14 December 2001

ELSEVIER

Chemical Physics Letters 350 (2001) 128–134

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

A full quantum embedded cluster study of proton siting in chabazite

Piti Treesukol [a,b], James P. Lewis [a], Jumras Limtrakul [b], Thanh N. Truong [a,*]

[a] *Department of Chemistry, Henry Eyring Center for Theoretical Chemistry, University of Utah, 315 S 1400 E, rm 2020, Salt Lake City, UT 84112, USA*

[b] *Laboratory for Computational and Applied Chemistry, Chemistry Department, Kasetsart University, Bangkok 10900, Thailand*

Received 10 July 2001; in final form 9 October 2001

Abstract

We propose a computational strategy within the full quantum embedded cluster methodology for modeling reactivity in extended systems. This method takes advantages of the embedded cluster methodology for treating interactions in the active region accurately while allowing interactions with the remaining crystal framework to be treated fully quantum mechanically by using the ab initio tight-binding theory. We have applied this method to study proton siting in chabazite. We found that our calculated relative stability of proton at four different oxygen sites agree well with those from previously periodic calculations, though the computational demand for the present approach is much less. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Despite rapid advances in computer technology and tremendous efforts in improving the efficiency of electronic structure methods, modeling reactivity in extended systems remains a challenge for quantum chemistry [1,2]. Periodic electronic structure methods provide an accurate framework to model interactions in extended systems such as crystals or surfaces. For porous materials such as zeolites, the unit cells are often larger than 100 heavy atoms. In such a case, the use of accurate periodic electronic structure methods is rather limited. A number of periodic density functional theory (DFT) studies of interactions in zeolites have been reported recently but only for small zeolitic systems [3–11]. These periodic DFT calculations used enormous computational resources.

Alternatively there are two other computational methodologies that are often employed, namely the cluster and embedded cluster methods. The cluster methodology treats the active region surrounding the active site (or defects) and the adsorbate quantum mechanically as an isolated system and totally ignores the effects of the remaining crystal framework. In many cases, such a treatment is sufficient in providing useful insights. However, there is sufficient evidence that the effects of the remaining crystal lattice, mainly the

* Corresponding author. Fax: +1-801-581-4353.
E-mail address: truong@chem.utah.edu (T.N. Truong).

PII: S0009-2614(01)01277-5

Madelung potential, are crucial for obtaining quantitative understanding on the mechanism of chemical processes that occur at the active sites (or defects) of the crystal. The embedded cluster methodology [12–17] takes advantages of the simplicity of the cluster approach but adds the effects of the crystal framework in an approximated manner. Two approximations known as the electronic embedding [12,14–17] and mechanical embedding [13] approaches have been developed. Both approaches have shown to perform quite well for many studies on adsorption and reactions at the Brønsted active sites of zeolites. Both, however, have inherent fundamental approximations. The electronic embedding neglects the crystal polarization and long-range structure relaxation effects whereas the mechanical embedding neglects the direct polarization of the wavefunction representing the active region and assumes certain accuracy of the potential force field, which was fitted to QM cluster results.

In this study we present a new computational strategy within the full quantum embedded cluster (FQEC) methodology that takes advantages of the embedded cluster methodology for accurate treatment of the active region and of the periodic electronic structure methods for rigorous representation of interactions in the extended system. Several different computational strategies within this general full quantum embedded methodology have been previously proposed [11,18,19]. The proposed computational strategy has its unique strength in crystals with large unit cells such as zeolites. For this reason, we select proton siting in H-chabazite as a model system for assessing its accuracy.

