

# Quantum chemistry study on small molecules adsorption and reactivity of Ga/SAPO-11 catalyst

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## Abstract

Quantum chemical calculations were carried out to determine the geometries and the adsorption energies of  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{SH}$ ,  $\text{H}_2$ , and  $\text{H}_2\text{O}$  molecules on a gallium-exchanged silicoaluminophosphate (SAPO) catalyst. The analysis of the results shows that the formation of the dihydride species  $[\text{GaH}_2]^+$  is thermodynamically unfavorable. Therefore, under  $\text{H}_2$  pressure, the  $\text{Ga}^+$  as well as  $[\text{GaH}_2]^+$  species are present simultaneously due to the thermodynamic equilibrium. On the other hand, the reduced Ga species behave like hard acids that react with hard bases such as  $\text{NH}_3$ , and  $\text{CH}_3\text{NH}_2$ , but do not react with  $\text{CH}_3\text{SH}$  which is a soft base. Calculations with small models of 3 tetrahedrons (T3) and with a model of 3 rings of 10 tetrahedrons (3T10) to simulate the SAPO-11 pore, show that in general, the cage effect only influences the magnitude of the reaction energies but not their endothermic or exothermic character.

**Key words:** Catalyst; calculations; DFT; Ga; theoretical.

## Estudio químico cuántico de la adsorción de moléculas pequeñas y su actividad sobre el catalizador de Ga/SAPO-11

### Resumen

Cálculos químico-cuánticos fueron realizados para determinar las geometrías y las energías de adsorción de las moléculas  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{SH}$ ,  $\text{H}_2$ , y  $\text{H}_2\text{O}$  sobre el catalizador de Ga intercambiado en silicoaluminofosfato (SAPO). El análisis de los resultados muestra que la formación de la especie di-hidruro  $[\text{GaH}_2]^+$  no está favorecida termodinámicamente. Por lo tanto, bajo presión de  $\text{H}_2$  las especies de  $\text{Ga}^+$  y  $[\text{GaH}_2]^+$  estarán presente simultáneamente debido a un equilibrio termodinámico. Por otro lado, los resultados muestran que la especie reducida de Ga se comporta como un ácido duro reaccionando con bases duras tales como el  $\text{NH}_3$ , y el  $\text{CH}_3\text{NH}_2$ , pero no con el  $\text{CH}_3\text{SH}$ , el cual es una base blanda. Cálculos con modelos de 3 tetraedros (T3) y con un modelo de 3 anillos de 10 tetraedros (3T10) para simular un poro del SAPO-11, muestran que en general, el efecto de la caja es sobre la magnitud de las energías de interacción pero no sobre el carácter endotérmico o exotérmico de las mismas.

**Palabras clave:** Cálculo químico-cuánticos; cálculos teóricos; catalizadores; DFT; Ga.

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## Introduction

Gallium based catalysts have been employed in many reaction types. For example,  $\text{Ga}_2\text{O}_3/\text{Al}_2\text{O}_3$  prepared by sol-gel method has shown excellent activity for the NO reduction with propane in presence of water (1). Ga-complexes that act as Schiff bases have been explored as potential catalysts for epoxide copolymerization (2). Other Ga complexes exhibit good Lewis acid features and catalyze the aldol-type reaction of silyl enol ethers with carbonyl compounds (3). Ga-modified and Ga-exchanged zeolites have been employed for alkylation of aromatic compounds (4), conversion of cycloalkanes (5), propane aromatization (6), and selective catalytic reduction of NO (7, 8). Recently, the Ga/SAPO-11 system has been employed for the direct transformation of *n*-butane to butenes (9).

In general, Ga-exchanged catalysts are prepared by incipient wetness. After impregnated, the solids are calcinated under dry air. Just before being used as catalysts, the solids are reduced under  $\text{H}_2$  atmosphere. The physical-chemical characterization of these solids has revealed the formation of Ga (III) oxide,  $\text{Ga}_2\text{O}_3$ , on their surfaces. After  $\text{H}_2$  treatment the Ga (III) is apparently reduced to  $\text{Ga}^{\text{II}}$  ion (10, 11) which occupy the Brønsted site of the support. The formation of  $\text{Ga}_2\text{O}_3$  occurs on the surface of the support; however, there are Ga atoms present inside the pores of the solid. In order to explain this, a migration mechanism of Ga from the surface into the framework of the support through the formation of gaseous  $\text{Ga}_2\text{O}$ , according to the following reaction set, has been proposed (6, 12, 13, 14)



where  $(\text{H}^+\text{Z})$  represents the Brønsted acid sites of the support. In spite of the extensive experimental data available, the structure of  $(\text{Ga}^+\text{Z})$  and the nature of the ac-

