Binding energy of H₂ to MOF-5: A Model Study

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Binding energy of H₂ to MOF-5: A Model Study

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Using models simulating the environment of two distinct adsorption sites of H_2 in metal-organic framework-5 (MOF-5), binding energies of H_2 to MOF-5 were evaluated at the MP2 and CCSD(T) level. For organic linker section modeled as dilithium 1,4-benzenedicarboxylate ($C_6H_4(COO)_2Li_2$), the MP2 and CCSD(T) basis set limit binding energies are estimated to be 5.1 and 4.4 kJ/mol, respectively. For metal oxide cluster section modeled as $Zn_4O(CO_2H)_6$, while the MP2 basis set limit binding energy estimate amounts to 5.4 kJ/mol, CCSD(T) correction to the MP2 results is shown to be insignificant with basis sets of small size. Substitution of benzene ring with pyrazine ring in the model for the organic linker section in MOF-5 is shown to decrease the H_2 binding energy noticeably at both the MP2 and CCSD(T) level, in contrast to the previous study based on DFT calculation results which manifested substantial increase of H_2 binding energies upon substitution of benzene ring with pyrazine ring in the similar model.

Key Words : MOF-5, Hydrogen adsorption, H_2, Binding energy

Introduction

Since its first synthesis by Yaghi and coworkers,[1] metal-organic framework MOF-5 has drawn a great deal of interests from academic and industrial communities due to its extraordinary storage capacity of hydrogen, becoming one of major candidates for future fuel carrier material. As a result, there have been numerous theoretical and experimental studies to understand the interactions between hydrogen molecules and MOF-5 and improve the storage capacity of IRMOF (isorecticular metal organic framework) class of molecules, especially in high temperature conditions.[2-27] For MOF-5, it has been known from previous studies[8,12,24] that there are two distinct hydrogen adsorption sites, metal (zinc) oxide cluster section and organic BDC (1,4-benzene dicarboxylate) linker section. albeit there are several different adsorption sites in metal (zinc) oxide cluster section (see Fig. 1). Since the interactions between hydrogen molecules and relevant adsorption sites in MOF-5 are mainly weak dispersion interactions, an accurate determination of H_2 binding energy to MOF-5 is a formidable task considering the size of the molecular system involved. Consequently, previous theoretical studies of hydrogen adsorption in MOF-5 often employed DFT (density functional theory) methods[12,15,22,24] or MP2 (second order Moller-Plesset perturbation theory) method.[4-6,13,26] However, even the use of MP2 method would not be sufficient to describe the weak dispersion interaction and high level correlation method would be required to accurately determine the binding energy of H_2 to relevant adsorption sites in MOF-5.

In a series of papers,[4-6] Ganz and coworkers performed a computational study of H_2 adsorption on MOF-5 and similar IRMOF molecules. Based on models representing the major adsorption sites cut from the entire MOF-5 framework, they found that the H_2 binding energy of the zinc oxide cluster section in MOF-5 could be stronger than the organic linker section by about 1.5 kJ/mol at the MP2 level. More recently, Sillar *et al.*,[26] using more sophisticated models for H_2 adsorption sites in MOF-5, reported that the difference between the binding energies of metal oxide cluster section and organic linker section could be larger, being about 2.9 kJ/mol at the MP2 level. The major difference between the former and latter models is that the latter models by Sillar *et al.* employed end groups which simulates the actual enviroment of MOF-5 more closely in their models for H_2 adsorption sites in MOF-5. However, considering weak nature of interactions between a hydrogen molecule and MOF-5, it would be necessary to employ a more sophisticated electron correlation method beyond MP2 method to determine the H_2 binding energy to MOF-5 accurately. Accurate determination of H_2 binding energies to relevant sites in MOF-5 is important to understand the thermochemical properties and isotherm behavior of H_2 adsorption on MOF-5. Employment of high level electron correlation method with appropriate basis set is also important to correctly evaluate the effect of substituting the metal atoms
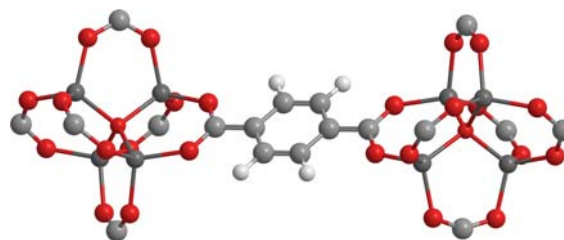