2. Methodology

The central idea of the embedded cluster methodology is to divide the physical system into two regions, the active and spectator regions. Most existent embedded cluster methods are based on the QM/MM methodology. In the present approach, the spectator region is also treated quantum mechanically by a periodic electronic structure theory. The partition of the physical system within the periodic boundary condition is illustrated in Fig. 1. The total energy of the system can be expressed within the framework of the ONIOM methodology developed by Morokuma and co-workers [20]

$$E_{\text{tot}} = E^{\text{Low}}_{\text{crystal}} + \left(E^{\text{High}}_{\text{cluster}} - E^{\text{Low}}_{\text{cluster}}\right) + \Delta E_{\text{boundary}}. \quad (1)$$

A physical interpretation for Eq. (1) is followed. In the first term, interactions in all regions, the active and spectator regions of the crystal and the cross-term interactions between the two regions are represented within a low level of periodic quantum mechanical formalism. The second term represents the correction to the local interactions

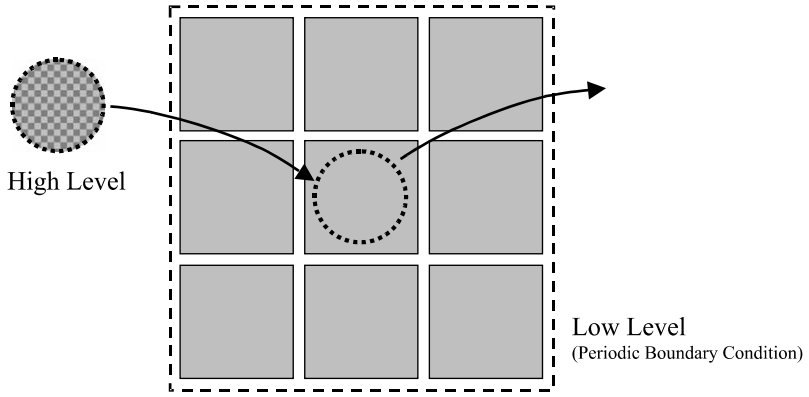

Fig. 1. Schematic description of the full quantum embedded cluster methodology.

in the active region by a more accurate level of electronic structure theory. The last term represents the difference in the energy of the boundary region calculated at the two levels of theory. With careful choice of the boundary region, the last term can be made to remain nearly constant in a chemical process and thus has no effect on the relative energy; consequently it can be ignored. We have shown that the ONIOM approach as in Eq. (1) can be used to improve the prediction for the adsorption energy of H_2O on Al_2O_3(0 0 0 1) surface calculated from our electronic embedded cluster method [21]. Sauer and co-workers also used the same energy correction expression both within the QM/MM methodology as in the QM–pot method [13] and within the full quantum embedded cluster methodology in their more recent study [11].

Correction for the local interactions in the active region can be done at any level of quantum chemistry methods available for isolated systems. Since we can correct the interactions in the most important region, it is possible to use a less accurate periodic electronic structure method to model interactions in the crystal. For the crystal energy term and the third term in Eq. (1), we propose to use the ab initio self-consistent tight-binding (AITB) method developed by Sankey and co-workers [22,23] called FIREBALL. The advantage of using this method is that systems with unit cells of order 1000 atoms can be easily considered on a Pentium III-based workstation. This is in fact the key strength of the present approach.

This AITB method is based on the generalized norm-conserving separable pseudopotentials of the Hamann type within a self-consistent density functional theory formalism. A tight-binding-like Hamiltonian is used to solve the generalized eigenvalue equation for determining the band-structure energy. This Hamiltonian consists of different density-functional interactions (i.e. kinetic, Coulomb, exchange-correlation, etc.). In solving the one-electron Schrödinger equation a set of slightly excited pseudoatomic 'fireball' wavefunctions are used. For the application discussed below, we employed the non-local Becke exchange and Lee-Yang-Parr correlation functional (BLYP) and the double numerical (DN) basis set of the sp^3 type. For convenience in the discussion below, we introduce a notation for AITB calculations similar to quantum chemistry methods for isolated systems, namely AITB calculations with the BLYP functional using the DN basis set as AITB(BLYP)/DN. The development of the DN basis set and the technical aspects of the AITB method have been described previously [23]. For the FQEC calculations, we used the ONIOM notation, i.e., high level:low level.

