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Energetics of Zn^{2+} adsorption in silicate MEL-type nanoporous material

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Abstract

Density-functional-based and ab initio calculations were implemented at different computational levels to estimate the binding energy of Zn^{2+} ion adsorbed on the available sites of a silicate MEL-type adsorbent. B3LYP and MP2 were used in combination with the 6-31G*, 6-31+G*, LanL2DZ, 6-311+G*, and Def2-TZVP basis sets. The zinc cation was found to preferentially occupy the 6MR sites followed by the cage-like positions. Nevertheles, all of the available sites exhibited negative amounts for the Gibbs free energy and enthalpy of adsorption with the corresponding population-averaged values of –160.84 and –169.53 kcal/molat the B3LYP/Def2-TZVP level. Overall, the B3LYP/LanL2DZ method illustrated the highest deviation from the others both in trends and absolute values of binding energy. While the absolute binding energy ranged from 131.23 to 230.79 kcal/mol over different sites, the population-averaged binding energies altered from 146.08 to 162.54 kcal/mol depending on the method employed.

Keywords: Zinc; silicalite-2; MEL-type nanoporous material; DFT; adsorption; binding energetics.

Introduction

Removal of heavy metal ions from wastewater [1-8] is a global concern from eco-friendly, health, and economic points of view. Metals such as Pb, Hg, Cd, As, Cr, Zn, Cu, and Mn are often classified as potentially hazardous elements when present in aquatic environment due to their toxicity to higher-life creatures and non-biodegradable nature [1, 3]. Examples of their hazard to human health include diseases like itai-itai disease (mass Cd poisoning), As and Cd induced cancer, mutations and genetic damage due to Hg, brain and bone damage by Cu, Pb, and Hg, and lead poisoning [1, 3].

Adsorption properties of Zn^{2+}cations on different clays, zeolites, silicates, and high-silica materials have been explored in the literature both experimentally and theoretically [7-27]. Hydrous oxides of aluminum and silicon in general, and clays and zeolite minerals in particular, may contribute

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to the adsorption potential of a soil or sediment [28]. Recently [10], we have investigated the available sites of the nanoporous material silicalite-2 (all-silica MEL-type zeolite) for adsorption of a substrate such as Zn^{2+}cations. This work aims at quantifying the binding energy of Zn^{2+}cations in the all-silica MEL structure at some different computational levels. To the best of our knowledge, there is no or at most rare detailed energetic data for this system.

Methods

The computational method used in this study was similar to that employed in our previous paper [10]. All terminal bonds of the cluster models were saturated by H atoms in compliance with the crystallographic data for all-silica MEL-type structure [29]. Gaussian 98 quantum mechanical software package [30] was employed for the calculations. The geometry optimizations were performed by using the hybrid functional B3LYP [31-33] and the *ab initio* MP2 [34-35] methods. Four basis sets were applied in combination with these methods including 6-31+G* [36-39], 6-311+G* [38-41], LanL2DZ [42-45], and Def2-TZVP basis set [46-48]. An estimation of the adhesion or binding energy ΔE_b of Zn^{2+} was made according to the following equation:

$$\Delta E_{\mathrm{b}} = E_{\mathrm{ZnS2}} - (E_{\mathrm{Zn}} + E_{\mathrm{S2}})$$

where symbols E_{Zn}, E_{S2} and E_{ZnS2} refer to the energies of Zn^{2+}, silicalite-2 model site, and cation plus silicalite-2, respectively.

Results and discussion

Different plausible sites for adsorption of a substrate in the nanoporous network of silicalite-2 have been shown in Figure 1 which include an intersection site I, ring sites M1, M2, M3, and M4 located in the main channels with an increasing number of T atoms from left to right, and cage-like location C that resembles a curved six-ring site inside the walls of silicalite-2. Hence, that the size of the investigated sites alters from T5 to T10.