Figure 1. Metal oxide cluster ($Zn_4O(CO_2)_6$) and organic linker (C_6H_4) sections in MOF-5. Metal oxide cluster sections are linked by organic linker in three dimensions to form an entire framework of MOF-5.

or linker molecule to improve the H_2 adsorption capacity of MOF-5. As an example, it will be shown from our high level electrom correlation study results that substittution of benzene ring by pyrazine in the organic linker section of MOF-5 appears to decrease the binding energy of H_2 to the linker section of metal-organic framework, in contrast to the results from previous DFT study on similar systems with different metals. The aim of this paper is to account the effect of higher electron correlation beyond MP2 by evaluating (estimating) the binding energies of H_2 to two distinct sites in MOF-5 at the CCSD(T) (singles and doubles coupled cluster method with perturbative triples correction) level.[28]

Theoretical and Computational Approach

To describe the interactions between the MOF-5 and hydrogen molecules accurately, proper account of weak dispersion attraction between sections of MOF-5 and hydrogen molecules is important, necessiating the use of a high level electron correlation method such as CCSD(T). However, accurate evaluation of binding energy between a single hydrogen molecule and MOF-5 at the CCSD(T) level is a formidable task considering the molecular system involved. Therefore, it is important to employ an effective approach which could yield a reliable estimate to the accurate binding energy of a hydrogen molecule to MOF-5 system from the results of the lower level calculations than the CCSD(T) level without direct calculation of binding energies at the CCSD(T) level.

Let ΔE_{MP2}^{TOT} and $\Delta E_{CCSD(T)}^{TOT}$ represent the total binding energies at the MP2 and CCSD(T) level including the Hartree-Fock contributions, respectively. The CCSD(T) correlation contribution beyond the MP2 level ($\Delta C(T)$) can be defined as follows;

$$\Delta C(T) = \Delta E_{CCSD(T)}^{TOT} - \Delta E_{MP2}^{TOT} \qquad (1)$$

The ratio (β) between MP2 correlation and CCSD(T) correlation contribution beyond the MP2 level is defined as

$$\beta = \Delta C(T)/\Delta E_{MP2}^{CORR} \qquad (2)$$

where ΔE_{MP2}^{CORR} represents the MP2 correlation contribution to the binding energy.

It has been shown[26] that the interactions with H_2 in MOF-5 originate mainly from the local environment around the adsorption site, suggesting that H_2 binding energies to local adsorption sites in MOF-5 could be calculated using the finite models cut from the MOF-5 framework and even a possibility of utilizing a similar system as local adsorption site in MOF-5 for H_2 interaction but with much smaller size than MOF-5. The basic approach adopted in this study is to utilize the relation between the MP2 and CCSD(T) correlation binding energies observed in a similar system as the organic linker section of MOF-5 but of smaller size. It has been suggested[29] that the ratio (β) between the MP2 correlation binding energy contribution (ΔE_{MP2}^{CORR}) and CCSD(T) correlation contribution beyond the MP2 level

($\Delta C(T)$) converges rather fast with basis set, enabling the prediction of this ratio value at the basis set limit from the results with limited basis sets. Therefore, if it could be assumed that these ratios for reference (smaller) model system and MOF-5 local adsorption site environment are similar for H_2 interaction, one would be able to predict the accurate H_2 binding energies to MOF-5 local environment using the ratio β obtained for smaller model system than actual MOF-5 system interacting with a hydrogen molecule. The H_2 binding energy to MOF-5 is obtained according to the following equation.