tive site remain unclear. Based on  $\text{H}_2$ -TPR profiles, Machado et al. (9) concluded that the extra-framework Ga atoms present as cationic  $[\text{GaO}]^+$  species, which are responsible for the catalytic behavior. On the other hand, Chao and col. (15) proposed that the Ga inside the pores doesn't exist as  $[\text{GaO}]^+$  but as some kind of Gallium hydride oligomers with bridging H atoms. Other authors used DRIFT spectroscopy (14) and *in-situ* X-ray absorption (16) to conclude that the reduced Ga is present in a highly dispersed form and probably as monomeric hydrides instead of oligomers. Védrine (12) and Su (17), using various experimental techniques, demonstrated the presence of oxyhydroxy species such as  $\text{GaO}(\text{OH})$ ,  $\text{Ga}_2(\text{OH})_x\text{O}_{3-x}$  that, after reduction with  $\text{H}_2$ , could transform into  $\text{Ga}^+$ ,  $[\text{GaO}]^+$  located at the ionic exchange positions of the support.

Considering all the abovementioned studies and contradictory conclusions, we performed the present work to aid in the understanding of the nature and the catalytic role of the possible extra-framework Ga species present in the Ga/SAPO-11 system. To achieve this objective, we performed a series of quantum chemical calculations of the  $[\text{GaO}]^+$ ,  $\text{Ga}^+$ ,  $[\text{HGaOH}]^+$ ,  $[\text{GaH}_2]^+$  and  $[\text{Ga}(\text{OH})_2]^+$  species and their interactions with  $\text{NH}_3$ ,  $\text{SO}_2$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{CH}_3\text{SH}$  probe molecules.

## Molecular Models and Methodology

Silicoaluminophosphates molecular sieves (SAPO) are structures that contain Si-O-Al, P-O-Al and Si-O-Si bonds but no Si-O-P bonds. In general, SAPO's Si atoms are grouped in regions called "Si islands". The Brønsted acid sites of these structures are protons attached to the oxygen bridges of the Si-O-Al triad. SAPO-11 has an AEL type framework (18) composed of rings of 10 tetrahedrons (T10). Therefore, a molecular structure built with three T10 rings served as model of this molecular sieve. The SM2-

SM3 rule (19, 20) and previous calculations results (21) were applied for the localization of the Si islands into the three rings system, and to avoid the formation of unstable Si-O-P bonds.

Calculations of thermodynamic properties were performed employing a small molecular aggregate composed of 3 tetrahedrons (T3),  $(\text{HO})_3\text{SiOAl}(\text{OH})_2\text{OP}(\text{O})(\text{OH})_2$ . Although in this model, physical-chemical effects such as electrostatics or van der Waals type interactions are not present, it is expected that these effects do not influence the qualitative results since the size of the adsorbed molecules is small in comparison with the pore or ring size. In most cases, geometry optimizations and energy calculations were performed using the Gaussian-03 program. For small molecular aggregates, the calculations were performed at B3LYP with the 6-31G\*\* basis set for N and O atoms. Steven's effective core potential (CEP-121) with the corresponding basis set was employed for Al, Si, P, S and Ga. A polarization function ( $\alpha_d = 0.55$ ) was added to the original P atom basis set. ONIOM(B3LYP/3-21G\*:uff) methodology was employed in the 3 T10-ring system. The

high level model corresponds to a T6 ring with the  $\text{Si}_3\text{Al}_2\text{PO}_{18}\text{H}$  formula as shown in Figure 1.

## Results and Discussions

### On the thermodynamics of Ga species

In order to analyze the thermodynamic properties of the different Ga possible species, quantum chemical calculations were performed using a 3T model  $(\text{HO})_3\text{SiOAl}(\text{OH})_2\text{OP}(\text{O})(\text{OH})_2$ . Figure 2 displays relevant geometric properties and net charges for T3-Ga (Figure 2a), T3-GaO (Figure 2b), T3-GaH<sub>2</sub> (Figure 2c), T3-HGaOH (Figure 2d) and T3-Ga(OH)<sub>2</sub> (Figure 2e) species. In general, the Ga-O(P) bond distance is larger than the Ga-O(Si) bond distance. Since P is more electronegative than Si, the bridging O atom of Al-O-P is more positive than the one of Si-O-Al. As a consequence, the Ga<sup>+</sup> ion is closer to the O(Si) bridge than to the O(P) bridge. The Ga-O distance of T3-GaO (Figure 2b) is smaller than the corresponding ones of T3-Ga-OH (Figures 2d and 2e), which reveals the presence of a double bond in Ga-O.

