

## An ab initio and DFT study of the interaction between ethanethiol and zeolites

Humberto Soscún<sup>a,e,\*</sup>, Olga Castellano<sup>b</sup>, Javier Hernandez<sup>b</sup>, Federico Arrieta<sup>a</sup>, Yaneth Bermúdez<sup>a</sup>, Alan Hinchliffe<sup>c</sup>, Marcos Rosa Brussin<sup>d</sup>, Morella Sanchez<sup>e</sup>, Anibal Sierraalta<sup>e</sup>, Fernando Ruetter<sup>e</sup>

<sup>a</sup> *Laboratorio de Química Inorgánica Teórica, Facultad Experimental de Ciencias, La Universidad del Zulia, Ap. 526, Grano de Oro, Módulo No. 2, Maracaibo, Venezuela*

<sup>b</sup> *PDVSA-INTEVEP, Departamento de Procesamiento de Residuales y Crudos Pesados, Urbanización Santa Rosa, Sector El Tambor, Los Teques, Edo. Miranda, Ap. 76343, Caracas 1070-A, Venezuela*

<sup>c</sup> *School of Chemistry, The University of Manchester, Oxford Road, Manchester M13 9PL, United Kingdom*

<sup>d</sup> *Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, Caracas, Venezuela*

<sup>e</sup> *Laboratorio de Química Computacional, Centro de Química, IVIC, Ap. 21827, Caracas 1020-A, Venezuela*

Received 20 March 2007; received in revised form 26 July 2007; accepted 27 July 2007

Available online 6 August 2007

### Abstract

The interaction of ethanethiol ( $C_2H_5SH$ ) with a model cluster of three tetrahedral zeolite sites (T3) and a larger zeolite model represented by a 12-membered ring with one hydroxyl Brønsted acid site (T12), has been investigated by Hartree–Fock (HF) and the B3LYP approach of the density functional theory methods using the 6-31+G(d,p) basis set. The molecular formula of the T12 cluster is  $Al(OH)_2(OH)(SiOH_2)_{11}$ . The deprotonation energy was evaluated for the T3 and T12 clusters as a criterion to account for the acidity strength of the zeolite models. The interaction between  $C_2H_5SH$  and these clusters leads to the formation of planar vander Waals 1:1 adsorption complexes, dominated by hydrogen bonding between the S atom of  $C_2H_5SH$  and the H atom of the hydroxyl group in the Al–O–Si zeolite bridge. The results of structures and interaction energies, show that these complexes are similar to other sulfur–zeolite complexes reported in the literature. A vibrational analysis was also performed to estimate the shift of frequency of the OH vibrational mode of the zeolite hydroxyl group on coordination, where the corresponding shifts are negative and are of the same order of magnitude as the corresponding experimental values shown by R–SH compounds adsorbed on  $SiO_2$  and acidic zeolites. Additionally, the SH mode frequency shift in ethanethiol complex is positive. The size of the cluster is significant for the estimation of the properties of the ethanethiol–zeolite adsorption complex.

© 2007 Elsevier B.V. All rights reserved.

**Keywords:** Ab initio; Density functional theory; Sulfur organic compounds; Zeolites; Interaction energy

### 1. Introduction

Studies of the surface chemistry and adsorption of sulfur organic compounds (SOC) on acid zeolites have long been of interest in catalysis, mainly because of implications in the areas of hydrotreatment of crude oils, catalytic cracking of fuels and because of the reactions of SOCs with molecular sieves

[1–4]. Such studies are topical because the SOC content in fuel transportation has been recently regulated by the environmental agencies of different countries; therefore, further research is timely in order to develop fuels with low SOC concentrations. For example, gasoline after the fluid catalytic cracking (FCC) process results in a fuel that can have as much as 2000 ppm sulfur content. This sulfur concentration is problematic because it generates high air pollution on automobile combustion. The origin of this S content in crude oil is due to the presence of aromatic compounds such as thiophene and benzothiophene derivatives and mercaptans or thiol compounds such as methanethiol ( $CH_3SH$ ) and ethanethiol ( $C_2H_5SH$ ). The modern hydrocracking processes are based in rational mixtures of

\* Corresponding author. Present address: Centro Nacional de Tecnología Química CNTQ, Ministerio del Poder Popular para Ciencia y Tecnología, Avenida Universidad, Esquina El Chorro, Torre MCT, Piso 18, Caracas, Venezuela. Tel.: +58 212 2103969; fax: +58 212 2103746.

E-mail addresses: [hsoscun@mct.gob.ve](mailto:hsoscun@mct.gob.ve), [hsoscun@yahoo.es](mailto:hsoscun@yahoo.es) (H. Soscún).

Ni-Mo and Ni-W catalysts supported in an acidic zeolitic phase, where removal of sulfur also occurs by catalytic action of the Brønsted acid sites of the zeolite support [5]. It is important to note that these processes are able to catalyze mainly the decomposition of the aromatic compounds. In this context, a novel catalytic gasoline desulfuration acting on thiols compounds has been recently developed via the so-called dehydrosulfidation (DHS) process which uses acidic zeolites; their performance is similar to that observed in the methanol dehydration process [1]. The products of this DHS process are hydrocarbon compounds, plus  $H_2S$ . The main advantage of DHS is to reduce drastically the sulfur content in gasoline without changing the octane number index and without using  $H_2$ . This is therefore a relevant topic of research because few experimental and theoretical works have been published in this area yet several patents have been registered [1].