$$\Delta E_{CCSD(T)}^{TOT}(\infty) = \Delta E_{MP2}^{TOT}(\infty) + \beta_{ref} \times \Delta E_{MP2}^{CORR}(\infty) \qquad (3)$$

where ∞ represents the basis set limit and β_{ref} implies that β value for smaller reference system is to be used in the equation. For H_2 binding to organic linker section in MOF-5, H_2-benzene system and H_2-BDCLi$_2$ (dilithium 1,4-benzene-dicarboxylate) were chosen as the reference model (where β is calculated) and actual model system representing the environment of organic linker section in MOF-5. (where $\Delta E_{MP2}^{TOT}(\infty)$ and $\Delta E_{MP2}^{CORR}(\infty)$ are calculated) were chosen, respectively. The H_2-BDCLi$_2$ system was also adopted as a model for H_2 interaction with the organic linker section in MOF-5 in ref. 4.

For H_2 binding to zinc oxide cluster section in MOF-5, however, it was difficult to choose a simpler reference model system. Therefore, in this case, only MP2 basis set limit binding energy for H_2-Zn$_4$O(CO$_2$H)$_6$, which was also a chosen model for H_2 interaction with metal oxide cluster section in MOF-5 in ref. 4 and 26, was estimated and CCSD(T) correlation effect beyond the MP2 level was evaluated using the results with the 6-31G and 6-31G* basis set. $\Delta E_{MP2}^{CORR}(\infty)$ for H_2-BDCLi$_2$ and H_2-Zn$_4$O(CO$_2$H)$_6$ were estimated from extrapolation of the results with aug'-cc-pVXZ (X=D,T) or aug*-cc-pVXZ basis sets which contained diffuse functions on selected atoms in addition to the cc-pVXZ basis sets.[30,31]

Only valence electrons were correlated in the correlation calculations. All binding energies were computed with the counterpoise correction[32] using Gaussian program package.[33]

Results and Discussion

In Table 1 the ratio for H_2-benzene system is presented along with the corresponding results for H_2-BDCLi$_2$ system as well as H_2 binding energy estimates at the MP2 level for two systems. The geometry of H_2 was optimized at the MP2/6-31++G* level with the fixed BDCLi$_2$ geometry which was obtained from the optimization at the MP2/6-31G* level. In Figure 2 a schematic view of the optimized BDCLi$_2$-H_2 system is presented. H_2 is almost perpendicular to the bezene plane with the distance of about 2.9 Å between the ring center and the H atom closer to the benzene ring. Therefore, for H_2-benzene interaction, the hydrogen molecule was placed perpendicular to benzene ring with a distance of 2.9 Å between the ring center and the H atom closer to the

Table 1. Total and correlation (in parentheses) binding energies (in kJ/mol) of H_2 to benzene and $BDCLi_2$

	H_2-Benzene				H_2-$BDCLi_2$			
Basis set	HF	MP2	CCSD(T)	β^a	HF	MP2	CCSD(T)	β^a
6-31G*	-1.25	0.38(1.63)	-0.10(1.15)	-0.29	-1.52	0.62(2.14)	0.08(1.60)	-0.25
aug-cc-pVDZ	-0.82	4.01(4.83)	3.45(4.27)	-0.12	-1.05	4.42(5.47)	3.79(4.84)	-0.11 $(-0.11)^b$
aug-cc-pVTZ^c	-0.91	4.45(5.36)	3.54(4.45)	-0.11	-1.17	4.79(5.96)		
CBS^d	-0.94^e	$4.81(5.75)^e$	4.18^g		-1.21^f	$5.10(6.31)^f$	4.41^g	

$^a\beta$ is the ratio between $\Delta C(T)$ and ΔE_{MP2}^{CORR} defined in eq. (2). ^{b}Value in parentheses corresponds to β value with aug'-cc-pVDZ basis set (see the text). ^{c}For H_2-$BDCLi_2$, diffuse functions for Li and oxygen were not included in the calculations. ^{d}Basis set limit estimates. ^{e}Basis set limit was obtained from extrapolation of aug-cc-pVDZ and aug-cc-pVTZ results (see the text). ^{f}Basis set limit was obtained from extrapolation of aug'-cc-pVDZ and aug'-cc-pVTZ results (see the text). ^{g}Basis set limit was obtained according to eq. 3 (see the text).