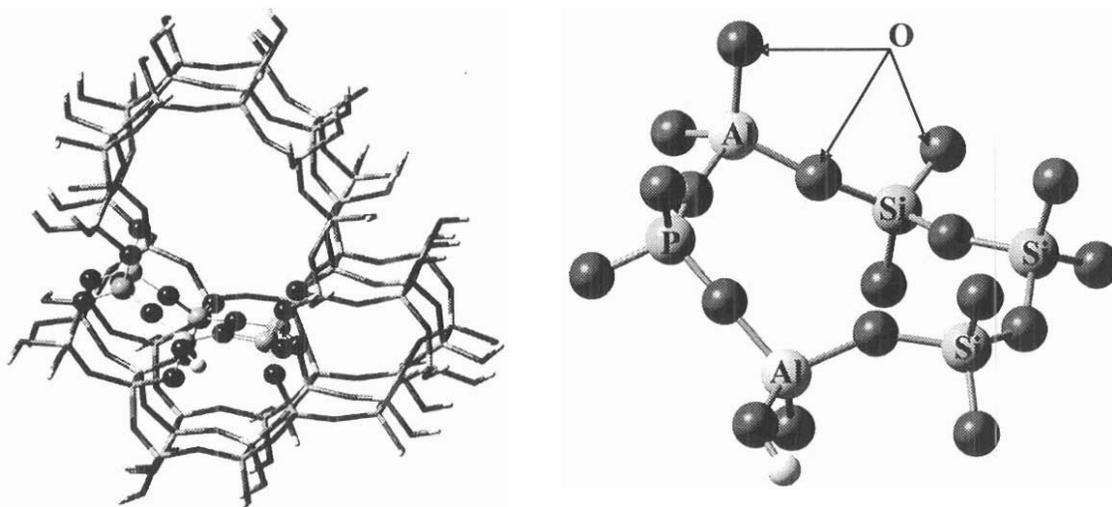


Figure 1. Three T10 rings system. Left: *high level*: ball&stick type. *low level*: wireframe. Right: detail view of the high level.

Figure 2 shows some selected charge values for the analyzed species. In T3-Ga, Ga is present as  $Ga^{+1}$  ion ( $Q_{Ga} = +0.83$ ); upon oxidation (T3-GaO,) its charge increases to a value close to +2 ( $Q_{Ga} = +1.58$ ). The H(Ga) atoms negative charge of the T3-GaH<sub>2</sub> and T3-HGaOH reveals their hydride character. In general, the calculated charge values agree with the expected values.

Table 1 shows that the reduction of T3-GaO to T3-Ga or to T3-HGaOH is thermodynamically very favorable, as well as the formation of the dihydroxy form, T3-Ga(OH)<sub>2</sub>, from the oxide species 3T-GaO. The direct formation of the dihydride from the reaction of H<sub>2</sub> with T3-Ga (reaction 5, Table 1) is not a thermodynamically spontaneous process ( $\Delta G = +12.7$  kcal/mol and  $\Delta S < 0$ ). However, the dihydride could be obtained from the reduction of the T3-HGaOH (reaction 9, Table 1) at high temperatures since this reaction is endothermic ( $\Delta H_{298.15} = +12.3$  kcal/mol) and  $\Delta S > 0$ . Summarizing, according to the results presented in Table 1, the formation of the dihydride species could proceed in two steps: first, the oxide reduces to HGaOH; then, this species reduces to GaH<sub>2</sub>. During the reduction process, part of the oxide is transformed into  $Ga^{+1}$  (reaction 3, Table 1). In addition, the dihydride decomposition is thermodynamically favorable (reaction 5, Table 1). Therefore, it is clear that not all the exchanged Ga turns into  $[GaH_2]^+$ ; necessarily, some Ga must be present simultaneously as  $Ga^{+1}$ .

To determine the hard or soft acid character of Ga in Ga/SAPO-11, adsorption energies were calculated for NH<sub>3</sub>, CH<sub>3</sub>NH<sub>2</sub> and CH<sub>3</sub>SH probe molecules, where the first two are hard bases, whereas the last is a soft base. The results show that the CH<sub>3</sub>SH does not interact with the T3-Ga system while the adsorption of both, NH<sub>3</sub> and CH<sub>3</sub>NH<sub>3</sub>, are thermodynamically favorable ( $\Delta G = -13.1$  and  $\Delta G = -4.4$  kcal/mol, respectively, Table 1). These results reveal that the Ga atom acts as a hard acid in the Ga/SAPO-11 system according to Pearson's empirical rule:

*hard bases prefer hard acids and soft bases prefer soft acids.*

It is well-known that when the molecules are adsorbed at low temperature, the free adsorption energy is lower than zero,  $\Delta G < 0$ . On the other hand, at high temperatures,  $\Delta G$  turns positive: therefore, the molecules are desorbed. At  $\Delta G = 0$ , the molecules start to adsorb/desorb depending on the temperature variations from this point. Consequently, the desorption/adsorption temperature ( $T_{sorp}$ ) can be estimated using the following equations:

$$T_{sorp} = \frac{\Delta H_{298.15}}{\Delta S_{298.15}}$$

$$\Delta S_{298.15} = \frac{\Delta H_{298.15} - \Delta G_{298.15}}{298.15K} \quad (2)$$

Using equations [1] and [2] and the data of Table 1, the  $T_{sorp}$  values obtained were 629.15K and 410.27K for NH<sub>3</sub>, and CH<sub>3</sub>NH<sub>2</sub>, respectively. Accordingly, in a NH<sub>3</sub>-TPD experiment, the signals corresponding to the NH<sub>3</sub> desorption should start around 356°C and those of the CH<sub>3</sub>NH<sub>2</sub> desorption around 137°C. Unfortunately there is no experimental data available to compare with the theoretical values.

An unexpected result was obtained for the SO<sub>2</sub> adsorption. According to the calculations, the SO<sub>2</sub> adsorption is highly exothermic, with  $\Delta G = -71.6$  kcal/mol and  $\Delta H = -86.8$  kcal/mol. Since SO<sub>2</sub> is a borderline acid between hard and soft, and Ga, in the T3-Ga system, is a hard acid, the interaction between them should not be strong. Conversely, the calculated adsorption enthalpy resulted larger than the corresponding one of the NH<sub>3</sub>.

Similarly, the results presented in Table 1 show that the SO<sub>2</sub> interaction with T3-GaO system is also thermodynamically very favorable ( $\Delta G = -84.5$  kcal/mol, reaction 13,) probably due to the formation of one SO<sub>3</sub> molecule. These striking results

