

Adsorption of Glycine Amino Acid in Zeolite: An Embedded QM/MM Study

B. Boekfa^{a,b}, J. Sirijaraensre^{a,b}, P. Limtrakul^a, P. Pantu^{a,b} and J. Limtrakul^{a,b*}

^aLaboratory for Computational and Applied Chemistry, Physical Chemistry Division,
Department of Chemistry, Faculty of Science, Kasetsart University, Bangkok 10900, Thailand and

^bCenter of Nanotechnology, Kasetsart University Research and Development Institute,
Bangkok 10900, Thailand

Phone: +66-2-562-5555 ext. 2169, Fax: +66-2-562-5555 ext. 2169

E-mail: jumras.l@ku.ac.th

ABSTRACT

Adsorption of glycine on the acid site of H-ZSM-5 has been studied at an embedded ONIOM (MP2/6-31G(d,p):UFF) level of theory. Four possible modes of adsorptions are considered. The zwitterionic adsorption is the most stable conformation with the highest adsorption energy of -47.22 kcal/mol. The glycine zwitterion is protonated and stabilized by the anionic zeolite framework. The second most stable complex of adsorbed glycine involves the interactions of the protonated amino group and the anionic zeolite surface with the adsorption energy of -33.41 kcal/mol. The next stable glycine/zeolite adsorbs via the carbonyl oxygen of glycine with the adsorption energy of -26.93 kcal/mol. The adsorption, via the glycine OH has the weakest interaction of -21.91 kcal/mol. The influence of the extended zeolite lattice ranges from -5.55 to -8.14 kcal/mol, depending on the modes of interactions. This finding suggests the important role of the zeolite framework as “solid solvent molecules” to stabilize the zwitterionic form of glycine which is normally present in aqueous solution.

Keywords: glycine, H-ZSM-5, zeolite, QM/MM, ONIOM

1 INTRODUCTION

The interactions of amino acids with silica alumina compounds and zeolites have long received great attention since these materials may play an important role in prebiotic chemical evolution [1-3] as catalysts for synthesis of polypeptides, polynucleotides. Smith [4] and Parson et al. [5] have suggested that silica as well as silica-rich zeolites might be responsible for generating the replicating bio-macromolecule which is due to the presence of surface silanol ($\equiv\text{SiOH}$) and surface hydroxyls ($\equiv\text{Si-OH-Al}\equiv$) embedded inside the nanopores of these materials. Zeolites are crystalline aluminosilicate microporous materials with high surface areas. Conventionally, they have important applications in catalysis, adsorption, and chemical separations due mainly to their shape-selectivity and Brønsted acidity [6]. Recently, zeolites have found potential

applications in amino acid separation [7-9], immobilized enzymatic peptide synthesis [10], biomedical sensors [11-12]. Numerous experimental [13-15] and theoretical studies [16-18] have investigated the interactions of biologically active molecules such as amino acids, peptides, proteins, with the surfaces of inorganic materials such as metals, oxides, clays, and zeolites, because this fundamental phenomenon may lead to applications in nanotechnology, biomaterials, and biotechnology processes [19].

Molecular modeling and simulations are important tools in the study of the interactions of probe molecules inside zeolites, providing detailed understanding of the molecular behavior and interactions within the nanocavity of the zeolite pore network. Some types of zeolites consist of a hundred atoms per unit cell; this makes accurate periodic calculation too expensive. Alternatively, hybrid methods, such as the embedded cluster or combined quantum mechanics/molecular mechanics (QM/MM) methods, as well as the more general our-Own-N-layered Integrated molecular Orbital + molecular Mechanics (ONIOM) method [20-21], have brought a larger system within reach and the benefit of obtaining accurate results with much more reasonable computational time [22-23].

In this study, structures, conformations, interactions of an amino acid adsorbed on the zeolite Brønsted acid site have been investigated. Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) is the simplest and smallest among the 20 most common amino acids found in proteins. Glycine is used as a basic adsorption model and is an important starting step for understanding interactions, structures and the reactivity of amino acids and peptides. To the best of our knowledge, the interaction of zeolites with amino acids adsorption has not been considered from a theoretical point of view. Although accurate experimental works on this topic have been reported [24] and a separation process of amino acids based on zeolites was claimed [8], the fundamental of interactions of amino acids with zeolites is still unknown.