The details of HDS acid catalyzed reactions are not well known and only have been reported theoretical studies dedicated to the mechanism of the S aromatic species, such as thiophene [6], alkylated thiophene [7] and dibenzothiophene [8] in presence of zeolite models. These investigations shown that acid zeolites are able to catalyze aromatic sulfur compounds in presence of hydrogen.

On the other hand, sulfur compounds such as thiols can interact – in absence of hydrogen – either chemically or physically with both ionic and acidic forms of zeolites [1–3] and the nature of these interactions are similar to those observed for alcohols [2]. Garcia and Lercher [3] have reported the adsorption of  $C_2H_5SH$  and *n*-butanethiol on H-ZSM5, Na-ZSM5 and on  $SiO_2$ . In this study, the authors investigated the nature of the complexes formed during the adsorption process using infrared spectroscopy, temperature programmed, and gravimetric techniques. From these experiments, it has been proposed that stable 1:1 reversible molecular thiol–zeolite can be formed. Three forms of adsorption structure have been proposed for these complexes: (a) a linear hydrogen-bonding complex between the thiol and the SiOHAl framework of the zeolite, (b) a cyclic hydrogen-bonding zeolite–thiol complex, and (c) a cyclic protonated zeolite–thiol complex, where the sulfur compound is hydrogen-bonded to oxygens on the zeolite surface. The structural forms of the linear (a), cyclic (b), and protonated (c) complexes are shown in Fig. 1.

Ziolek and Decyk have reported the adsorption and transformation of  $C_2H_5SH$  and diethyl sulfide on faujazite-type zeolites, both alkali-metal-exchanged and protonated types [4]. These

studies have demonstrated that protonated forms of zeolites are highly active in the transformation of sulfur compounds due to the formation of hydrogen bonding complexes. The existence of this hydrogen bonding between the SOC S atom and the acid proton of zeolites has been studied by theoretical methods, where the zeolites have been represented by cluster models of finite dimension. Modeling studies of the  $CH_3SH$  [2] and the  $C_2H_5SH$  adsorption on HZSM-5 zeolites have been recently reported by Soscún et al. [2] and by Lu et al. [9], using Hartree–Fock (HF) and density functional theory (DFT) methods, respectively. Soscún et al. employed a 10 membered cluster ring as a zeolite model with 43 atoms and only one Brønsted acid site (BAS), and in this investigation was found that the interaction of  $CH_3SH$  with acidic zeolite site leads to the formation of a complex that is dominated by the bonding between the SOC S atom and the H atom of the O bridged between the Al and Si atoms [2]. On the other hand, Lu et al. [9] employed a series of three tetrahedral atoms (two Si and one Al atoms only) to model the ZSM5 acid zeolite and reported the formation of a weak vander Waals bond between the sulfur molecule ( $C_2H_5SH$ ) and the zeolite clusters. It is important to note that the calculated structures of the observed complexes correspond to the linear conformation (a) of Fig. 1, and not cyclic ones (Fig. 1(b and c)).

The present paper is dedicated to a theoretical study of the interactions of  $C_2H_5SH$  molecule with acid zeolites of large size. Our aim is to gain an understanding at the molecular electronic level of the interaction mechanism in SOC and zeolites. We chose  $C_2H_5SH$  as the SOC model is because it represents the second most important industrial RSH compound in the series of mercaptans, after  $CH_3SH$ .

It is well known that the intrinsic acidity of the OH groups in a zeolite model depends on the size of the model cluster [10], therefore two models were used to represent the zeolite, the T3 and T12 that will be explained in the next section. The cluster of three tetrahedral sites, referred as T3 and shown in Fig. 2, has been chosen as the simplest zeolite model. A more realistic representation of the zeolite structure, a ring of 12 tetrahedral with 11 Si atoms and only one Al atom to simulate an isolated Brønsted acid site that will be referred as T12 membered ring has been also employed. The structure of T12 is shown in Fig. 3.

The main objectives of this work is therefore the structural, energetic and vibrational characterization of the complex formed between ethanethiol and the zeolite models, and to make the corresponding comparison with previously reported values for the complex between  $CH_3SH$  and acidic zeolites [2].

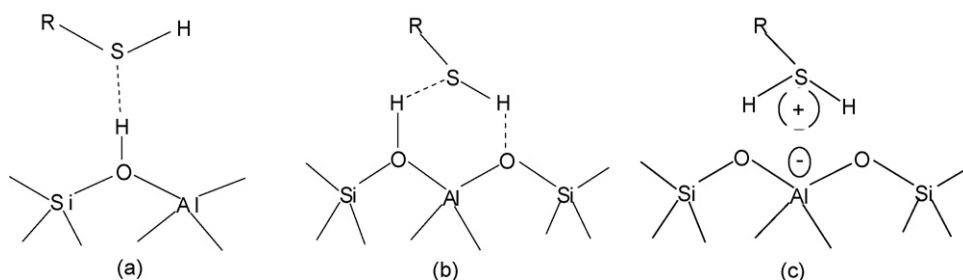


Fig. 1. Structural forms of the adsorption complexes between R-SH sulfur compounds and acidic zeolites: (a) linear complex; (b) cyclic complex; (c) cyclic protonated complex Ref. [3].