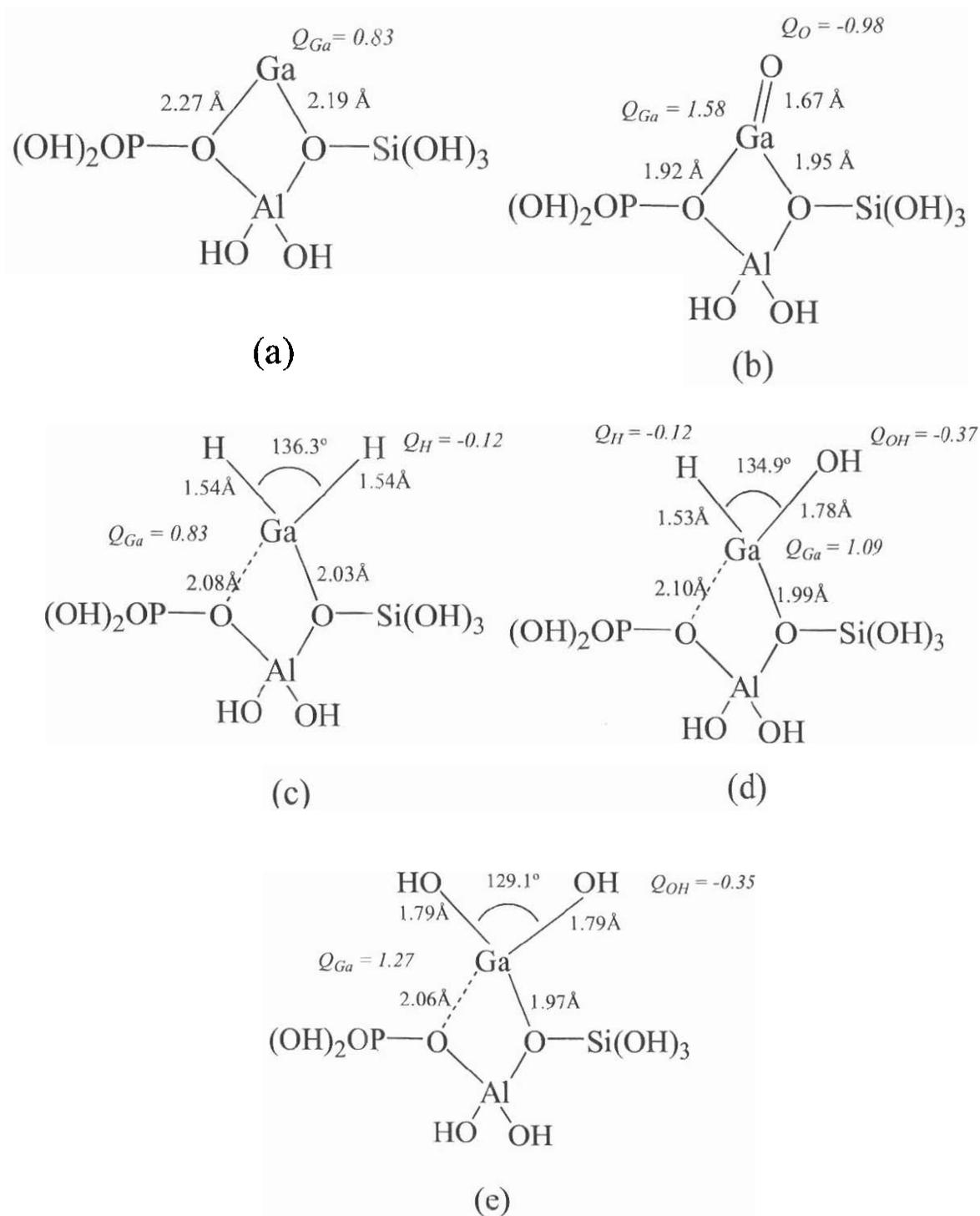


Figure 2. Schematic representation of Ga species showing relevant bond distances, angles and charges.

Table 1  
Free energies, enthalpies and reaction energy changes for various Ga species, calculated using the T3 model (kcal/mol)

Reaction	$\Delta G_{298.15}$	$\Delta H_{298.15}$	$\Delta E_{zpc}$
3) T3-GaO + H <sub>2</sub> → T3-Ga + H <sub>2</sub> O	-51.6	-46.7	-46.7
4) T3-GaO + H <sub>2</sub> → T3-HGaOH	-48.7	-55.9	-54.9
5) T3-Ga + H <sub>2</sub> → T3-GaH <sub>2</sub>	+12.7	+3.1	+4.9
6) T3-HGaOH → T3-Ga + H <sub>2</sub> O	-2.9	+9.2	+8.2
7) T3-GaO + H <sub>2</sub> O → T3-Ga(OH) <sub>2</sub>	-59.1	-70.0	-69.1
8) T3-Ga(OH) <sub>2</sub> + H <sub>2</sub> → T3-Ga + 2H <sub>2</sub> O	+7.5	+23.3	+22.4
9) T3-HGaOH + H <sub>2</sub> → T3-GaH <sub>2</sub> + H <sub>2</sub> O	+9.9	+12.3	+13.0
10) T3-Ga + NH <sub>3</sub> → T3-GaNH <sub>3</sub>	-13.1	-24.9	-24.1
11) T3-Ga + CH <sub>3</sub> -NH <sub>2</sub> → T3-GaNH <sub>2</sub> CH <sub>3</sub>	-4.4	-16.1	-15.9
12) T3-Ga + SO <sub>2</sub> → T3-GaO <sub>2</sub> S	-71.6	-86.8	-86.0
13) T3-GaO + SO <sub>2</sub> → T3-GaO <sub>3</sub> S	-84.5	-97.6	-97.3

seem to open the possibility that the Ga/SAPO-11 system could be used as a DeSox catalyst due to this highly favourable interaction. Figure 3 shows that after SO<sub>2</sub> adsorption, there is a charge transfer of -1.19e from the T3-Ga system to the SO<sub>2</sub> molecule. The charge analysis showed that the charge is transferred mainly to the O atoms since  $Q_s = +0.57e$  and  $Q_o = -0.285e$  for the free SO<sub>2</sub> molecule while  $Q_s = +0.69e$  and  $Q_o = -0.94e$  for the adsorbed molecule.

#### On the Ga<sub>2</sub>O reactivity inside a SAPO-11 pore

As mentioned in the introduction, during the H<sub>2</sub> treatment of the Ga/SAPO-11 catalyst, the gallium (III) oxide, Ga<sub>2</sub>O<sub>3</sub>, is converted to Ga<sub>2</sub>O(g), which migrates into the cavities of the support and reacts with the Brønsted acid sites to form different Ga species such as GaO<sup>+</sup> (9, 10, 12, 14), Ga<sup>+</sup> (9, 10, 12), HGaOH<sup>+</sup> (12, 17), and (GaH<sub>2</sub>)<sup>+</sup> (14, 16). These latter species have been proposed in the literature as the active sites of the Ga/ZSM5 and GA/SAPO-11 catalysts (22,

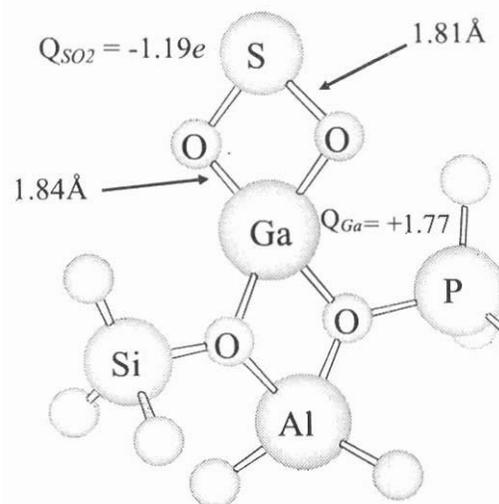


Figure 3. Lowest energy structure for T3-GaO<sub>2</sub>S model. The H atoms are not shown for clarity.