2 METHODOLOGY

The 128T nanocluster model of ZSM-5 zeolite which covers the pore network was taken from the lattice structure

of ZSM-5 zeolite [25]. The 12T quantum cluster model, covering the 10-membered-ring window at the zigzag nanochannel of the structure, was treated at the 6-31G(d,p) level of theory while the rest of the framework, which is a main contribution of the van der Waals interaction, was carefully calibrated and represented by the universal force field (UFF). The Brønsted acid 5T cluster and the interacting probe molecule were allowed to relax while the rest was fixed along to the crystallographic coordinate [25].

In order to derive the full description of the adsorption properties of amino acids in nanopores of zeolites, it is necessary to take into account the long range interactions of the infinite zeolitic lattice, which is important for adsorption-desorption in zeolites [22-23, 26-29]. The Madelung potential from the zeolite lattice beyond the 12T quantum cluster was introduced by employing the newly developed approach called “embedded ONIOM2” which has previously been successfully employed [26-27]. This model is subdivided into three parts. The inner part is a 12-tetrahedral (12T) quantum cluster representing the active reaction center. The second part is the universal force field accounting for the confinement effect of the zeolitic pore. The outermost part of the model is a set of optimized point charges representing the remaining Madelung potential generated from the infinite zeolite lattice. In order to achieve more reliable adsorption energies, the single point energy calculated at MP2/6-31G(d,p):UFF//B3LYP/6-31G(d,p):UFF corrected for the basis set superposition errors (BSSE) is carried out.

3 RESULTS AND DISCUSSION

3.1 Structures of glycine adsorption complexes

Figures 1-4 illustrate the four possible structures of glycine adsorbed on H-ZSM-5 via, (i) the amino group, (ii) the carbonyl oxygen of the carboxylic group, (iii) the hydroxyl (-OH) of carboxylic group and (iv) the carboxylate ion of glycine zwitterion. The ONIOM (MP2/6-31G (d, p): UFF) energies of adsorption with the embedded charges are calculated on the structure of ONIOM (B3LYP/6-31G (d, p): UFF) and gives interaction energies with BSSE as shown in Table 1.

	amino group	carbonyl group	hydroxyl group	carboxylic group
QM	-27.85	-19.95	-13.77	-40.47
UFF	-5.55	-6.98	-8.14	-6.75
ΔE_{ads}	-33.41	-26.93	-21.91	-47.22

Table 1: The adsorption energy, ΔE_{ads} , of glycine/zeolite complexes, (kcal/mol)

The neutral form of glycine is adsorbed in its most stable conformation via the interactions of its amino group with the zeolite Brønsted acid (Fig. 1). Upon the adsorption, the Brønsted acid protonates to the amino group as indicated by the break of the acidic O1-Hz bond (1.863 Å) and the formation of the N-Hz bond (1.046 Å). The protonation of the amino group generates the ion-pair adduct with two hetero-hydrogen bonds (N-H---O) and one homo-hydrogen bond (O-H---O). The two hydrogen bonds (N-Hz---O1 and N-H4---O2) are computed to be 2.735 and 2.692 Å, respectively. The N-Hz and N-H4 bonds have virtually equal distances (1.046 and 1.050 Å) which indicate the complete proton transfer to the glycine amino group. The Al-O1 and Al-O2 distances are very close (1.688 and 1.698 Å) and also close to that found for the average of four Al-O bonds, $\langle \text{Al-O} \rangle$, of 1.682 Å. The hydroxyl (O4-H1) of carboxylic group of glycine is lengthened (from 0.972 to 1.006 Å) as it interacts with the nearby bridging oxygen (O5) of the zeolite. The O4-H1---O5 hydrogen bond distance is 2.605 Å. The adsorption energy of the glycine cation $[\text{H}_2\text{NH}_2\text{CH}_2\text{COOH}]^+$ binding with three H-bonds toward the anionic zeolite is calculated to be -33.41 kcal/mol. This value is comparable to the adsorption of the ammonia/zeolite complex (-34.5 to -39.5 kcal/mol) [30].

