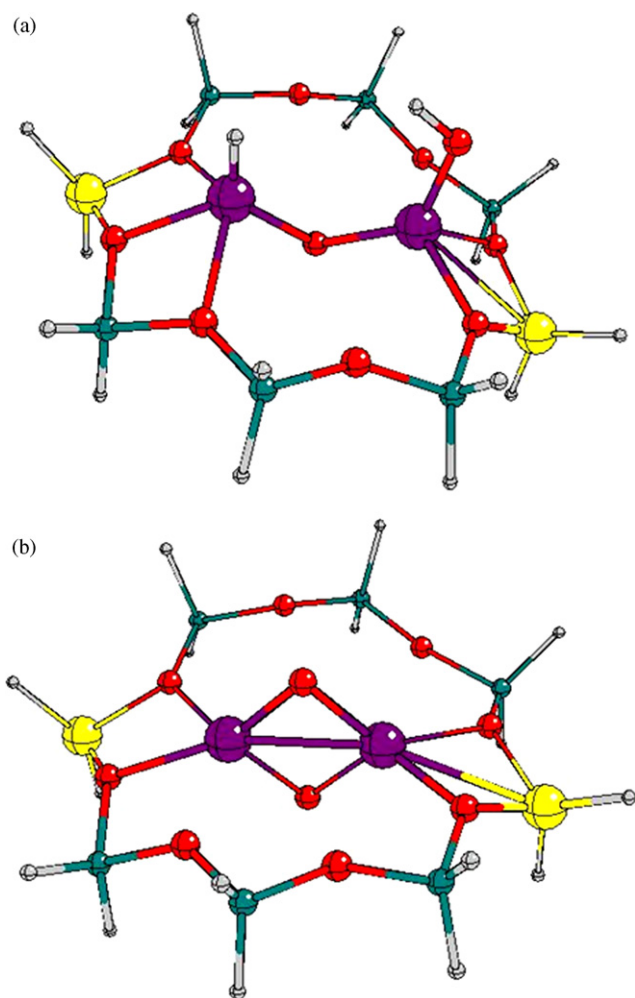


Fig. 3. Most stable hydrogenation HGa–O–GaOH (8R) product (a) and initial Ga₂O₂ (8R) cluster (b) with Al–(Si)₂–Al alternation in the 8R window. The color code corresponds to the one in Fig. 1.

which is better adopted within the 8R window with Al–(Si)₂–Al alternation owing to smaller Al radii. Respective product of hydrogenation of Ga-clusters in the zeolite (Fig. 3a) is the most stable one (–24.6 kcal/mol in Table 2) as compared to other possible type of hydrogen addition (–18.0 kcal/mol) to the Ga-clusters in the MOR 8R window. The HGa–O–GaOH (Fig. 3a) is the product of exothermic Ga₂O₂ hydrogenation (Fig. 3b) with the heat of –34.6 kcal/mol at the B3LYP/basis set 1 level.

One should emphasize the difference of geometry between the rectangular Ga–(OH)₂–Ga configuration in Fig. 2b and d, on one hand, and the Ga–O(H)–GaOH configuration in Fig. 2c, e, and h, on the other hand. The rectangular Ga–(OH)₂–Ga form (Fig. 2b and d) becomes the most stable upon C₃H₈ dissociative adsorption on Ga₂O₂, while the HGa–O–GaOH is the most stable form for hydrogen atoms (Fig. 3a, Table 2 for *n* = 3). The geometry of the mentioned Ga–(OH)₂–Ga type is observed in the bi-dentate products of C₃H₈ dissociative adsorption via both primary carbons (Fig. 2b) or via primary and secondary carbons (Fig. 2d).

The 6Ra product of dissociative adsorption is the most stable by –5.9 kcal/mol (Fig. 2b). It corresponds to the conservation of all Ga–O bonds as in the initial Ga₂O₂ complex (Fig. 3b). Two C–Ga bonds between different Ga atoms and the primary carbons are formed while both H atoms from propane remain on the O atoms of the Ga₂O₂ part and do not point toward the 8R window. The cycle with two primary carbons (–5.9 kcal/mol) is less distorted, corresponding to minimal strains relative to the 5R complex with

primary and secondary carbons in the –C₂–C₃–Ga–O–Ga– cycle (Fig. 2d, 13.8 kcal/mol). The 5R complex presents a rectangular Ga–(OH)₂–Ga geometry very similar to the initial Ga₂O₂ complex (Fig. 3b). This 5R complex can serve as initial configuration for propylene formation. Propylene can also be formed via simultaneous hydrogen transfer from C₂ to C₁ in the “chain” or 4R models. The “chain” is a conventional name for the structure obtained by breaking the initial Ga–O bond in the 6Rb moiety (shown by arrow in Fig. 2c). Such a rupture of the Ga–O bonds leads to a minimal energy loss from –5.9 to –2.8 kcal/mol provided that both H atoms form hydroxyl groups linked to the Ga atoms (Fig. 2g). The 6Rb type structure presents a stable geometry with basis sets 2 and 3 only. It is however less stable at the respective levels than the “chain” geometry, i.e., 16.2 and 18.5 kcal/mol versus 3.6 and 10.1 kcal/mol (Table 1).

As we noted in the Introduction, the 4R GaC₃ cycle type could be a promising product of dissociative adsorption with both C–Ga bonds related to one Ga atom only. We observed such 4Ra complex with a lower energy, 13.2 kcal/mol, as compared to physisorbed *c*-propane, 14.7 kcal/mol (Table 1). The preferential H-position at the O atoms of the Ga₂O₂ part versus the O atoms of the 8R is also confirmed by the 4Ra case. The Ga–O bonds with the oxygens of the 8R are of extreme importance for the total energy; the rupture of two Ga bonds with the framework O atoms in the 4Rb model strongly destabilizes the system, 32.7 kcal/mol, which is much less stable than the 4Ra one, 13.2 kcal/mol (Table 1). Regarding the drastic difference between the energies of the 4Ra and 4Rb complexes which present a different Ga₂O₂ cluster geometry in the reaction, one can suspect that an even more favored intermediate for the cycle opening can be found as compared to that of 4Ra.

It is worth to mention that relative energies of the 5R (13.8 kcal/mol), 4Ra (13.2 kcal/mol), and physisorbed *c*-propane (14.7 kcal/mol) are pretty close. With a moderate increase of temperature, all these products of dissociative adsorption become the reaction steps which explain the way of the C migration in the propane framework. The dynamic equilibrium between the adsorbed forms like 4Ra and physisorbed *c*-propane allows the re-opening of the *c*-propane re-adsorbed via the opposite –¹²C–¹³C– side as compared to the initial adsorption via the two ¹²CH₃– groups of ¹²C–¹³C propane (4Ra). Hence, the re-opening through the –¹²C–¹³C– side results in the ¹³C atom at the primary position instead of the secondary one in the initial ¹²C–¹³C–¹²C propane.

4. Conclusions

Propane and cyclo-propane complexes over binuclear Ga₂O₂ clusters at the cation positions of Ga-exchanged mordenite zeolites are modeled using DFT calculations via the isolated cluster approach. The relative energies of the bidentate complexes, i.e., via both primary C atoms of propane to both Ga atoms, show the most stable 6Ra and chain products of dissociative adsorption of propane in the system. A series of 5R and 4Ra complexes possessing close energies is observed as possible candidates of dissociative adsorption for propane cyclization as suggested by experimentalists on the basis of the quick ¹³C/¹²C exchange in propane molecule.

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