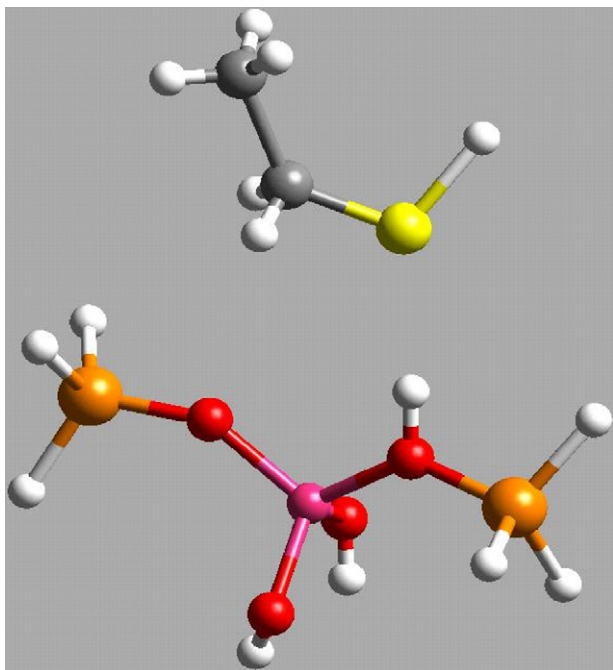


Fig. 2. Model of the T3 cluster and the interaction with the  $\text{CH}_3\text{CH}_2\text{SH}$  molecule ( $\text{C}_2\text{H}_5\text{SH-T3}$  complex).

## 2. Methods and models

The zeolite models used in this work therefore consist of two clusters: one formed by three tetrahedral with only one acid site, named T3 with the chemical composition of  $\text{Al}(\text{OH})_2(\text{OH}_p)(\text{OSiH}_3)_2$  (See Fig. 2), and other with 11 Si tetrahedral and one Al atom in the window of 12 O atoms (12-membered ring cluster),  $\text{Al}(\text{OH})_2(\text{OH}_p)(\text{SiOH})_{11}$  named T12,

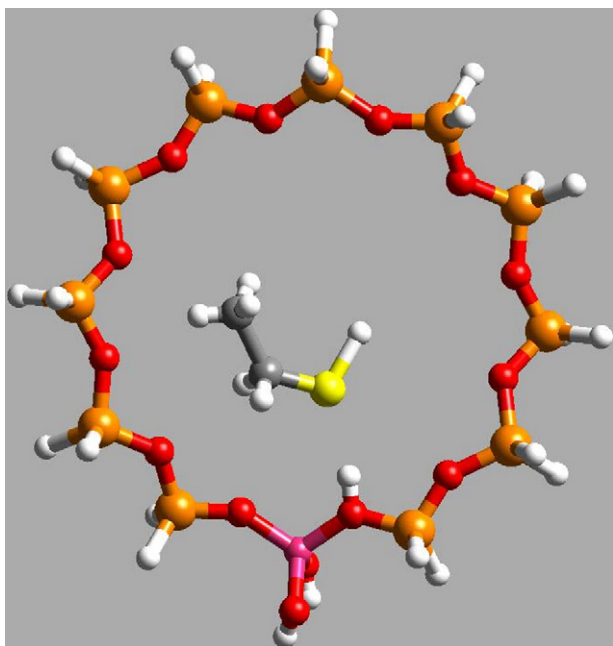


Fig. 3. Model of the zeolite structure (T12 cluster) and the interaction with the  $\text{CH}_3\text{CH}_2\text{SH}$  molecule ( $\text{C}_2\text{H}_5\text{SH-T12}$  complex).

with  $C_s$  symmetry (See Fig. 3). The advantage of using the T12 model is that besides the interaction between the adsorbate molecule and the acid site, further interactions are possible with the O atoms of the pore. In both models each Si atom has been capped with H atoms and the Al one has been saturated with two OH groups. The catalytic activity of zeolites is mainly due to the Brønsted acidic sites (BAS). These are formed when a silicon atom is replaced by an aluminum atom and a proton  $\text{H}_p$  is attached to the bridge oxygen atom between Al and the adjacent Si atom, giving a chemically stable structure,  $\text{Al}(\text{OH}_p)\text{Si}$ , where the Si and Al atoms are four-coordinated structures. In this sense, we expect that a four-oxygen coordination around the Al atom in the studied clusters will give a more realistic representation of the  $\text{OH}_p$  acid site and this feature allows a better representation of the zeolite adsorption site.

The interaction of  $\text{C}_2\text{H}_5\text{SH}$  with the T3 and T12 zeolite ring has been considered as a planar interaction, i.e., the C, S and H atoms of  $\text{C}_2\text{H}_5\text{SH}$  and the Al, O, Si and H of the BAS of the zeolite cluster lie in the same plane, such as the linear adsorption complex shown in Fig. 1(a). The corresponding complexes are referred as  $\text{C}_2\text{H}_5\text{SH-T3}$  and  $\text{C}_2\text{H}_5\text{SH-T12}$  models.

Our calculation strategy was performed with full optimization of the T3 and T12 clusters,  $\text{C}_2\text{H}_5\text{SH}$  molecule and the  $\text{C}_2\text{H}_5\text{SH-T3}$  and  $\text{C}_2\text{H}_5\text{SH-T12}$  complexes, constrained to  $C_s$  symmetry, with HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) levels of theory [11,12]. Additionally, harmonic vibrational analysis was performed for the T3 cluster,  $\text{C}_2\text{H}_5\text{SH}$  and the complex structure at both levels of approximations. For the T12-complex the IR frequencies were calculated at HF level of theory only. All calculations were carried out with the Gaussian98 suite of programs [13].