benzene ring. For the benzene-H_2 system, the basis set limit MP2 binding energy was obtained from separate extrapolations of Hartree-Fock and correlation contributions with the aug-cc-pVDZ and aug-cc-pVTZ basis sets[30,31] by $X^{-3.4}$ and $(X+1)^{-3}$ (X=D(2),T(3)) formulas,[34,35] respectively. Similarly, the MP2 basis set limit binding energy for the $BDCLi_2$-H_2 system was obtained from extrapolations of HF and correlation contributions with the aug'-cc-pVDZ and aug'-cc-pVTZ basis sets (which were similar to the aug-cc-pVXZ basis set but did not contain diffuse functions for O and Li atoms in the system) by $X^{-3.4}$ and $(X+1)^{-3}$ (X= D(2),T(3)) formulas, respectively. From the binding energy results in Table 1, it is clear that employment of higher level electron correlation method beyond the HF and even the MP2 level along with proper basis sets is important for correct description of the interaction between a hydrogen molecule and $BDCLi_2$ (as well as benzene) as the HF and MP2 level binding energies are not close to the corresponding CCSD(T) level binding energies. Considering the major contribution to the interaction energies at the HF level would be electrostatic, the negative binding energy at the HF limit well manifests the failure of the electrostatic description of such molecular systems.

Although CCSD(T) calculations for $BDCLi_2$-H_2 system could be performed only with the aug'-cc-pVDZ basis set and aug-cc-pVDZ basis set, the agreement of β values for both basis sets appears to suggest that β value of -0.11 with these basis sets is close to the converged value for $BDCLi_2$-H_2 system. Since the converged β value for benzene-H_2 system also appears to be close to -0.11, β value at the basis set limit for H_2-benzene system could be used to derive the CCSD(T) basis set limit binding energy of the $BDCLi_2$-H_2 system according to eq. (3). If one adopts β value of -0.11

for the estimation of the $BDCLi_2$-H_2 basis set limit binding energy at the CCSD(T) level, application of eq. (3) yields 4.41 kJ/mol of the bais set limit CCSD(T) binding energy for the H_2-$BDCLi_2$ system. Alternatively, one may add the $\Delta C(T)$ value of -0.63 kJ/mol with the aug-cc-pVDZ basis set to the MP2 basis set limit result of 5.10 kJ/mol, which yields 4.47 kJ/mol for the CCSD(T) basis set limit binding energy for the $BDCLi_2$-H_2 interaction. Since $\Delta C(T)$ appears to increase with basis set (in magnitude), this value could be considered as the upper limit and we conclude that the binding energy of a hydrogen molecule to the $BDCLi_2$ would be very close to 4.4 kJ/mol, and, accordingly, hydrogen binding energy to organic linker section in MOF-5 would be close to 4.4 kJ/mol, considering the recent finding that the interaction of H_2 with relevant adsorption site is dominated by the local environment around the adsorption site in MOF-5.[26]

It was suggested from DFT study[15] that presence of nitrogen in the benzene ring would substantially increase the binding energy of H_2 to organic linker section. To investigate the effect of presence of the nitrogen atom in the benzene ring, pyrazine was introduced in $BDCLi_2$, thus forming $PDCLi_2$ (dilithium 1,4-pyrazinedicarboxylate, $C_4N_2H_2(CO_2)_2Li_2$) for interaction with H_2. As in the H_2-$BDCLi_2$ system, H_2 geometry in H_2-$PDCLi_2$ system was optimized at the MP2/6-31++G* level with the fixed $PDCLi_2$ geometry which corresponded to the MP2/6-31G* optimized geometry. The binding energy of H_2 to $PDCLi_2$ was calculated at the MP2 and CCSD(T) level with the aug-cc-pVDZ basis set, which yielded 3.19 and 2.67 kJ/mol, respectively. These results are smaller than the corresponding H_2 binding energies to $BDCLi_2$. by 0.63 and 1.12 kJ/mol, respectively (see Table 1), suggesting presence of nitrogen would decrease H_2 binding to the organic linker section in MOF-5. It is interesting to note that the difference between the H_2 binding energies to $BDCLi_2$ and $PDCLi_2$ is more prominent at the CCSD(T) level. Although previous DFT study explored different metals M other than Li in $PDCM_2$,[15] it appears from our high level correlation results that presence of nitrogen would not enhance H_2 binding to the organic linker section in MOF-5.