23). Therefore, the study of the reactions of Ga<sub>2</sub>O(g) with the SAPO-11 cavities is very important to understand the process of active site formation. To investigate this process

we performed quantum chemical calculation using ONIOM(B3LYP/3-21G\*:uff) methodology. Previous results using MSINDO approach (21) in similar systems showed that the  $\text{Ga}_2\text{O}$  molecule reacts and further anchors in the SAPO pores, at the surroundings of the ion-exchanged positions. Figure 4 shows the minimum energy geometry obtained herein for the  $\text{Ga}_2\text{O}$  anchored into a SAPO-11 pore. Table 2 summarizes the relevant geometric parameters. As Figure 4 shows, there is one highly coordinated Ga atom bonded to the oxygen atom of the SAPO-11 structure. The second Ga atom is less coordinated and is bonded only to the O atom of the  $\text{Ga}_2\text{O}$  molecule.

The  $\text{Ga}_2\text{O}(\text{g})$  triatomic molecule is approximately linear with an angle of  $174.6^\circ$  and identical Ga-O distances of 1.81 Å. When the  $\text{Ga}_2\text{O}$  bonds to the SAPO-11 structure, the molecule bends, yielding an angle of  $137.9^\circ$ . As shown in the Figure 4, an enlargement of the Ga-O bond occurs, changing from 1.81 Å in the free molecule to 1.87 Å in the anchored molecule. This enlargement persists in the different  $\text{Ga}_2\text{O}$  derived species  $\text{HO}(\text{H})\text{Ga}-\text{OGa}-\text{Surf}$ ,  $\text{H}_2\text{Ga}-\text{O}-\text{Ga}-\text{Surf}$ ,  $(\text{HO})_2\text{Ga}-\text{OGa}-\text{Surf}$ , with the corresponding reduction of the bending angle to  $132.1^\circ$ ,  $131.8^\circ$  and  $129.3^\circ$ .

Conversion of  $\text{Ga}-\text{OGa}-\text{Surf}$  to the above-mentioned species may take place through reactions with either  $\text{H}_2$  or water according to the following equations, presented with the corresponding calculated energy changes:

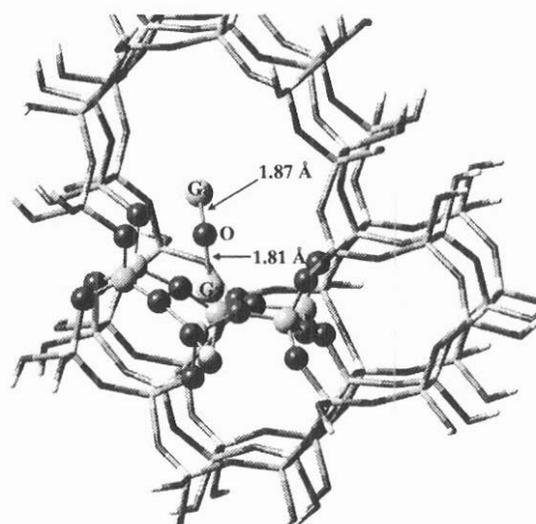
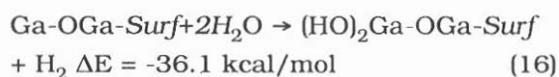
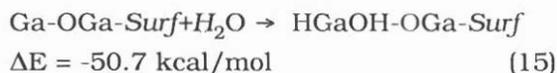
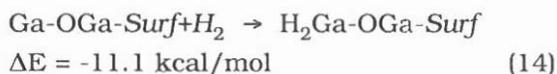
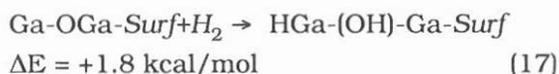


Figure 4. Lowest energy structure for the  $\text{Ga}_2\text{O}$  anchored into a SAPO-11 pore ( $\text{Ga}-\text{OGa}-\text{Surf}$ ).