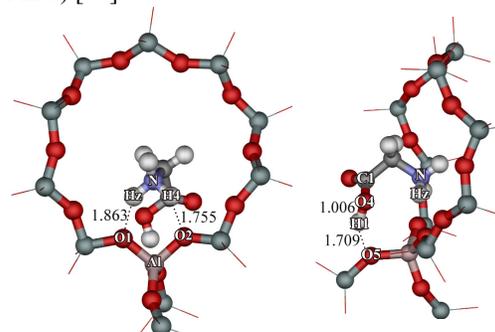


Figure 1: The glycine adsorbs on H-ZSM-5 via amino group of glycine (bond length in Å)

The second most stable conformation of the adsorption of glycine in its neutral form is the complex where the glycine carbonyl group interacts with the zeolite Brønsted acid (Fig. 2). The glycine molecule interacts with O1-Hz of H-ZSM via the carbonyl oxygen of the carboxylic group forming a cyclic double hydrogen bonded structure. The carbonyl C=O act as an H-bond acceptor whereas the zeolite Brønsted acid O1Hz group is an H-bonded donor. Two homo-hydrogen bonds are formed. The zeolite Brønsted O1-Hz is lengthened by 0.077 Å while the acidic hydroxyl group of glycine, O4-H1, is lengthened by 0.023 Å. The corresponding hydrogen bond distances are O1-Hz---O3 ($r = 2.509$ Å) and O4-H1---O2 ($r = 2.746$ Å). The adsorption energy of this adsorbed conformation is -26.93 kcal/mol which is reasonably comparable to the adsorption energy of the acetone/ZSM-5 complex of -31.2 kcal/mol [31].

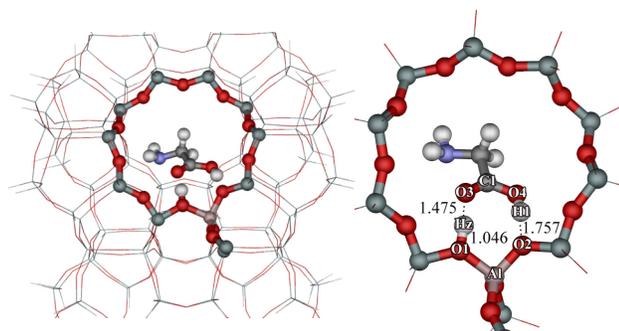


Figure 2: The glycine adsorbs on H-ZSM-5 via carbonyl group of glycine (bond length in Å)

The glycine molecule can also adsorb via interactions of its hydroxyl (-OH) of the carboxylic group and the zeolite acid site (Fig. 3). The interactions of the oxygen atom (O4) of glycine OH moiety with the Brønsted acid of zeolite yield two hydrogen bonds (O1-Hz---O4 and O4-H1---O2). The acidic proton of zeolite, O1-Hz, is slightly elongated by about 0.03 Å. This indicates that the interaction of the Brønsted acid of zeolite with the glycine hydroxyl group is not as strong as the interaction with the glycine carbonyl oxygen. The hydrogen bond distance (O1-Hz---O4) is 2.665 Å which is significantly longer than the O1-Hz---O3 ($r = 2.509$ Å) in the adsorption via the carbonyl oxygen. Another hydrogen bond distance (O4-H1---O2) is 2.736 Å with the bond angle of 121.5 degree which is also a rather weak hydrogen bond. The adsorption energy of this complex is calculated to be -21.9 kcal/mol.

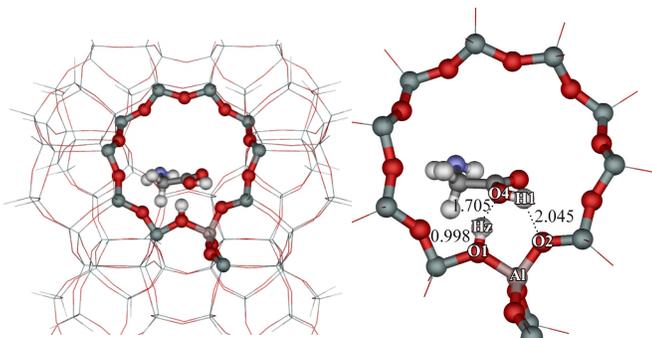


Figure 3: The glycine adsorbs on H-ZSM-5 via hydroxyl group of glycine (bond length in Å)

In aqueous solution, glycine is mostly present in a zwitterionic form in a neutral or slightly acidic or slightly basic solution. Therefore, the adsorption of the glycine zwitterionic form on the acid site of zeolite is considered as one of the possible conformations of the adsorption complexes. In this study, the glycine zwitterion is stabilized by the zeolite framework which acts as “counter ions” or “solid solvent molecules”. Upon the adsorption, the acidic proton of zeolite is completely transferred to the oxygen (O4) atom of the carboxylate group of the zwitterions molecule and a strong hydrogen bond toward the anionic zeolite is formed. The hydrogen bond O4-Hz---O1 has a

distance of 2.429 Å and an almost linear hydrogen-bonded angle of 176.5 degrees. The short hydrogen-bonded distance and linear hydrogen-bonded angle found in the zwitterions/zeolite adduct implies a much stronger hydrogen bond than their corresponding interaction of the carboxyl-bound complex of neutral glycine. Indeed, the adsorption energy of this complex is calculated to be -47.2 kcal/mol which is the highest among these four possible conformations.