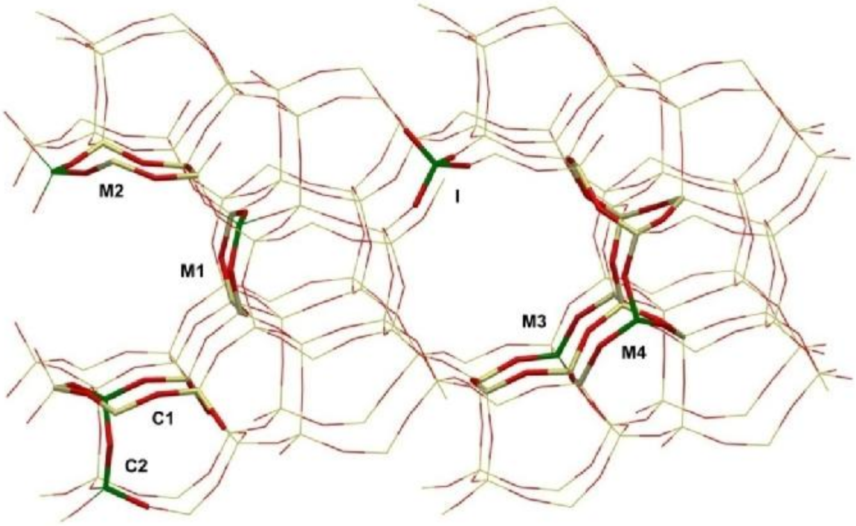

Figure 1. The available sites for the placement of the Zn^{2+}cations in the silicate MEL-type material viewed at the (010) layer [10]

Table 1. Zinc ion binding energies calculated for Zn/silicalite-2 system at different computational levels (kcal/mol).

		Methods				
Adsorption Sites	**Population Percentage**	**B3LYP/ 6-311+G***	**B3LYP/ LanL2DZ**	**B3LYP/ Def2-TZVP**	**B3LYP/ 6-31+G***	**MP2/ 6-31G***
I	48.1	–142.22	–143.37	–141.40	–145.84	–131.23
M1	11.1	–155.11	–132.90	–156.53	–161.89	–143.92
M2	14.8	–187.49	–143.41	–192.86	–195.22	–200.13
M3	7.4	–218.85	–191.13	–222.86	–224.82	–230.97
M4	7.4	–186.95	–161.20	–189.89	–194.81	–195.81
C	11.1	–195.79	–147.11	–203.99	–206.84	–210.12
Overall [a]	100	–165.30	–147.49	–167.29	–171.19	–163.78

[a] assuming a uniform monolayer coverage

Table 1 reports the binding energy for the investigated clusters at different computational levels. As can be seen, the adsorption (binding) of Zn^{2+} ion is expected to be exothermic on all of the sites by all of the methods. Moreover, the binding energies all fall into the range of a chemical adsorption. At most, the binding energy altered from –230.79 to –131.23 kcal/mol, respectively, for M3 and I adsorption complexes, both calculated with the MP2/6-31G* method. Except for the B3LYP/LanL2DZ level of theory, the sequence of the thermodynamic privilege for this binding is M3 > C > M2 > M4 > M1 > I with all of the methods employed. The most thermodynamically favored adsorption to occur is hence the six-membered ring M3 site, which is also more convenient to access by the cations when compared to the cage-like C site.

The overall behavior of the solid matrix can be estimated from the individual site-based data provided that the population of every site is known. Assuming a uniform monolayer coverage, the overall population-based behavior of the adsorbent demonstrates an absolute value of binding energy ranging from 147.49 to 171.19 kcal/mol following the sequence of B3LYP/LanL2DZ < MP2/6-31G* < B3LYP/6-311+G* < B3LYP/Def2-TZVP < B3LYP/6-31+G* with that of B3LYP/LanL2DZ deviating much more largely from the rest of the methods. Table 1 also shows that the average behavior is closest to the energy on M1 for all of the methods except B3LYP/LanL2DZ in which the overall binding energy is close to that on the C site. An interesting observation in Table 1 is that the B3LYP/Def2-TZVP method which involves a valence triple-zeta plus polarization TZVP basis set and the B3LYP/6-31+G* method which incorporates a valence double-zeta polarized basis set predict very similar energetic data in terms of both magnitudes and trends. Comparing the results of the ab initio Hartree-Fock calculation method of MP2/6-31G* against those of B3LYP/6-31+G* in Figure 2, however, one can see that the former predicts lower binding energies on I and M1 sites and slightly higher energies on the rest of the sites, so that the average binding energy will be lower. This difference should be mainly attributed to the level of functional/theory used in the methods and also to the absence of the diffuse function in the basis set employed in the former case.