These results demonstrate that the less coordinated Ga atom is very reactive. For example, according to the T3 model, the formation of the dihydride is not energetically favored ( $\Delta E = +4.9 \text{ kcal/mol}$ ). On the contrary, the formation of  $\text{H}_2\text{Ga}-\text{OGa}-\text{Surf}$  from the anchored  $\text{Ga}_2\text{O}$  in the 3T10 ring model is energetically favorable ( $\Delta E = -11.1 \text{ kcal/mol}$ ). This difference results from the fact there is a single bicoordinated Ga atom in the T3 model, whereas in the 3T10 model, the dihydride is formed from the less coordinated Ga atom of the  $\text{Ga}-\text{OGa}-\text{Surf}$  species, as shown in Figure 5.

To test if this inversion of the reaction energy; that is, endothermic to exothermic, is due to the  $\text{Ga}_2\text{O}$  molecule itself or to the cage effect included in the three T10 ring model, calculations were repeated using one  $\text{Ga}^{\text{III}}$  atom instead of the  $\text{Ga}_2\text{O}$  molecule and compared with the results of the T3 model (Table 1). As shown in Table 3, endother-

Table 2  
Relevant bond distances (Å) and bond angles (in degrees) for the Ga<sub>2</sub>O and related species anchored on the 3T10 model.

Ga <sub>2</sub> O/SAPO-11 system			
<b>RGa-OGaS<sup>a</sup></b> 1.87 Å	<b>RGaO-GaS</b> 1.81 Å	<b>Ga-O-GaS</b> 137.9°	
HO(H)GaOGa/SAPO-11 system			
<b>RHO(H)Ga-OGaS</b> 1.86 Å	<b>RHO(H)GaO-GaS</b> 1.81 Å	<b>R(H)HO-GaOGaS</b> 1.81 Å	<b>HO(H)Ga-O-GaS</b> 132.1°
H <sub>2</sub> GaOGa/SAPO-11 system			
<b>RH<sub>2</sub>Ga-OGaS</b> 1.86 Å	<b>RH<sub>2</sub>GaO-GaS</b> 1.81 Å	<b>RH-GaOGaS</b> 1.60 Å	<b>H<sub>2</sub>Ga-O-GaS</b> 131.8°
(HO) <sub>2</sub> GaOGa/SAPO-11 system			
<b>R(HO)<sub>2</sub>Ga-OGaS</b> 1.85 Å	<b>R(HO)<sub>2</sub>GaO-GaS</b> 1.81 Å	<b>RHO-Ga(OH)OGaS</b> 1.81 Å	<b>HO<sub>2</sub>Ga-O-GaS</b> 129.3°
		<b>RHO(H)GaOGaS</b> 1.59 Å	

a) S means surface.

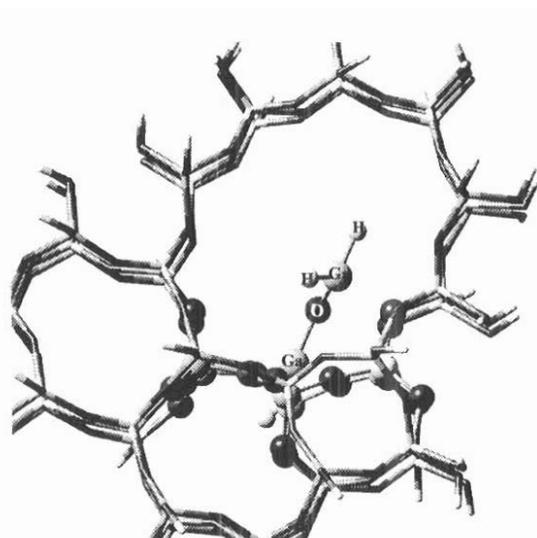


Figure 5. Lowest energy structure for the [H<sub>2</sub>GaOGa] species anchored into a SAPO-11 pore (H<sub>2</sub>Ga-OGa-Surf).

mic/exothermic tendencies of the 3T10-Ga model follow the same trend than those of the T3-Ga model. In other words, if for the

T3-Ga system the reaction is not favored (endothermic), it is not favored either for the 3T10-Ga model. For example, in the 3T10-Ga model the formation of the dihydride (DE = +12.0 kcal/mol) as well as the H<sub>2</sub> reduction of Ga(OH)<sub>2</sub> (DE = +76.1 kcal/mol) are endothermic, as they are in the T3-Ga model (ΔE = +4.9 and +22.4 kcal/mol, respectively.) In conclusion, the change endothermic to exothermic is due to the nature of the anchored species (Ga<sub>2</sub>O or Ga) and not to a pore effect.

Figure 6 shows the lowest energy structure for the 3T10-GaH<sub>2</sub> system. This structure is quite similar to the one found for the T3-Ga model (Figure 2c). These results indicate that, in general, the cage effect affects the magnitude but not the sign of the reaction energies; i.e. reactions do not change from endothermic to exothermic. The magnitude change may result from stabilizing interactions of the adsorbed species with the oxygen atom located close to the interaction site. This is the case for the NH<sub>3</sub> adsorption where the H atom interacts with the O atoms

Table 3  
Reaction Energy changes values ( $\Delta E$ ) for Ga/SAPO-11 Catalyst using the 3T10 model.