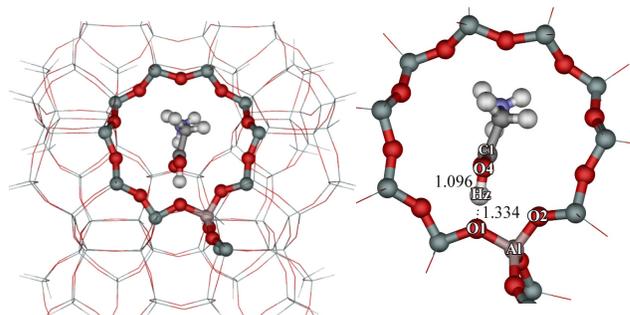


Figure 4: The glycine adsorbs on H-ZSM-5 via carboxylate ion of glycine zwitterions (bond length in Å)

3.2 Energetics of glycine adsorption complexes

Table 1 summarizes the adsorption energies of the four possible adsorption complexes considered in this study. The adsorption energy obtained from the ONIOM calculation can be partitioned into (i) the interaction energy of the adsorbate and the acid site at the quantum region and (ii) the interaction energy of the adsorbate with the extended framework of the zeolite which is modeled by the UFF force field. The interactions of the acid site and the glycine amino acid are the main contribution to the overall adsorption energies. The ion-pair interactions of the protonated zwitterions and the anionic zeolite cluster yield the strongest interaction. The ion-pair interactions of the protonated glycine and the anionic zeolite cluster also yield significantly higher interaction energy than those of the hydrogen bond complexes. The influence of the extended zeolite lattice ranges from -5.55 kcal/mol up to -8.14 kcal/mol or accounts for 14-37% of the overall adsorption energies, depending on the modes of interactions.

From the energetic point of view, the most stable and, thus, the most favorable adsorption conformation is the zwitterionic form which is the agreement with the experimental observation of the adsorption of glycine aqueous solution on silica [15] that glycine was specifically adsorbed in the form of zwitterions at the low loading condition and that the zwitterions were also predominant in the high loading where precipitation of glycine took place. Whereas, in the theoretical calculation of glycine adsorption on isolated hydroxyl groups at the silica surface zwitterions were not found at the low loading condition [17]. This finding suggests the important role of the zeolite framework as “solid solvent molecules.”

4 CONCLUSIONS

The adsorption of neutral and zwitterionic forms of glycine have been carried out at an embedded ONIOM(MP2/6-31G(d,p):UFF) level of theory. Four possible configurations involving the H-bond formation between glycine and its zwitterionic form with H-ZSM-5 have been reported.

For the neutral form, one of the favorable H-bondings of glycine with zeolite occurs via the amino and the acid OH groups which lead to an ion-pair formation having a six-membered-ring structure in which the amino group acts as a proton acceptor whereas the acidic proton of zeolite is a proton donor ($\Delta E = -33.41$ kcal/mol). Two other modes of interactions for the neutral glycine are: a mode of hydrogen bonding of COOH moiety (via C=O) interacted with the active region of zeolite which has been observed to be -26.93 kcal/mol, while another interaction occurs via glycine OH with zeolite, the adsorption energy ΔE , being -21.91 kcal/mol.

The most favorable modes of interaction occur through the zwitterionic form of glycine. The complete proton transfer from zeolite to the carboxylate group of zwitterion is obtained leading to an increased adsorption energy ($\Delta E = -47.22$ kcal/mol). It is important to note that the zwitterionic form of glycine is not observed in the gas-phase. Our findings demonstrate that the zwitterion of amino acid is stabilized by cooperatively building up hydrogen bonding within the zeolitic framework, which is in line with those found in solvent molecules and/or in counter ions.

ACKNOWLEDGMENTS

This work was supported in part by grants from the Thailand Research Fund (TRF Senior Research Scholar to J.L.) and the Kasetsart University Research and Development Institute (KURDI) as well as the Ministry of University Affairs under the Science and Technology Higher Education Development Project (MUA-ADB funds). Support from the National Nanotechnology Center of the National Science Technology Development Agency is also acknowledged.