In Table 2 binding energies of H_2 to $Zn_4O(HCO_2)_6$ at the MP2 level are presented, which represents a model for metal oxide cluster section in MOF-5. The binding energy was
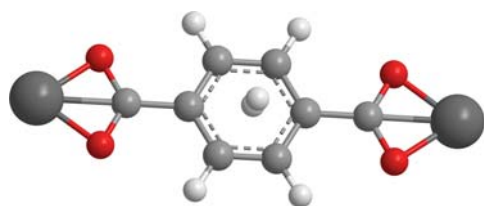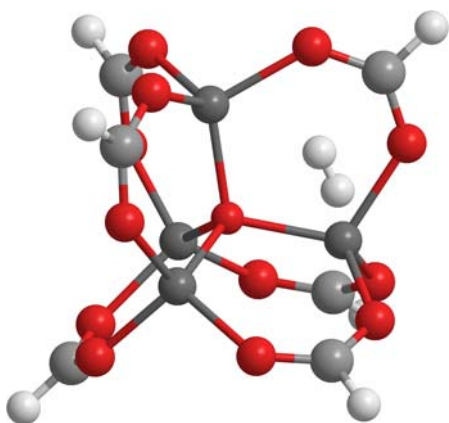

Figure 2. A schematic view of an adsorbed H_2 on $BDCLi_2$ (dilithium 1,4-benzenedicarboxylate). Two lithium atoms are placed at each side of the molecule.

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Table 2. Binding energies (in kJ/mol) of H_2 to $Zn_4O(HCO_2)_6$ at the HF, MP2 and CCSD(T) level

Basis set	HF	MP2	CCSD(T)
6-31G	-2.96	-1.09	-0.96
6-31G[*]	-3.10	-0.33	-0.44
aug[*]-cc-pVDZ[a]	-2.47	3.42(5.89)[b]	
aug[*]-cc-pVTZ[a]	-2.44	4.59(7.03)[b]	
CBS estimate[c]	-2.43[d]	5.43(7.86)[e]	

[a]cc-pVXZ basis set added by extra diffuse functions for Zn and O atoms from the aug-cc-pVXZ basis sets (X=D,T). [b]Values in parentheses represent the coorelation contributions to the binding energy. [c]Basis set limit estimates. [d]Basis set limit was obtained from extrapolation of the aug[*]-cc-pVDZ and aug[*]-cc-pVTZ results by $X^{-3.4}$ (X=D(2),T(3)) (see the text). [e]Basis set limit was obtained from extrapolation of the aug[*]-cc-pVDZ and aug[*]-cc-pVTZ results by $(X+1)^{-3}$ (X=D(2),T(3)) (see the text)

computed at the MP2/6-31G[*] optimized geometry of H_2-$Zn_4O(HCO_2)_6$ system, which is depicted in Figure 3. In Table 3 bond lengths and angles for the model systems are compared to the experimental results for pure MOF-5 with the corresponding bond lengths and angles shown in Figure 4. Although the angle between O(10)-C(1)-O(10) is different from the experimental value by more than 4^0 (4.6^0) in case of BDCLi$_2$ where Li replaced the metal cluster section in MOF-5, other geometrical parameter values for the model systems appear to be in good agreement with the experimental values, exhibiting the similarity of the model systems to the local environments of the MOF-5. The basis set limit Hartree-Fock and MP2 correlation contributions to the binding energies were estimated by extrapolating the corresponding HF and correlation contributions with the aug[*]-cc-pVDZ and aug[*]-cc-pVTZ basis sets by $X^{-3.4}$ and $(X+1)^{-3}$ formulas (X=2 for DZ, 3 for TZ), respectively. The aug[*]-cc-pVXZ basis sets contain extra diffusion functions for Zn and O atoms in addition to the cc-pVXZ basis sets (X=D,T). As in the case of H_2-BDCLi$_2$ interaction, the negative binding energies at the HF level well manifest the importance of employing high level correlation method along with proper basis set for this system.

