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Adsorption of dihydroxybenzenes inside the UiO-66-SO_3H, UiO-66 and defect-UiO-66 Metal Organic Framework: An ONIOM study

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Abstract The confinement effect on the adsorption of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on the UiO-66 Metal Organic Framework (MOF), has been investigated by a multi-layered chemistry calculation approach called our own n-layered integrated molecular orbital and molecular mechanics (ONIOM). The effect of two Brønsted acid sites of the UiO-66-SO_3H and UiO-66 MOF has been studied together with the effect of the Lewis acid site at the defected UiO-66 MOF. The high level calculation area covered a reactive site which included a functionalized benzene sulfonic group with two metal-oxide clusters. This area was calculated through M06-L/6-31G(d,p)+LANL2DZ method. The low level area was the outer six metal-oxide clusters which were treated with PM6 semi-empirical method of calculation. To improve the adsorption energies, the overall optimized structures from the ONIOM were recalculated using single point energy calculations using ONIOM(M06-L/6-311+G(2df,2p)+LANL2DZ:M06-L/LANL2DZ). Dihydroxybenzene molecule adsorbed inside the pore via a hydrogen bond between hydroxyl group and acid sites of MOF. The strong interactions were found more on the Lewis acid site than on the Brønsted acid sites. Natural bond orbital analysis indicated that electrons from ion pair of hydroxyl group transfer to the antibonding orbital of the Brønsted acid while electrons from Lewis acid site Zr-O bond transfer to the hydroxyl group of dihydroxybenzene. This data is able to reflect tendency in diffusion coefficients which corresponded to chemical reactions for dihydroxybenzene and its derivatives.

MSC: 03C57; 81V70; 82M36

Keywords: UiO-66-SO_3H; defect-UiO-66; Metal Organic Framework; dihydroxybenzenes; ONIOM, M06-L

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INTRODUCTION

Over the past decades, the development of catalysts for fuel storage materials has been intensively studied, for example, selective separations and chemical catalysts. [1-3] Several Metal-Organic Frameworks (MOFs) have been designed to obtain large pore volumes with high catalytic activity and stability. Their structures are composed of various inorganic metal clusters such as Fe, Cu, Cr and Zr connected together with organic linkers. Among these materials, Zr-based MOFs have been intensively studied due to their catalytic performance and corrosion resistant. UiO-66 is one of the Zr MOFs family which includes a $Zr_6O_4(OH)_4$ octahedron unit connected to12-fold 1,4-benzene-dicarboxylate (BDC) linker.[4-7] This type of MOF has been reported to be stable under high temperature and it can be compatible with typical solvents such as water, ethanol and acetone. Functionalization of UiO-66 is a method to improve the catalytic activity of this catalyst to be applied in many more reactions. [3] The development of metal nodes and ligand design have been extensively driving the potential for MOF applications. A sulfate functionalized zirconium based MOFs such as UiO-66-SO_3H and MOF-808-SO_3H were shown to be a strong solid Brønsted acid for broad types of chemical reaction. [8] Recently, the Lewis pair on defective UiO-66, created by removing one organic linker, was used to study the CO_2 dehydrogenation to methanol. [9]

The dihydroxybenzene are a group of organic compound which contains two hydroxyl groups substituted at an aromatic benzene ring. The compounds include benzene-1,2-diol (Catechol), benzene-1,3-diol (Resorcinol) and benzene-1,4-diol (Hydroquinone). These compounds have been used for medical purposes and for several chemical reactions. For example, the benzene-1,3-diol has been widely used as a reactant for coumarin synthesis using several catalysts such as sulfuric acid [10, 11] and zeolite [12]. The reaction of dihydroxybenzene over zeolites and MOFs have been studied.[13-15] The resorcinol was used to synthesis coumarin with Cu-MOF. [13]

To understand physical and chemical properties inside the catalysts, quantum calculations have been used to study structures, energies and related properties. Density Functional Theory (DFT) has been widely used to calculate the adsorption and reaction. The DFT functional has been applied for the aldol condensation of benzaldehyde and heptanal on UiO-66-NH_2 in 2015. [16] However, a remarkable point to concern about the B3LYP functional is that the lack of dispersion energy. Also, B3LYP is one of post Hartree-Fock methods which consumes high computational resource. In 2006, Zhao and Thular has developed the Minnesota functional [17]which yield reasonable results in adsorption and reactions in zeolite system [18], Metal catalysts [19] and MOF[20]. Up until now, the M06-L functional is a local function in this M06 family which is mostly used for transition metal, inorganic and organometallic compounds. The method has been broadly applied to study various adsorption system, reaction mechanism, as well as the framework effect of MOFs. The M06-L functional has been proved to be very beneficial for studying the adsorption and reaction mechanisms of hydrocarbon on MOFs such as Glucose-to-Hydroxylmethylfurfural transformation[20] and the aldol condensation reaction of acetone [21].