Finally, despite extensive searches for a cyclic adsorption structure such as that illustrated in Fig. 1(b), no stable structure for this coordination mode was found.

## 3. Results and discussions

### 3.1. Structure and energetics

Relevant optimized geometric results of the structures of T3 and T12 clusters of zeolite are displayed in Table 1. The BAS for our T3 and T12 models are structurally characterized by the Al–O, Si–O and O– $\text{H}_p$  bond distances. The corresponding optimized values for T12 are 1.9298 Å (1.9389 Å), 1.6983 Å (1.7170 Å) and 0.9496 Å (0.9693 Å) determined at HF/6-31+G(d,p) (and B3LYP/6-31+G(d,p) in parenthesis), respectively. The optimized Al–O–Si and Al–O– $\text{H}_p$  bond angles are 124.9° (124.2°) and 115.6° (116.1°), respectively. This indicates that the acid proton  $\text{H}_p$  is located in the same plane that Si, O and Al atoms. The rest of Si–O bonds (not reported in Table 1) for the T12 structure varies in the range of 1.6041 Å (1.6253 Å) to 1.6447 Å (1.6658 Å), and the complementary Al–O bond that does not participate in the BAS have the values of 1.7195 Å (1.7350 Å). The results illustrate well-known behavior that the DFT geometry optimization consistently produces bond lengths greater than HF and in some cases smaller

Table 1  
Relevant optimized geometric parameters of the T3, T12, C<sub>2</sub>H<sub>5</sub>SH–T3 and C<sub>2</sub>H<sub>5</sub>SH–T12 structures, total energies  $E_T$  and interaction energies  $E_i$

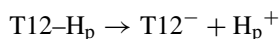
	T12 cluster		C <sub>2</sub> H <sub>5</sub> SH–T12 complex	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
<b>Bond length (Å)</b>				
Al–O	1.9298 1.9479 <sup>a</sup>	1.9389 1.9529 <sup>a</sup>	1.9150 1.9369	1.9187 1.9369 <sup>a</sup>
Si–O	1.6983 1.7047 <sup>a</sup>	1.7170 1.7227 <sup>a</sup>	1.6934 1.7023 <sup>a</sup>	1.6453 1.7205 <sup>c</sup>
O–H <sub>p</sub>	0.9496 0.9485 <sup>a</sup>	0.9693 0.9692 <sup>a</sup>	0.9560 0.9518 <sup>a</sup>	0.9843 0.9763 <sup>a</sup>
<b>Bond angles (°)</b>				
Al–O–Si	124.9 132.9 <sup>a</sup>	124.2 133.8 <sup>a</sup>	124.7 130.5 <sup>a</sup>	123.5 130.0 <sup>a</sup>
Al–O–H <sub>p</sub>	115.6 107.7 <sup>a</sup>	116.1 106.4 <sup>a</sup>	116.6 111.6 <sup>a</sup>	118.0 113.8 <sup>a</sup>
Si–O–H <sub>p</sub>	119.7 119.4 <sup>a</sup>	119.5 119.8 <sup>a</sup>	118.7 118.0 <sup>a</sup>	118.5 117.2 <sup>a</sup>
<b>Bond length (Å) and Bond angle (°)</b>				
S···H <sub>p</sub>			2.4607 2.6513 <sup>a</sup>	2.2441 2.3947 <sup>a</sup>
S···H <sub>p</sub> –O			167.0 161.7 <sup>a</sup>	171.0 165.9 <sup>a</sup>
<b>Total and interaction energies</b>				
$E_T$ (a.u.)	–4483.992106 –1124.737436 <sup>a</sup>	–4496.290991 –1128.026119 <sup>a</sup>	–4960.748019 –1601.489464 <sup>a</sup>	–4974.326716 –1606.057580 <sup>a</sup>
$E_i$ (kJ/mol)			–19.1 –14.8 <sup>a</sup>	–23.5 –12.4 <sup>a</sup>

<sup>a</sup> With the T3 cluster.

bond angles (Al–O–Si, Si–O–H<sub>p</sub>). However, the differences are smaller than 0.02 Å for the bond lengths and less of 1° for the bond angles. It is important to note that there are small variations in the optimized Al–O, Si–O and O–H<sub>p</sub> bond lengths between T3 and T12 clusters. However, large differences are observed for the Al–O–Si and Al–O–H<sub>p</sub> bond angles of these clusters, being these changes in about 8°, where in the T12 cluster these angles are closer than in T3 one.

On the other hand, the optimized structural results of the T12 cluster indicate that the diameter of the 12 tetrahedral windows has a value of 7.4 Å at HF and B3LYP levels of theory which is in excellent concordance with experimental results for the 12-member ring window of the faujasite (FAU) structure (7.4 Å [14]).