Comparison of the MP2 results in Table 1 and Table 2

Figure 3. A schematic view of an adsorbed H_2 on Zn_4O-$(CO_2H)_6$. Zn_4O core is represented by a tetrahedron at the center of the molecule.

Table 3. Bond length and angle values for model systems

Bond lengths (Å)/ Bond angles (°)	$Zn_4O(HCO_2)_6$	BDCLi$_2$	Exp.[b]
Zn(23)-O(11)[a]	1.96 Å		1.92 Å
Zn(23)-O(16)	1.95 Å		1.94 Å
C(3)-O(16)	1.27 Å	1.28 Å	1.30 Å
C(3)-C(9)		1.49 Å	1.49 Å
C(5)-C(9)		1.40 Å	1.39 Å
C(5)-H(24)		1.09 Å	1.10 Å
Zn(22)-O(11)-Zn(23)	107.3°		109.5°
O(11)-Zn(23)-O(16)	111.7°		112.6°
O(15)-Zn(23)-O(16)	107.0°		106.2°
Zn(23)-O(16)-C(3)	129.6°		129.5°
O(16)-C(3)-O(17)	128.0°	121.8°	126.4°
O(16)-C(3)-C(9)		119.1°	116.8°

[a]The numbers in parentheses represent the numbers for the corresponding atoms in Fig. 4. [b]Ref. 2.

shows that H_2 appears to bind more strongly to zinc oxide cluster section than organic linker section in MOF-5 as expected. Since direct calculations at the CCSD(T) level with large basis sets are computationally too demanding for this complex, CCSD(T) correction to the MP2 level result was made only with the 6-31G and 6-31G[*] basis set, which showed only ~0.1 kJ/mol change (increase for 6-31G and decrease for 6-31G[*]) of MP2 binding energy at the CCSD(T) level. Recently Sillar *et al.* also reported 0.06 kJ/mol increase of H_2 binding energy to $Zn_4O(CO_2H)_6$ from the MP2 to the CCSD(T) level with the cc-pVDZ basis set.[26] They also reported that substitution of end hydrogen in Zn_4O-$(CO_2H)_6$ with phenyl (-C_6H_5, Ph) ring increased the H_2 binding energy by about 2 kJ/mol at the MP2 level. This would give the MP2 basis set limit binding energy estimate of more than 7 kJ/mol for H_2-$Zn_4O(CO_2Ph)_6$ interaction. Thus, the H_2 binding energy difference between the linker and metal oxide cluster section in MOF-5 appears to be more than 2 kJ/mol at the MP2 level. With regard to accurate evaluation of H_2 binding energy to the metal oxide cluster section in MOF-5, although it cannot be precluded that a large basis set calculation close to the basis set limit at the CCSD(T) level could decrease the corresponding MP2 level H_2 binding energy to $Zn_4O(CO_2H)_6$ (or $Zn_4O(CO_2Ph)_6$)
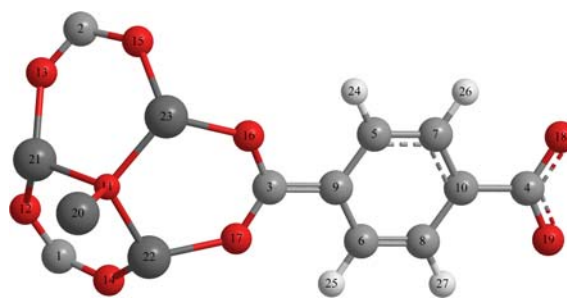
Figure 4. Part of the metal core and BDC linker section in MOF-5. Atoms are represented by numbers. carbon: 1-10, oxygen: 11-19, Zn: 20-23, hydrogen: 24-27.