REFERENCES

- [1] J. D. Bernal, *The Physical Basis of Life*. 1951.
- [2] M. Rao, D. G. Odom and J. Oro, *J. Mol. Evol.*, 15, 317, 1980.
- [3] L. E. Orgel, *Origins Life Evol. Biosphere*, 28, 227, 1998.
- [4] J. V. Smith, *Proc. Natl. Acad. Sci. U.S.A.*, 95, 3370, 1998.
- [5] I. Parson, M. R. Lee, J. V. Smith, *Proc. Natl. Acad. Sci. U.S.A.*, 95, 15173, 1998.
- [6] A. Corma and H. Garcia, *Chem. Rev.*, 103, 4307, 2003.
- [7] J. E. Krohn and M. Tsapatsis, *Langmuir*, 21, 8743, 2005.
- [8] S. Yonsel, W. Schaefer-Treffendorf, A. Kiss, E. Sextl and H. Naujok, DE Patent, 4217203, 1993.
- [9] S. Munsch, M. Hartmann and S. Ernst, *Chem. Comm.*, 1978, 2001.
- [10] G.-W. Xing, X.-W. Li, G.-L. Tian and Y.-H. Ye, *Tetrahedron*, 56, 3517, 2000.
- [11] Y. Cui, Q. Wei, H. Park and C. M. Lieber, *Science*, 293, 1289, 2001.
- [12] J. Kong, N. R. Franklin, C. Zhou, M. G. Chapline, S. Peng, K. Cho and H. Dault, *Science*, 287, 622, 2000.
- [13] G. Tzvetkov, G. Koller, Y. Zubavichus, O. Fuchs, M. B. Casu, C. Heske, E. Umbach, M. Grunze, M. G. Ramsey and F. P. Netzer, *Langmuir*, 20, 10551, 2004.
- [14] S. M. Barlow, K. J. Kitching, S. Haq and N. V. Richardson, *Surface Science*, 401, 322, 1998.
- [15] M. Meng, L. Stievano and J.-F. Lambert, *Langmuir*, 20, 914, 2004.
- [16] A. J. A. Aquino, D. Tunega, M. H. Gerzabek and H. Lischka, *J. Phys. Chem. B*, 108, 10120, 2004.
- [17] A. Rimola, M. Sodupe, S. Tosoni, B. Civalleri and P. Ugliengo, *Langmuir*, 22, 6593, 2006.
- [18] A. Rimola, S. Tosoni, M. Sodupe and P. Ugliengo, *ChemPhysChem*, 7, 157, 2006.
- [19] J. J. Gray, *Curr. Opin. Chem. Biol.*, 14, 110, 2004.
- [20] M. Svensson, S. Humbel, R. D. J. Froese, T. Matsubara, S. Sieber and K. Morokuma, *J. Phys. Chem.*, 100, 19357, 1996.
- [21] S. Dapprich, I. Komiro, K. S. Byun, K. Morokuma and M. J. Frisch, *Theochem*, 461-462, 1, 1999.
- [22] S. Namuangruk, P. Khongpracha, P. Pantu and J. Limtrakul, *J. Phys. Chem. B*, 110, 25950, 2006.
- [23] S. Kasuriya, S. Namuangruk, P. Treesukol, M. Tirtowidjojo and J. Limtrakul, *J. Catal.*, 219, 320, 2003.
- [24] V. A. Basiuk, "Adsorption of Biomolecules at Silica. In *Encyclopedia of Surface and Colloid Science*," Marcel Dekker, 277, 2002.
- [25] H. Van Koningsveld, H. Van Bekkum and J. C. Jansen, *Acta Crystallogr. B*, B43, 127, 1987.
- [26] B. Jansang, T. Nanok and J. Limtrakul, *J. Phys. Chem. B*, 110, 12626, 2006.
- [27] W. Panyaburapa, T. Nanok and J. Limtrakul, *J. Phys. Chem. C*, 111, 3433, 2007.
- [28] J. Sirijaraensre, T. N. Truong and J. Limtrakul, *J. Phys. Chem. B*, 109, 12099, 2005.
- [29] V. Dungsrikaew, J. Limtrakul, K. Hermansson and M. Probst, *Int. J. Quantum Chem.*, 96, 17, 2003.
- [30] D. J. Parrillo and R. J. Gorte, *J. Phys. Chem.*, 97, 8786, 1993.
- [31] J. Sepa, C. Lee, R. J. Gorte, D. White, E. Kassab, E. M. Evleth, H. Jessri and M. Allavena, *J. Phys. Chem.*, 100, 18515, 1996.