The degree of acidity was evaluated for the T12 cluster in terms of the deprotonation energy (DPE) of the acid zeolite model; this determines the ability of the cluster to release the acid proton of the BAS. This property is defined for the process

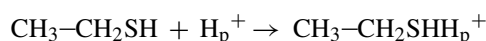


as

$$\text{DPE} = E_T(\text{T12}^-) - E_T(\text{T12-H}_p) \quad (1)$$

where  $E_T(\text{T12}^-)$  and  $E_T(\text{T12-H}_p)$  are the total energies of the deprotonated species and the neutral cluster, respectively. The results obtained for DPE of T12 evaluated at HF/6-31+G(d,p) (B3LYP/6-31+G(d,p)) is 339.7 kcal/mol (330.6 kcal/mol). The B3LYP value is within the accepted range of the faujasite deprotonation energy (321–330 kcal/mol) as shown in reference [2] for a great variety of zeolites using different methods of determination. For the particular case of T3 the corresponding DPE is 340.9 kcal/mol (332.9 kcal/mol). These results suggest that the acidity of both clusters, T3 and T12, are reasonable values for a protonated zeolite cluster and these models are appropriate to study the interaction of BAS of zeolites with polar molecules.

With respect to the feasibility of the formation of the (c) complex (see Fig. 1(c)), we expect that this process depends not only on the zeolite DPE value but on the energetic gain due to the protonation of the thiol, according to the following reaction:



$$\text{PE} = E_T(\text{CH}_3\text{-CH}_2\text{SHH}_p^+) - E_T(\text{CH}_3\text{-CH}_2\text{SH}) \quad (2)$$

The (c) complex formation can be described in two steps: deprotonation of the zeolite (Eq. (1)) and the thiol protonation (Eq. (2)). The calculated protonation energy PE value (Eq. (2)) at

Table 2  
Optimized relevant geometric parameters of CH<sub>3</sub>CH<sub>2</sub>SH and interacting with T12 and total energy

	Isolated CH <sub>3</sub> CH <sub>2</sub> SH		CH <sub>3</sub> CH <sub>2</sub> SH in the C <sub>2</sub> H <sub>5</sub> SH–T12 complex	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Bond lengths (Å)				
C–C	1.5248	1.5273	1.5228	1.5246
C–S	1.8276	1.8490	1.8354	1.8545
S–H	1.3275	1.3489	1.3249	1.3444
Total energy (a.u.)				
<i>E<sub>T</sub></i> (a.u.)	–476.748645	–478.026757		

B3LYP/6-31+G(d,p) is –193.9 kcal/mol. Therefore, the energy gain in this step (PE = –193.9 kcal/mol) does not compensate the energy loss (DPE = 330.6 kcal/mol) required to deprotonated the zeolite and consequently the (c) complex can not be formed.

The structure of ethanethiol was fully optimized under the C<sub>s</sub> symmetry constraint, and the main results are shown in Table 2. These results are in agreement with the standard geometry of C<sub>2</sub>H<sub>5</sub>SH (<http://webbook.nist.gov>). We observe longer equilibrium bond lengths in calculations carried out with DFT compared to HF, particularly for the S–X bonds (X = C, H).

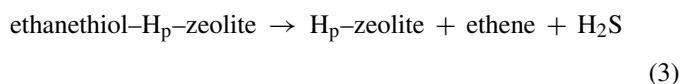
Relevant results of the C<sub>s</sub> optimization of the geometry of the C<sub>2</sub>H<sub>5</sub>SH–T3 and C<sub>2</sub>H<sub>5</sub>SH–T12 complexes, at HF/6-31+G(d,p) and B3LYP/6-31+G(d,p) levels are displayed also in Table 1. The corresponding optimized lengths of the Al–O, Si–O and O–H bonds indicate that, by effect of the interaction between C<sub>2</sub>H<sub>5</sub>SH and the OH bridge group of the zeolite model the two first bonds decrease, whereas the OH bond increases. This last feature could be an indication of a partial ethanethiol–H<sub>p</sub> bond formation. The weakening of the O–H<sub>p</sub> zeolite bond brings as a consequence a strengthened of other bonds attached to O, i.e., O–Si and O–Al bonds. It is important to note that these effects are not quantitatively significant, indicating that the interaction C<sub>2</sub>H<sub>5</sub>SH–zeolite is a weak *van der Waals* type bonding (physisorption). It is important to note that for the T3 and T12 clusters, the observed changes in the geometries are similar when the SOC is adsorbed.

The calculated S···H<sub>p</sub> bond distance of 2.6513 Å (2.3947 Å) for the T3 cluster, and 2.4607 Å (2.2441 Å) for the T12 complex (Table 1) indicate that the size of the cluster is important in the stabilization of the complex giving shorter S···H<sub>p</sub> bond distances, in T12 than in T3, at HF as well as DFT level. In addition, the combined exchanged and correlation effects that were accounted for with the B3LYP hybrid functional gives a major structural stabilization of T3 and T12 compared to HF, which is reflected in shorter S···H<sub>p</sub> bond distance of about 0.2 Å. A comparison with the CH<sub>3</sub>SH–zeolite complex [2] shows similarity in the S···H<sub>p</sub> distance of 2.4265 Å compared to 2.4607 Å at HF level and 2.2499 Å compared to 2.2411 Å using DFT. As one would expect chemically, the adsorption complex geometries of C<sub>2</sub>H<sub>5</sub>SH–zeolite and CH<sub>3</sub>SH–zeolite are structurally analogous.

Additionally to the S···H<sub>p</sub> hydrogen bonding in the C<sub>2</sub>H<sub>5</sub>SH–T12 complex, the distances between the H atoms of the CH<sub>3</sub> group of the sulfur compound and the neighbor O atoms of the T12 cluster are about of 3.3 Å, showing that there is no

chemical bonding between these units. These structural results show that the interaction between C<sub>2</sub>H<sub>5</sub>SH and acid zeolites is mainly determined by the dipole-induced hydrogen bonding interaction between the S atom with the Brnsted acid site of the zeolite.