noticeably, in view of the CCSD(T) results with smaller basis sets and recent finding that H_2 binding energy for similar system to $Zn_4O(CO_2H)_6$ increased at the CCSD(T) level compared to the MP2 level with the aug-cc-pVDZ basis set,[26] there is a possibility the H_2 binding energy to zinc oxide cluster section in MOF-5 would be close to 7.4 kJ/mol or even larger. In such case, the difference in H_2 binding energies between the two sites in MOF-5 would be close to 3 kJ/mol or larger. These estimates are not expected to change noticeably upon inclusion of vibrational contributions as the zero point vibrational energies of H_2 at both sites were shown to make similar contributions to the electronic binding energies.[26]

Summary

In this paper, using models representing the H_2 adsorption sites in MOF-5 and employing high level ab initio CCSD(T) method, we focused on accurate evaluation of H_2 binding energy to two distinct adsorption sites, organic linker section and metal oxide cluster section, in MOF-5. For organic linker section which was modeled as 1,4-benzene dicarboxylate lithium (Li-O_2C-C_6H_4-CO_2-Li), H_2 basis set limit binding energy estimate at the CCSD(T) level amounts to about 4.4 kJ/mol. For metal oxide cluster section which was modeled as $Zn_4O(CO_2H)_6$, while the MP2 basis set limit binding energy of H_2 was estimated to be 5.4 kJ/mol from basis set extrapolation, CCSD(T) calculations with relatively small basis sets such as 6-31G or 6-31G* showed negligible change from the corresponding MP2 binding energies of H_2. If this tendency of negligible difference between the MP2 and CCSD(T) binding energies also holds true for large basis set calculations, the binding energy of H_2 to metal oxide cluster section in MOF-5 could be expected to be close to 5.4 kJ/mol. However, if one adopts $Zn_4O(CO_2C_6H_5)_6$ as a model for metal oxide cluster section in MOF-5 (which would be more similar to the actual environment in MOF-5 than $Zn_4O(CO_2H)_6$), H_2 binding energy to metal oxide cluster section in MOF-5 could be more than 7 kJ/mol as the substitution of hydrogen with phenyl group in $Zn_4O(CO_2H)_6$ was shown to increase the H_2 binding energy by about 2 kJ/mol at the MP2 level.[14] Therefore, it appears that the metal oxide cluster section could bind the H_2 molecule more strongly than the organic linker section by about 3 kJ/mol as long as the CCSD(T) binding energy of H_2 near the basis set limit for metal oxide cluster section does not decrease the corresponding MP2 results significantly. Although accurate estimate of large basis set effect at the CCSD(T) level on H_2 adsorption affinity to metal oxide cluster section in MOF-5 cannot be made at the present time, increase of basis set in similar but smaller H_2-$Zn_3O(CO_2H)_3OH$) system than H_2-$Zn_4O(CO_2H)_6$ system appears to increase the binding energy of H_2 at the CCSD(T) level,[26] suggesting that the difference in binding energies of H_2 to the metal oxide cluster and organic linker section in MOF-5 could be larger than 3 kJ/mol. This result also appears to be in accord with the previous neutron powder diffraction study which found the metal oxide cluster as the primary adsorption site while organic linker only plays a secondary role for the hydrogen adsorption in MOF-5.[8]

We also found that presence of nitrogen in the benzene ring would decrease the H_2 binding energy to the organic linker section in MOF-5, which is in contrast to the previous prediction based on DFT calculations. This finding, along with the accurate estimate to the H_2 binding affinity to the organic linker section and metal oxide cluster section in MOF-5 using ab initio methods, illustrates the danger in relying on results based on DFT methods in cases where weak dispersion attraction is a dominant interaction force and illuminates the utility of the methodology employed in this study in such cases.

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