

Interaction between NaY Zeolite and boric Acid: a preliminary computational study

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ABSTRACT

A computational study of the electronic structure and stability of complexes formed between Zeolite Y and boric acid was carried out at the HF and B3LYP levels using 6-31G* basis set. Five structures located as local minimum in PES of complex (structures d, e, f, g, and h). The most stable structure is formed due to hydrogen bonding between two hydroxyl of boric acid and both oxygen of AlO₂ in Zeolite (structure e).

Keywords: Zeolite Y; H₃BO₃; ab initio; DFT

1. INTRODUCTION

High catalytic activity of steamed forms of NaY zeolites, Mordenite and ZSM-5 in many reactions are usually attributed to Bronsted and Lewis sites acids [1]. These sites are believed to be a result of interaction between Bronsted sites and Lewis sites created during steaming procedures, since both are present, and since it is known that in solution, enhanced Bronsted acidity can be generated by adding Lewis acid to Bronsted acid [2]. Recently, nature of these sites has been investigated by a range of experimental [3] and theoretical techniques [4]. For example ab-initio study investigated for interaction of water with Bronsted acidic sites of zeolite [5, 6] and in other work investigated interaction of BF₃ with zeolite [1]. Recently, Muller et al investigated application to the system thionine in zeolite NaY [7]. Nature of

acids sites have been characterized by adsorption of pyrole using Fourier Transform Infrared FT-IR, XPS, and microcalorimetry technique. The passivity of zeolite has important roles in a variety of base-catalyst reactions [8, 9]. Hence, these sites basicity of zeolite was characterized by adsorption of boric acid trimethyl ester [10]. Thus, there is some report about interaction of boric acid by other material such as Hydride Acids [11-15]. So far, to our best knowledge there is no theoretical or experimental work about interaction of acid boric with acid and base sites of zeolite for characterized of these sites. This has motivated us search for electronic structure, and stability of complexes on the model system, NaY zeolite and HY (protonated form of zeolite NaY) and H₃BO₃ for the first time. The purpose of this study is to determine the structure and relative

stability of the H_3BO_3 adsorption on this catalyst and help experimentalist for performing experimental study about acid and base sites in zeolite.

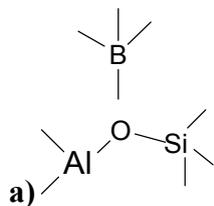
2. Computational details

Calculations were performed using the GAUSSIAN98 program system [16]. The geometric optimizations and frequency calculations were performed at the HF and B3LYP levels using 6-31G* basis set. The harmonic vibrational frequency calculations were performed to confirm whether the predicted structures are minima and to evaluate the zero-point vibrational energies (ZPE) corrections. The counterpoise (CP) method (using "Massage" keyword in Gaussian package) was used to correct basis set superposition error (BSSE) in the calculation of the binding energy.

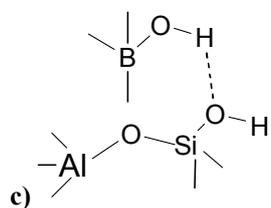
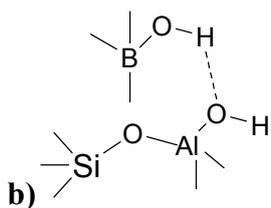
3. RESULTS AND DISCUSSION

In principle, a zeolite molecule can interact with H_3BO_3 as the following forms:

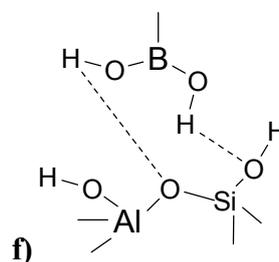
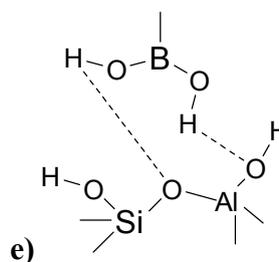
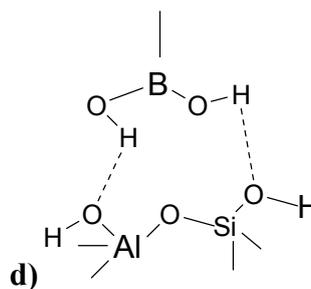
1. as a donor



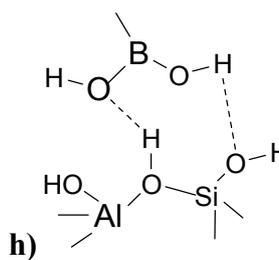
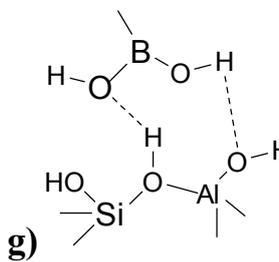
2. as a base (with one hydrogen bond)



3. as a base (with two hydrogen bond)



4. as an acid (proton of zeolite with two hydrogen bond)



There are zeolites in two forms. In the first form (NaY) oxygen in zeolite is a base sites (a, b, c, d and e) and the second form (HY) oxygen protonated and created a Bronsted acid sites (g and h). Our calculation shows that both **a** and **b** structures after optimization changed to structure **e** and **c** change to **f** structure. These observations indicate that no stable complex formed as a result of interaction between B atom with the framework oxygen by hydrogen and without hydrogen bond. It seems that the b and c structures are not formed because of the repulsion between the framework and the out of plane-OH atoms of zeolite. The calculated energies of complexes along with interaction energies at the HF and B3LYP levels are shown in Tables 1, 2 and 3. As shown in Tables 1, 2 and 3,

the most stable structure among possible ones is structure **e**. The results of selected bond lengths for structures **d**, **e**, **f**, and **g** are listed in Table 4. Noting to Table 4, we understand that in structures **e**, **f**, **g**, and **h**, H...O bond length in BOH...OAl is shorter than H...O bond length in BOH...OSi. In all of the structures (**d**, **e**, **f**, **g**, and **h**) planer structure of H₃BO₃ does not change upon complex formation however, the elongation of O-H of H₃BO₃ is observed due to complex formation when calculated O-H values are compared with experimental value reported in Ref 13 for O-H bond length. The more stability of structure **e** (Table 2) is consistent with the calculated values of O-H bond lengths (Table 4).