3. Test system and computational details

To test the proposed method we have applied it to study proton siting in H-chabazite. Due to its small unit cell of 37 atoms, several theoretical studies [3,5,8–11] using different periodic electronic structure methods have been carried out for the proton siting in this zeolite. Results from these studies are valuable for comparison purposes here. For chabazite, all tetrahedral sites (T-sites) (Al or Si tetrahedral sites) are equivalent by symmetry. At a given Al T-site, the Brønsted proton can reside on any of the four non-equivalent neighboring oxygen (O_1 through O_4) atoms as shown in Fig. 2a. Since these oxygen atoms are non-equivalent in the zeolite framework, Brønsted protons at different sites have different physical properties such as acidity and stability. In other words, the effect of the zeolite framework is perhaps the sole factor that distinguishes the differences among these sites and thus the relative stability of proton at these four sites provides a stringent test of the new methodology.

To calculate the relative stability of proton at the four oxygen sites, four different H-chabazite structures, where the Brønsted acidic proton is located at different sites, were first fully optimized at the periodic AITB(BLYP) level. To correct the local interactions near the Brønsted acid site, clusters of 13T surrounding the four oxygen sites (Fig. 2b) were selected from the optimized H-chabazite structures. The hybrid B3LYP/6-31G(d,p) method was used as the high level in this test case.

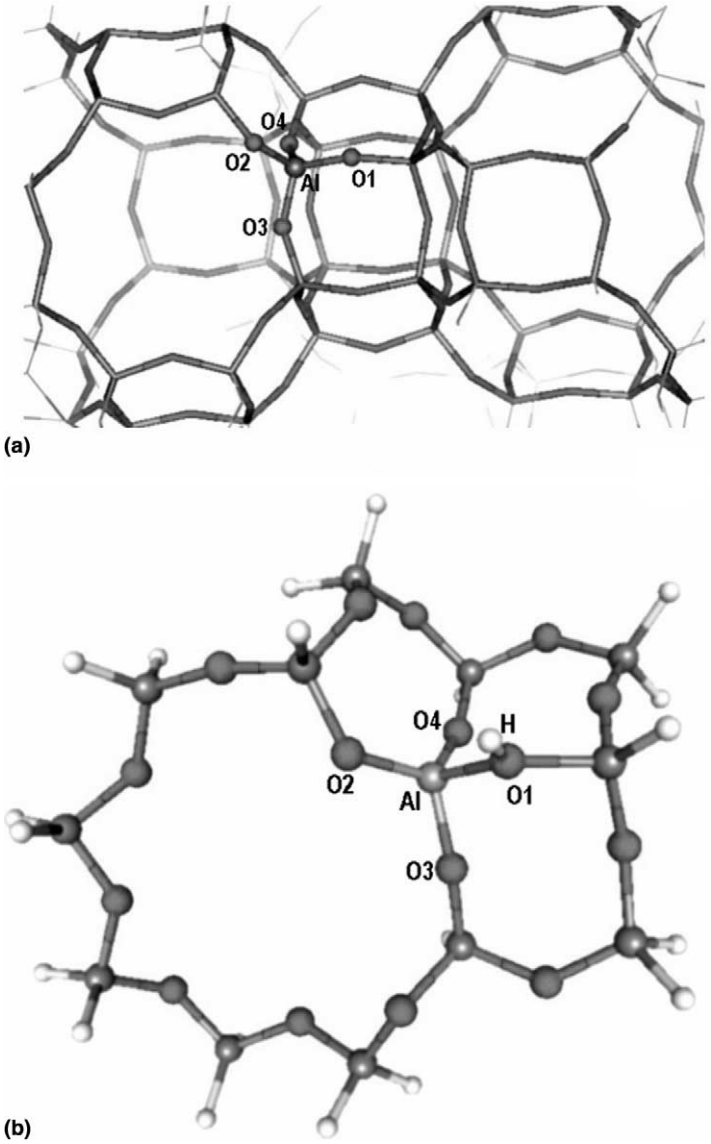

Fig. 2. (a) Perspective view of four non-equivalent oxygen atoms in the chabazite framework. (b) 13T cluster used in FQEC calculations.