Reaction	$\Delta E$ kcal/mol
18) 3T10-GaO + H <sub>2</sub> $\longrightarrow$ 3T10-Ga + H <sub>2</sub> O	-8.1
19) 3T10-Ga + H <sub>2</sub> $\longrightarrow$ 3T10-GaH <sub>2</sub>	+12.0
20) 3T10-GaO + H <sub>2</sub> O $\longrightarrow$ 3T10-Ga(OH) <sub>2</sub>	-84.1
21) 3T10-Ga(OH) <sub>2</sub> + H <sub>2</sub> $\longrightarrow$ 3T10-Ga + 2H <sub>2</sub> O	+76.1
22) 3T10-Ga + NH <sub>3</sub> $\longrightarrow$ 3T10-GaNH	-29.4

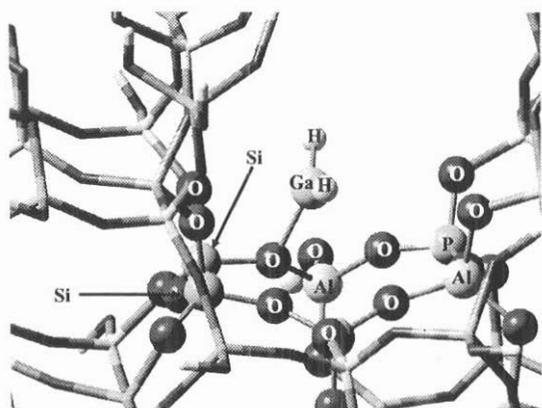


Figure 6. Lowest Energy Structure for the [H<sub>2</sub>Ga] species anchored into a SAPO-11 pore (3T10-GaH<sub>2</sub>).

of the 3T10 structure, providing an extra stabilization to the system that is not present in the T3 model. Consequently, the absolute reaction energy for the NH<sub>3</sub> adsorption ( $\Delta E = -29.4$  kcal/mol; reaction 23) is larger than that of the GaO reduction ( $\Delta E = -8.1$  kcal/mol; reaction 18) in the 3T10 system, whereas for the T3 system, the absolute reaction energy for the NH<sub>3</sub> adsorption ( $\Delta E = -24.1$  kcal/mol; reaction 10) is lower than that of GaO reduction ( $\Delta E = -46.7$  kcal/mol; reaction 3). In conclusion, the abovementioned results confirm the hypothesis that the less coordinated Ga atom in the anchored Ga<sub>2</sub>O molecule is more reactive than a single Ga atom anchored to the structure, such as T3-Ga (Figure 2a).

## Conclusions

Minimum energy structures, thermodynamic properties and net charges for various Ga species supported on SAPO-11 were determined using *ab initio* calculations at density functional level. The analysis of the results shows that: 1) The formation of the dihydride species [GaH<sub>2</sub>]<sup>+</sup> from the Ga oxide seems to proceed via a two step reduction: First, the formation of HGaOH species takes place afterwards, these species are reduced by H<sub>2</sub> to yield [GaH<sub>2</sub>]<sup>+</sup>. Taking into account that the decomposition of the [GaH<sub>2</sub>]<sup>+</sup> into Ga<sup>+</sup> + H<sub>2</sub> is thermodynamically favourable, simultaneous presence of Ga<sup>+</sup> and [GaH<sub>2</sub>]<sup>+</sup> is expected for the Ga/SAPO-11 system under H<sub>2</sub> pressure, as a result of the thermodynamic equilibrium 2) The reduced Ga in the SAPO-11 behaves as a hard acid since it interacts strongly with hard bases such as NH<sub>3</sub>, ROH, RNH<sub>2</sub>, etc. 3) The supported Ga<sup>+</sup> and [GaO]<sup>+</sup> species interact strongly with SO<sub>2</sub>, which suggests that Ga/SAPO-11 catalysts could be candidates for DeSOx reactions. 4) The Ga<sub>2</sub>O(g) can migrate into the SAPO-11 pores and react with the Brønsted sites producing an anchored Ga species, Ga-OGa-Surf, with one low coordinated, very reactive Ga atom. The formation of the Ga dihydride from this species is energetically favorable. 5) The cage effect does not alter qualitatively the results obtained with small models such as the T3 model unless an interaction with the O atoms of the

structures takes place, as is the case of  $\text{NH}_3$ , where H bridges helps to stabilize the adsorbed  $\text{NH}_3$  molecule.

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