Table1: Calculated energy (kcal/mol) of H₃BO₃, Zeolite Y, and complex **d** along with the interaction energies at HF and B3LYP levels using 6-31G* basis set.

	HF/6-31G*	B3LYP/6-31G*
d :Y- H ₃ BO ₃	-1310.03329024	-1315.0854321
Y	-1058.8291789	-1062.5739728
H ₃ BO ₃	-251.1817159	-252.4751184
ΔE_{int}	-14.05	-22.80
BSSE	5.22	3.21
ZPVE	1.96	4.64
$\Delta E_{\text{int}}+\text{ZPVE}+\text{BSSE}$	-6.87	-14.95

Table 2: Calculated energy (kcal/mol) of H₃BO₃, Zeolite Y, and complexes e and f along with the interaction energies at HF and B3LYP levels using 6-31G* basis set.

	HF/6-31G*	B3LYP/6-31G*
e: Y- H ₃ BO ₃	-1310.04392866	-1315.09058235
Y	-1058.8291789	-1062.5739728
H ₃ BO ₃	-251.1817159	-252.4751184
ΔE_{int}	-20.73	-26.04
BSSE	7.12	5.03
ZPVE	1.54	3.91
$\Delta E_{\text{int}}+\text{ZPVE}+\text{BSSE}$	-12.07	-17.10
f: Y- H ₃ BO ₃	-1310.03722756	-1315.0824937
Y	-1058.8291789	-1062.5739728
H ₃ BO ₃	-251.1817159	-252.4751184
ΔE_{int}	-16.52	-20.96
BSSE	7.68	6.11
ZPVE	1.61	4.13
$\Delta E_{\text{int}}+\text{ZPVE}+\text{BSSE}$	-7.23	-10.72

Table 3: Calculated energy (kcal/mol) of H₃BO₃, Zeolite Y, and complexes g and h along with the interaction energies at HF and B3LYP levels using 6-31G* basis set.

	HF/6-31G*	B3LYP/6-31G*
g: HY- H ₃ BO ₃	-1310.54015881	-1315.584300
HY	-1059.3324809	-1063.0744871
H ₃ BO ₃	-251.1817159	-252.4751184
ΔE_{int}	-16.29	-21.77
BSSE	1.80	4.51
ZPVE	1.69	1.28
$\Delta E_{\text{int}}+\text{ZPVE}+\text{BSSE}$	-12.80	-15.98
h: HY- H ₃ BO ₃	-1310.538200	-1315.582349
HY	-1059.3324809	-1063.0744871
H ₃ BO ₃	-251.1817159	-252.4751184
ΔE_{int}	-15.06	-20.55
BSSE	5.43	3.67
ZPVE	2.06	1.98
$\Delta E_{\text{int}}+\text{ZPVE}+\text{BSSE}$	-7.57	-14.90

Table 4: Selected calculated bond lengths for structures d, e, f, and g B3LYP/6-31G* level.

structure	H bond	B-O	O-H	H...O
D	BOH...OSi	1.381	0.988	1.748
	BOH...OAl	1.361	0.985	1.807
E	BOH...OT	1.376	0.986	1.796
	BOH...OAl	1.363	0.996	1.686
F	BOH...OT	1.377	0.983	4.361
	BOH...OSi	1.360	0.980	1.800
G	BO...HOT	1.385	0.948	1.733
	BOH...OAl	1.335	0.963	1.804
h	BO...HOT	1.400	0.969	1.635
	BOH...OSi	1.351	0.980	1.846

It is believed that the basicity of Y zeolite is dependent on their cations. In Y zeolite, Na^+ is of the lower electronegative and is more delocalized than H^+ , so the oxygen anions in NaY may be more uniform. On the contrary, H^+ is localized on some of the oxygen anions and results in different types oxygen anions in HY [10] and may be adsorbed of H_3BO_3 gives strong splitting in B-O stretching vibration region when interact by base sites in NaY zeolite. It seems, there are good interaction between H_3BO_3 and unprotonated oxygen in zeolite (NaY, HY) and this material can be used for characterize basicity sites of zeolite.

4. CONCLUSION

Finally we hope results of the present theoretical study encouraging and help experimentalists for performing experimental study about interaction of zeolite with boric acid and other molecular moieties [17].

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بررسی برهم‌کنش میان زئولیت و اسید بوریک با استفاده از محاسبات کامپیوتری

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چکیده:

در این کار محاسبات کامپیوتری با روش HF و B3LYP و برنامه ریزی اولیه *6-31G روی ساختار الکترونی کمپلکس‌های تشکیل شده از زئولیت و اسید بوریک انجام شده و میزان پایداری آنها مورد بررسی قرار گرفت. پنج ساختار پایه ای d, e, f, g, h برای این کمپلکس‌ها پیشنهاد شده است که نتایج نشان داد پایدارترین حالت مربوط به تشکیل پیوند هیدروژنی بین گروه‌های هیدروکسیل اسید بوریک و AlO_2 در زئولیت می باشد.

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