4. Results and discussion

4.1. Structure relaxation

Brønsted acidic site is created when the Si atom at a tetrahedral site is substituted by an Al atom. Due to the change in the valency at the tetrahedral site, one can expect such a substitution would induce a large structure relaxation on the zeolite framework. As expected we found a large structure relaxation upon Al substitution in chabazite from the periodic AITB calculations. Selected optimized geometrical parameters are listed in Table 1 along with those from previous studies. The degree of relaxation is different when the proton is located at one of the four different neighbor oxygen sites. In particular, the Si–O bond distance in the chabazite SiO_2 crystal lattice is 1.65 Å. Upon substitution,

Table 1
Selected structural parameters of Brønsted acid sites in H-chabazites (Å and degree)

H-site	Method	O–H	Si–O(H)	Al–O(H)	∠Al–O(H)–Si	OUT(OH)[a]
O1	Periodic AITB	1.007	1.748	1.894	121.0	9.7
	QM–pot[b]	0.976	1.725	1.910	128.4	2.8
	Periodic DFT[c]	0.974	1.702	1.904	132.9	0.6
	Periodic DFT[d]	0.972	1.680	1.838	132.8	–
O2	Periodic AITB	1.004	1.723	1.846	129.7	8.0
	QM–pot[b]	0.977	1.721	1.876	133.4	12.3
	Periodic DFT[c]	0.976	1.701	1.876	135.2	20.5
	Periodic DFT[d]	0.971	1.681	1.807	132.6	–
O3	Periodic AITB	1.011	1.714	1.858	139.9	3.8
	QM–pot[b]	0.978	1.722	1.883	134.0	5.3
	Periodic DFT[c]	0.976	1.697	1.876	136.8	13.7
	Periodic DFT[d]	0.973	1.678	1.808	134.1	–
O4	Periodic AITB	1.059	1.748	1.912	148.9	1.9
	QM–pot[b]	0.980	1.738	1.921	129.9	7.4
	Periodic DFT[c]	0.975	1.714	1.938	135.2	11.6
	Periodic DFT[d]	0.972	1.697	1.857	134.4	–

[a] Out-of-plane angle.
[b] Taken from [3].
[c] Taken from [8].
[d] Taken from [9].

the Al–O(H) bond distance (O(H) is the oxygen atom of the hydroxyl group) varies from 1.846 to 1.912 Å. The large elongation in this particular lattice bond creates a local strain to the framework and induces changes in coordinates of the nearby atoms, particularly the Al–O(H)–Si angle. This angle is compressed from the original value of about 145° by as much as 26°.

The Al–O(H)–Si angle can be used to compare the differences between different computational methods in predicting the crystal structure relaxation upon Al substitution. It is interesting to note that the QM–pot method was able to reproduce the large structure relaxation upon Al substitution [3]. The variation in the magnitude of such relaxation when the Brønsted acidic proton located at four different sites is rather small as indicated by the range in the Al–O(H)–Si angle from 128° to 134° as compared to the range 121–149° from the periodic AITB calculations. However, the plane-wave periodic DFT results have a much smaller range 133–137° [8]. In our periodic AITB calculations, experimental crystal parameters from SiO_2 chabazite crystal (volume of 798 $Å^3$) were used. Periodic plane-wave DFT calculations [8] have shown that upon Al substitution the unit-cell volume is expanded from 800 to 821 $Å^3$. Thus, constraining the unit-cell volume at 798 $Å^3$ would introduce an external pressure on the system and thus would induce larger structure changes. That is in fact observed in our AITB calculations. Optimizing the crystal parameters using the periodic AITB method is being carried out and the results will be reported in a forthcoming paper.