Table 2 displays the optimization results for the relevant geometric parameters of isolated C<sub>2</sub>H<sub>5</sub>SH and C<sub>2</sub>H<sub>5</sub>SH–zeolite complex. These results show that the structure of C<sub>2</sub>H<sub>5</sub>SH remains almost constant on complex formation in the zeolite network because the strength of this interaction is rather weak. However, in spite of this weak interaction an increasing of the C–S bond and a shortening of the S–H bond in C<sub>2</sub>H<sub>5</sub>SH occur. These facts suggest that a strong S···H<sub>p</sub> interaction (for example at high temperatures) could lead to the formation of H<sub>2</sub>S and therefore the DHS process would take place. It may be possible to visualize the C<sub>2</sub>H<sub>5</sub>SH physisorption as a precursor state for the surface reaction:



At this point it is important to mention that the structure of C<sub>2</sub>H<sub>5</sub>SH in the zeolite complex does not correspond to the most stable conformation of this sulfur compound in the gas phase. In fact, it can be inferred that in the process of complexation, a change occurs in the position of the S–H bond with respect to the CH<sub>2</sub> group that leads to a more stable conformation, where the S atom can interact freely with the hydroxyl group of the BAS of the zeolite network to form the adsorption complex represented in Fig. 3.

The total energies of the species involved in the interaction C<sub>2</sub>H<sub>5</sub>SH, T3, and T12 are also presented in Tables 1 and 2. The values of the ethanethiol–zeolite adsorption energy defined as the difference between the total energy of the complex and that of the isolated species and evaluated at HF and B3LYP levels are –14.8 and –12.4 kJ/mol for T3 and of –19.1 and –23.5 kJ/mol for T12, respectively. On the other hand, the low value of the interaction energy (*E<sub>i</sub>*) between the T12 ring and the C<sub>2</sub>H<sub>5</sub>SH thiol to give the C<sub>2</sub>H<sub>5</sub>SH–T12 complex reported in Table 1 confirm the *van der Waals* interaction type. Also, the difference in the interaction energy at DFT level is 11.1 kJ/mol in spite of the cluster size difference, where the increasing of the cluster model gives larger adsorption energies because of the electrostatic contribution of the rest of atoms of the T12

Table 3  
Mulliken atomic population MAP of the atoms involved in the BAS of the T12 cluster

Mulliken atomic populations	T12 cluster		C <sub>2</sub> H <sub>5</sub> SH–T12 complex	
	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Q(Al) (e)	+0.034	–0.446	+0.033	–0.456
Q(Si) (e)	+0.767	–0.464	+0.740	+0.441
Q(O) (e)	–0.319	–0.157	–0.254	–0.060
Q(H <sub>p</sub> ) (e)	+0.468	+0.448	+0.460	+0.390
C <sub>2</sub> H <sub>5</sub> SH compound				
Q(H) (e)	+0.040	+0.060	+0.070	+0.092
Q(S) (e)	–0.085	–0.058	–0.433	–0.248
Q (c) <sub>α</sub>	–0.294	–0.363	–0.127	–0.272
Q (c) <sub>β</sub>	–0.335	–0.393	–0.287	–0.445

window. Additionally, binding energies for the C<sub>2</sub>H<sub>5</sub>SH–T12 complex are larger than the corresponding values obtained for the interaction of the CH<sub>3</sub>SH–T10 acid zeolite cluster, which value at the BLYP/6-31+G(d,p) level of theory is –17.6 kJ/mol [2]. These results suggest that the interaction between the proton (H<sup>+</sup>) and the thiol S atom increases with the molecular size of the sulfur compound. Likely, the size of the zeolite cluster also participates in some degree in the nature of the S · · · H interaction.

Additionally it is worth to mention, that it is expected that larger clusters that include extra atomic interactions between the organic compounds and O atoms of the zeolite windows can lead to lower adsorption energies than those calculated in this work because of the long range *van der Waals* interactions are ignored.

### 3.2. Mulliken atomic populations

Mulliken atomic populations (MAP) give a chemical intuitive representation of the degree of charge on one atom in a molecule and should be regarded as a qualitative tool for interpreting tendencies about intramolecular charge transfer in a molecular system. The MAP of the atoms involved in the interaction between C<sub>2</sub>H<sub>5</sub>SH and the T12 cluster are reported in Table 3. The most important changes in these atomic charges are observed in the O atom of the T12 OH hydroxyl group and the S atom of the C<sub>2</sub>H<sub>5</sub>SH. These MAPs suggest that the formation of the C<sub>2</sub>H<sub>5</sub>SH–T12 complex induces electronic charge reorganization where the O atom of the BAS acts as electron donor with a polarization charge of +0.07e (HF) or +0.10e (B3LYP). On the other hand, the S operates as an electron acceptor, where the corresponding polarization charge values are –0.34e (HF) and –0.19e (B3LYP). Fig. 4 displays the model of the charge polarization of the C<sub>2</sub>H<sub>5</sub>SH–zeolite adsorption complex with the corresponding charge variations. These values are in the same order of magnitude reported for the CH<sub>3</sub>SH–zeolite interaction [2].