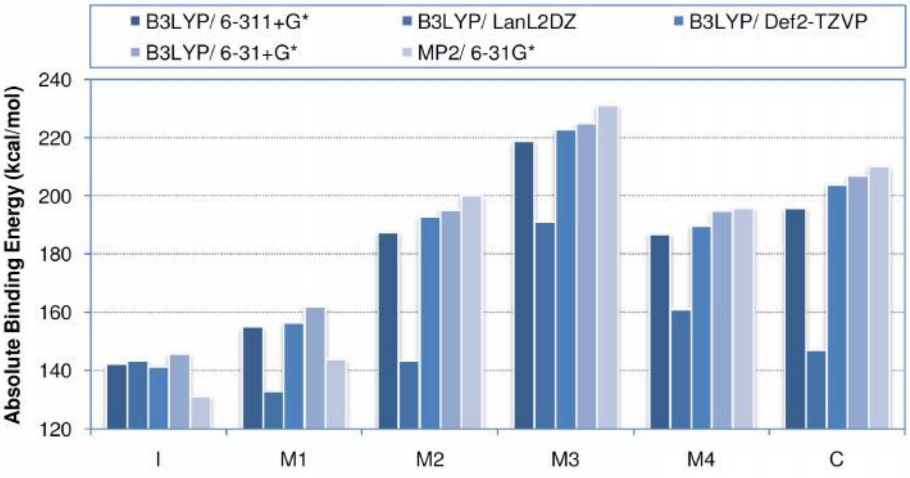

Figure 2. Absolute of binding energies predicted by different methods

Table 2 demonstrates the energetics of Zn^{2+} in silicalite-2 from a thermodynamics point of view. As evinced by the negative sign of the Gibbs free energy change and the enthalpy change on adsorption, the adsorption of zinc ions onto the available sites of silicalite-2 would be spontaneously favorable. The trends of both the Gibbs free energy and enthalpy were almost the same with the two methods such that the lower the Gibbs free energy (ΔG_b), the more negative the enthalpy of the reaction (ΔH_b). As such, both of the methods suggest that the M3 and I clusters are the most and least favorable sites to form, respectively. Moreover, the trends of the thermodynamic data were similar to those of the binding energy for the two methods. At the B3LYP/Def2-TZVP level of theory, the enthalpy of adsorption was found to vary from–144.50to –224.66 kcal/mol according to the sequence of I>M1> M4 ~ M2 > C > M3. Interestingly, the enthalpies of adsorption fall into the chemisorption range. In addition, the Gibbs free energy ranges from –136.70 to –213.43 kcal/mol. Obviously, negative entropies of adsorption are manifested by the difference of the Gibbs free energy and enthalpy of adsorption which is the largest at M3 and the lowest at the I location. It is also notable from Table 2 that the average enthalpy and Gibbs free energy change of adsorption using the B3LYP/Def2-TZVP method are –169.53 and –160.84 kcal/mol, respectively, which are closest to the values on M1 location.

Table 2. Gibbs free energy (ΔG_b) and enthalpy of binding(ΔH_b) for a Zn/silicalite-2 system (kcal/mol)

Adsorption Sites	**B3LYP/6-311+G***		**B3LYP/Def2-TZVP**	
	ΔH_b	ΔG_b	ΔH_b	ΔG_b
I	–146.56	–138.84	–144.50	–136.70
M1	–159.25	–148.37	–160.79	–150.97
M2	–187.11	–178.65	–192.49	–183.95
M3	–219.82	–208.60	–224.66	–213.43
M4	–189.32	–176.35	–191.12	–182.89
C	–195.52	–187.12	–205.01	–194.76
Overall [a]	–168.01	–159.11	–169.53	–160.84

[a] see Table 1 for the estimated population of each site.

Also apparent in the results of this study is that the relativistic effective core potential basis set LanL2DZ in combination with B3LYP predicts M1 and M2 as less strongly interacted sites for Zn^{2+} binding when compared to the other methods. In contrast, the intersections (I positions) provide the loosest binding for the adsorbed Zn ion in all of the other cases in agreement with the Gibbs free energy data. Finally, the binding energies and the thermodynamic data reported here cannot be compared against any similar data from the literature because no such information is available to the best of our knowledge for Zn^{2+} deposition over silicate adsorbents.

Conclusion

This paper has investigated energetic properties of Zn^{2+} adsorption complexes with different available sites in a silicate nanoporous MEL-type material through a hybrid density functional and an ab initio method in conjunction with four basis sets. The zinc cation was most favorably adsorbed on M3 sites followed by the C positions. While the B3LYP/Def2-TZVP and B3LYP/6-31+G* methods illustrated very similar data, the B3LYP/LanL2DZ method exhibited the largest deviation from the others both in terms of trends and absolute values of binding energy. The population-averaged binding energies ranged from 146.08 to 162.54 kcal/mol depending on the method employed. All of the sites exhibited negative changes in the Gibbs free energy and enthalpy upon zinc adsorption with the corresponding population-averaged values of –160.84 and –169.53 kcal/mol at the B3LYP/Def2-TZVP level.

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