Table 2
Relative stability for the Brønsted acidic proton located at the four distinct oxygen atoms O1–O4 in the active site of chabazite

Methods	Relative energy (kcal/mol)			
	O1	O2	O3	O4
Periodic AITB(BLYP)	0.00	3.78	3.99	3.81
Cluster AITB(BLYP)[a]	10.49	8.08	0.00	0.33
Cluster B3LYP[a]	8.50	6.65	0.00	5.28
B3LYP:AITB//AITB	0.00	4.35	5.98	10.75
Periodic HF//QM–pot[b]	0.00	4.07	3.09	3.01
Periodic HF[c]	(0.0)	(16.0)	(76.7)	(80.1)
Periodic DFT//QM–pot[d]	(0.0)	2.75	1.72	3.21
Periodic DFT[e]	0.00	2.10	1.25	1.43
Periodic DFT[f]	0.00	1.61	0.92	2.08
CCSD(T):DFT//QM–pot[g]	0.00	9.00	5.20	12.90

[a] Using 13T clusters selected from the periodic AITB(BLYP)/DN optimized crystal structures.
[b] Taken from [5].
[c] Taken from [10]; partial optimization; site specific information was not given explicitly.
[d] Taken from [3].
[e] Taken from [8].
[f] Taken from [9].
[g] Taken from [11].

4.2. Energetics

Relative stability for the Brønsted acidic proton located at the four distinct oxygen atoms O1–O4 (denoted as H1–H4, respectively) in the active site of chabazite calculated by different methods is listed in Table 2. Our calculated results can be compared to those from previous periodic HF//QM–pot [5], B3LYP//QM–pot [3,11] and plane-wave PZPW91 [8,9] calculations. Larin and Vercauteren [10] reported a periodic HF study with partial optimization for this system. All periodic methods including the present periodic AITB and B3LYP:AITB ones predict H1 to be the most stable. This is in consistent with the observation from a powder neutron diffraction study that found two distinct acid sites at O1 and O3 in the unit cell [24]. Different methods, however, yield slightly different order of relative stability for the remaining sites H2–H4. The differences in the spread of relative stability between B3LYP:AITB results of 10.7 kcal/mol and those of periodic HF//QM–pot, B3LYP//QM–pot, and plane-wave PZPW91 results of less than 4.1 kcal/mol can be due to (1) the degree of structure relaxation upon Al substitution in chabazite discussed above and/or (2) the differences in the local interactions. The later is supported by the recent the periodic DFT study when the interaction in the active region (1T) is corrected at the CCSD(T) level the larger spread of 12.9 kcal/mol was observed [11].

Results from AITB and B3LYP single-point energy calculations for 13T clusters used in the determination of the B3LYP:AITB energy can also provide information on the contributions of the electronic component of the zeolite framework, local interactions, and structure relaxation in the relative stability of proton at these four sites. First of all, comparing the cluster and periodic AITB results, we found that the electronic component of the zeolite framework, i.e. Madelung potential and crystal polarization, has a significant effect on the relative stability of the H1–H4 Brønsted acidic protons. Without it, the AITB method predicts the H3 and H4 protons to be more stable while H1 and H2 protons to be much higher in energy. This is in fact totally opposite to results from periodic calculations. In particular, this component stabilizes the H1–H4 protons by 14.5, 8.3, 0.0, and 0.5 kcal/mol relative to that of the H3 proton, respectively. Comparing the B3LYP and AITB cluster results, we found that improving the accuracy for interactions in the active site region stabilizes the H1 and H2 protons by 2.0 and

1.4 kcal/mol, respectively, while it destabilizes the H4 proton by 5.0 kcal/mol relative to that of the H3 proton. Thus the local corrections for interactions in the active region further spread the relative stability of these protons as mentioned above.