Additionally, the charges located at the C atom of the CH<sub>3</sub> group of C<sub>2</sub>H<sub>5</sub>SH are slightly affected by the very weak interactions with the neighbor O atoms of the T12 cluster, where the MAP of Table 3 show for the C<sub>β</sub> atom a small charge transfer at HF (+0.048e) and at B3LYP (–0.054e) levels of theory occur in the complex.

### 3.3. Vibrational frequencies

The vibrational frequency of the OH normal mode ( $\nu_{\text{OH}}$ ) of the BAS in zeolites is a quantitative measure of the acidity of the zeolite and the shift of this frequency ( $\delta_{\text{OH}}$ ) on interaction with a neutral molecule is a measure of the degree of the strength of the interaction. In this work, we calculated the harmonic frequencies for the optimized T3 and T12 clusters and the optimized C<sub>2</sub>H<sub>5</sub>SH–T3 and C<sub>2</sub>H<sub>5</sub>SH–T12 complexes. Calculations with the T3 cluster were performed at HF and B3LYP levels of theory. However, for the T12 complex these calculations were performed only at HF/6-31+G(d,p) level of theory. The results for  $\nu_{\text{OH}}$  are displayed in Table 4. We have scaled the calculated values by a factor of 0.90, following a well-documented procedure [14]. The HF/6-31+G(d,p) values for T3 and T12 are 3659 and 3706 cm<sup>–1</sup>. The interaction with C<sub>2</sub>H<sub>5</sub>SH leads to a shift of the frequency  $\delta_{\text{OH}}$  of 0 cm<sup>–1</sup> for T3 and 127 cm<sup>–1</sup> for the T12 complex at HF level, respectively. This result illustrates the importance of cluster size for studies on the frequency of the acid site. In fact, by effect of the interaction between the S atom of C<sub>2</sub>H<sub>5</sub>SH and the OH<sub>p</sub> zeolite group the OH vibrational frequency mode decreases, as it does in the case of other S–H<sub>p</sub> zeolite interaction complexes [2]. This frequency shift may be higher when electron correlation effects are taken into account (not considered here for T12). For example, for T3 at B3LYP

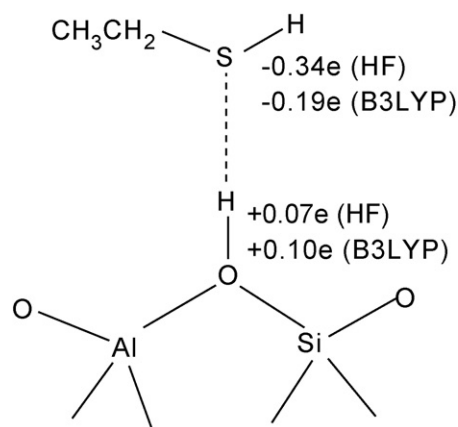


Fig. 4. Model for charge polarization for the O atom of the BAS of the T12 zeolite cluster and the S atom of the ethanethiol molecule.

Table 4

Frequency of the OH vibrational mode  $\nu_{\text{OH}}$  ( $\text{cm}^{-1}$ ) and the shift of the frequency  $\delta_{\text{OH}}$  ( $\text{cm}^{-1}$ ) of the T3 and T12 clusters, vibrational frequency  $\nu_{\text{SH}}$  ( $\text{cm}^{-1}$ ) and frequency shift  $\delta_{\text{SH}}/\text{cm}^{-1}$  of the SH normal mode of the ethanethiol molecule

	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)	HF/6-31+G(d,p)	B3LYP/6-31+G(d,p)
Vibrational frequency of the $\text{OH}_p$ normal mode of the T12 cluster				
$\nu_{\text{OH}}$ ( $\text{cm}^{-1}$ )	3706		3579	
	3659 <sup>a</sup>	3809 <sup>a</sup>	3659.0 <sup>a</sup>	3659 <sup>a</sup>
Frequency shift ( $\delta_{\text{OH}}$ , $\text{cm}^{-1}$ )				
			−127	
			0 <sup>a</sup>	−150 <sup>a</sup>
Vibrational frequency of the SH normal mode of the ethanethiol molecule				
$\nu_{\text{SH}}$ ( $\text{cm}^{-1}$ )			2617 (2601) <sup>b</sup>	
Frequency shift ( $\delta_{\text{SH}}$ , $\text{cm}^{-1}$ )			16	

<sup>a</sup> With the T3 cluster.

<sup>b</sup> The values between parentheses correspond to the vibration frequency mode in the isolated molecule. Ref. [15].

the  $\delta_{\text{OH}}$  is  $-150 \text{ cm}^{-1}$ , and the interaction of a cluster of four tetrahedral (T4) with  $\text{C}_2\text{H}_5\text{SH}$  evaluated at B3LYP/6-31+G(d,p) level gives a value of  $-328$  was found for  $\delta_{\text{OH}}$ . From these results the  $\delta_{\text{OH}}$  of  $335 \text{ cm}^{-1}$  at B3LYP for T12 was estimated. Qualitatively, these results are in the same order of magnitude as the experimentally measured frequency shift for the  $\text{C}_2\text{H}_5\text{SH}$  interaction with  $\text{SiO}_2$  and ZSM5 zeolite, which values corresponds to  $-283$  and  $-769 \text{ cm}^{-1}$ , respectively [3]. It is important to note that the SH normal mode of the sulfur compound is slightly affected by the interaction with the zeolite network, where the shift for this mode is  $16 \text{ cm}^{-1}$ .