5. Conclusion

We presented a computational strategy within the full quantum embedded cluster (FQEC) methodology for studying reactivity of extended systems. This method takes advantages of the embedded cluster methodology for treating interactions in the active region accurately while allowing interactions with the remaining crystal framework to be treated fully quantum mechanically but at a less accurate level, particularly by the use of an ab initio tight-binding theory. To illustrate the applicability and accuracy of this method, we performed a study on proton siting in chabazite. The non-local hybrid B3LYP level of theory was used for the active region while a self-consistent tight-binding AITB method was used for determining the crystal structure when the Brønsted proton is located at four different oxygen atoms O1–O4 in the active site. We found that the FQEC results are consistent with previously published full periodic HF and DFT results. This is particularly encouraging since the present approach is computationally much less demanding compared to the periodic HF or DFT methods, thus allowing consideration of crystals with large unit cells such as zeolites. Furthermore, the availability of analytical gradient and Hessian for the AITB method opens many opportunities for the FQEC method in studying reactivity of extended systems. This study so far only provides proof of the concept. More studies however are required to fully access its range of applicability and limitations. Such studies are currently being considered in our lab.

Acknowledgements

This work is supported in part by the Thailand Research Fund, ACS Petroleum Research Fund, the National Science Foundation, and the Science and Technology Higher Education Development Project funded by the MUA-ADB. The computer support from the Center of High Performance Computing at University of Utah is gratefully acknowledged.

References

[1] R.A. van Santen, G.J. Kramer, Chem. Rev. 95 (1995) 637.
[2] C.R.A. Catlow (Ed.), Modeling of Structure and Reactivity in Zeolites, Academic Press, San Diego, 1992.
[3] M. Sierka, J. Sauer, J. Chem. Phys. 112 (2000) 6983.
[4] J.-R. Hill, C.M. Freeman, B. Delley, J. Phys. Chem. A 103 (1999) 3772.
[5] M. Brändle, J. Sauer, J. Chem. Phys. 109 (1998) 10379.
[6] E.H. Teunissen, C. Roetti, C. Pisani, A.J.M. deMan, A.P.J. Jansen, R. Orlando, R.A. vanSanten, R. Dovesi, Model. Sim. Mater. Sci. Eng. 2 (1994) 921.
[7] L. Campana, A. Selloni, J. Weber, A. Pasquarello, I. Papai, A. Goursot, Chem. Phys. Lett. 226 (1994) 245.
[8] Y. Jeanvoine, J.G. Angyan, G. Kresse, J. Hafner, J. Phys. Chem. B 102 (1998) 5573.
[9] R. Shah, J.D. Gale, M.C. Payne, Phase Transitions 61 (1997) 67.
[10] A.V. Larin, D.P. Vercauteren, J. Mol. Catal. A 168 (2001) 123.
[11] M. Sierka, J. Sauer, J. Phys. Chem. B 105 (2001) 1603.
[12] M. Allavena, K. Seiti, E. Kassab, G. Ferenczy, J.G. Angyan, Chem. Phys. Lett. 168 (1990) 461.
[13] M. Brändle, J. Sauer, J. Mol. Catal. A 119 (1997) 19.
[14] T. Bredow, G. Geudtner, K. Jug, J. Chem. Phys. 105 (1996) 6395.
[15] S.P. Greatbanks, P. Sherwood, I.H. Hillier, J. Phys. Chem. 98 (1994) 8134.
[16] C. Pisani, U. Birkenheuer, Int. J. Quantum Chem. S 29 (1995) 221.
[17] E.V. Stefanovich, T.N. Truong, J. Phys. Chem. B 102 (1998) 3018.
[18] N. Govind, Y.A. Wang, A.J.R. da Silva, E.A. Carter, Chem. Phys. Lett. 295 (1998) 129.
[19] E.V. Stefanovich, T.N. Truong, J. Chem. Phys. 104 (1996) 2946.
[20] M. Svensson, S. Humbel, K. Morokuma, J. Chem. Phys. 105 (1996) 3654.
[21] V. Shapovalov, T.N. Truong, J. Phys. Chem. B 104 (2000) 9859.
[22] O.F. Sankey, D.J. Niklewski, Phys. Rev. B 40 (1989) 3979.
[23] J.P. Lewis, K.R. Glaesemann, G.A. Voth, J. Fritsch, A.A. Demkov, J. Ortega, O.F. Sankey, Phys. Rev. B 64 (2001) 195103.
[24] L.J. Smith, A. Davidson, A.K. Cheetham, Catal. Lett. 49 (1997) 143.