In order to reproduce theoretically the experimental frequency shifts due to the  $\text{S} \cdots \text{H}_p\text{O}(\text{zeolite})$  interaction it is necessary to take in account post Hartree–Fock levels of theory with extended basis sets and to consider model zeolite clusters of larger size where the long range interactions can be properly treated. Further works in this direction are being performed in our laboratory.

#### 4. Conclusions

In this paper we carried out a theoretical study about the interaction of  $\text{C}_2\text{H}_5\text{SH}$  with acid zeolites leading to the formation of the *van der Waals* adsorption  $\text{C}_2\text{H}_5\text{SH}$ –zeolite complex. Ab initio Hartree–Fock and B3LYP methods were employed for the calculations with the standard 6-31+G(d,p) basis set. Zeolite structure clusters of three tetrahedral (T3) and a 12-membered ring (T12) containing one hydroxyl Brönsted acid site were used. The isolated molecules, zeolite clusters and complexes were restricted to maintain  $\text{C}_s$  symmetry. For these species the geometries, energies, and vibrational properties were analyzed. Results for B3LYP show smaller bond distances and stronger interactions than HF. Comparison of calculated values of DPE with literature are within the accepted range for acid zeolites. It was also found that the adsorption of  $\text{C}_2\text{H}_5\text{SH}$  in model zeolites gives a linear structure complex that is similar to previously reported one for  $\text{CH}_3\text{SH}$ –zeolite. The adsorption energy and geometry structure results show that model clusters of large size as T12 have a more stabilizing interaction (higher adsorption energy) and shorter  $\text{S} \cdots \text{H}_p$  and  $\text{H}_p\text{—O}$  bond distances than small ones (T3). The  $\text{C}_2\text{H}_5\text{SH}$  adsorption energy in a faujasite zeolite

model is slightly stronger than that of  $\text{CH}_3\text{SH}$  in a ZSM5 zeolite model. A comparison with results reported in the literature indicates that the nature of  $\text{C}_2\text{H}_5\text{SH}$  adsorption in zeolites is similar to other sulfur–zeolite complexes. The increase of the S–C and the decreases of the S–H bond of ethanethiol by effects of zeolite complexation suggest that  $\text{C}_2\text{H}_5\text{SH}$ –zeolite complex can be considered as a precursor state for the DHs process.

The analysis of the charge distribution of the isolated molecules and cluster models and the corresponding complexes through the MAP shows that there is an important charge polarization in the O atom of the BAS hydroxyl group and the in the S atom of the thiol molecule. The O acts as an electron donor and S as an electron acceptor.

The O– $\text{H}_p$  vibrational frequency mode decreases by the effect of the acid coordination and theoretical shifts are comparable to the corresponding experimental values of the adsorption of ethanethiol in  $\text{SiO}_2$  and acidic zeolites, whereas the SH vibrational mode of the sulfur compound increases by effect of the interaction.

The results presented in this work are limited because the vander Waals interactions are ignored. In this sense, further work is under development in our laboratory in order to account the effects of large zeolite clusters – including periodic models – in the adsorption process of organic compounds in mesoporous systems.

#### Acknowledgments

This research was partially supported by the CONIPET under project of Agenda Petróleo, contract grant No. 97003734, and La Universidad del Zulia LUZ. We thank deeply Jesus Rodriguez (IVIC) for useful help.

#### References

- [1] H. de Lasa, R. Hernandez Enrique, G. Tonetto, Ind. Eng. Chem. Res. 45 (2006) 1291–1299.
- [2] H. Soscún, O. Castellano, J. Hernandez, J. Phys. Chem. B 108 (2004) 5620. See references there in for other theoretical studies about sulfur compounds in zeolites.
- [3] C.L. Garcia, J.A. Lercher, J. Phys. Chem. 95 (1991) 10729–10736.
- [4] M. Ziolek, P. Decyk, Langmuir 15 (1999) 5781–5784.

- [5] A. López Agudo, A. Benitez, J.L.G. Fierro, J.M. Palacios, J. Neira, R. Cid, *J. Chem. Soc., Faraday Trans.* 88 (1999) 385.
- [6] X. Santigny, R.A. van Santen, S. Clémendot, F. Hutschka, *J. Catal.* 183 (1999) 107–118.
- [7] X. Rozanska, X. Santigny, R.A. van Santen, F. Hutschka, *J. Catal.* 202 (2001) 141–155.
- [8] X. Rozanska, X. Santigny, R.A. van Santen, S. Clémendot, F. Hutschka, *J. Catal.* 208 (2002) 89–99.
- [9] R. Lu, G. Qiu, C. Liu, *J. Nat. Gás. Chem.* 14 (2005) 119–214.
- [10] H. Soscún, O. Castellano, J. Hernández, A. Hinchliffe, *Int. J. Quantum Chem.* 82 (2001) 143–150.
- [11] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098; C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785; B. Mihlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* 157 (1989) 200.
- [12] M.J. Frisch, J.A. Pople, J.S. Binkley, *J. Chem. Phys.* 80 (1984) 3265, and references therein.
- [13] M.J. Frisch, et al., *Gaussian 98, Revision A. 7*, Gaussian, Inc., Pittsburgh, PA, 1998.
- [14] T. Yamazaki, K. Hasegawa, K. Honma, S. Ozawa, *Phys. Chem. Chem. Phys.* 3 (2001) 2686–2691.
- [15] <http://srdata.nist.gov/cccbdb/vs.f.asp> and references therein.