ONIOM is a multi-layered calculation approach which has been developed by Morokuma and coworker.[22] The two-layer ONIOM method, or ONIOM2, has been used to compensate computational efficiency and time.[23] The ONIOM2 has been successfully applied to study the confinement effect on the adsorption and reaction mechanism of unsaturated aliphatic, aromatic and heterocyclic compounds on zeolites.[18] The method was also used to study the similar types of reaction over MOFs. [20] Previous results confirmed that the calculation method covered weak interactions such as the Van der Waals and some short-ranged interactions. Therefore the method is an effective choice to describe the confinement effect [24] of large framework materials such as zeolite and MOF catalysts.

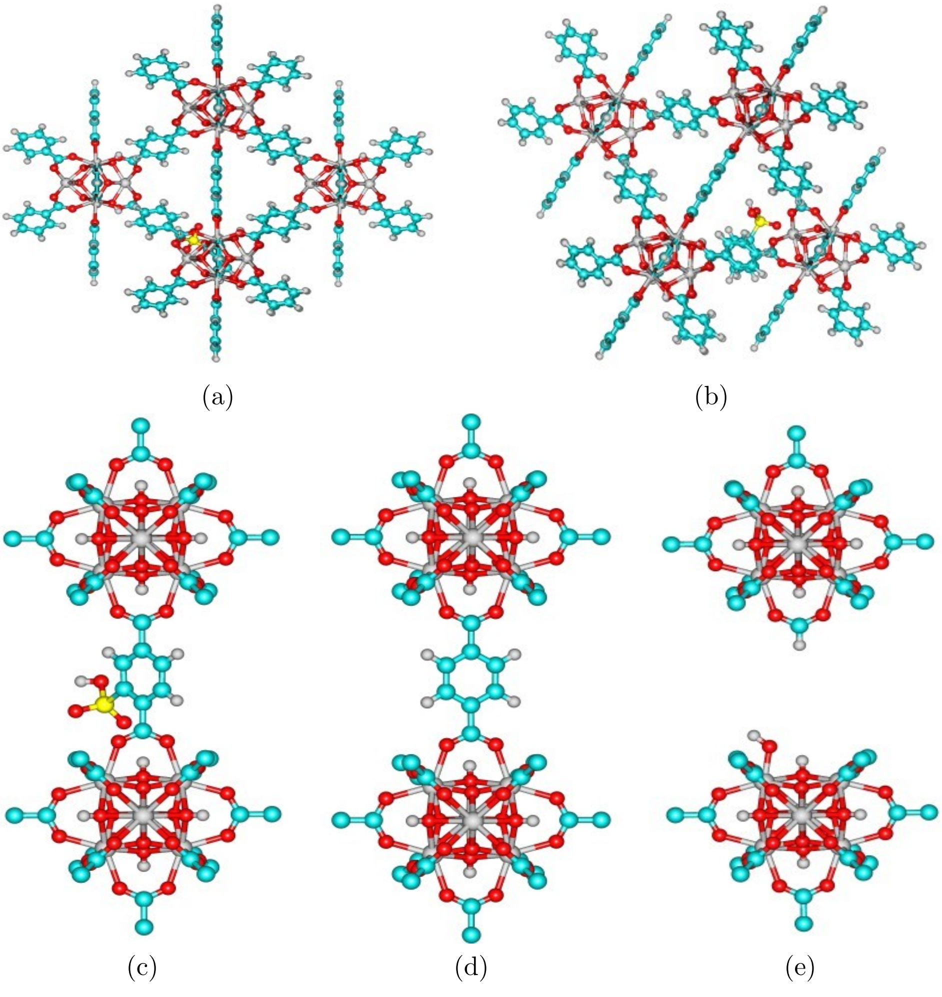
In this study, the adsorption of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on the UiO-66 MOF has been investigated by the ONIOM approach. The effect of two Brønsted acid sites from a sulfonic group and Zr metal cluster in the UiO-66-SO_3H and UiO-66 MOF were studied. Besides, the effect of the Lewis acid site on the defect-UiO-66 MOF was also studied. The inner layer of the ONIOM2 demonstrated the adsorptive active region and was treated by M06-L functional, while the outer layer was calculated by semi-empirical PM6 method. The details for the adsorption of dihydroxybenzene molecules on MOF will be analyzed via natural bond orbital analysis.

METHOD

Geometrical structures and adsorption properties of dihydroxybenzenes over UiO-66, UiO-66-SO_3H and defected-UiO-66 has been studied by ONIOM approach. It is important for the framework to be large enough to represent the confinement effect of the whole MOF structure. Also, the accuracy for the interaction at the active region has to be precise. The selected MOFs has been divided into two regions represented by ONIOM2 scheme as shown in figure 1a and 1b. For UiO-66, the active site covered the two octahedral metal-oxide nodes ($Zr_6O_4(OH)_4$ with six carboxylic group) and 1,4-benzene-dicarboxylate (BDC) linker. [4, 20, 21, 27] The outer layer was connected with six octahedral metal-oxide nodes and calculated with a lower level of theory PM6. For UiO-66-SO_3H, one BDC linker was replaced with HSO_3-BDC to represent the Brønsted acid at sulfonic group as shown in figure 1c. The cluster is composed of $Zr_{36}O_{192}C_{432}H_{311}SO_3H$ model. The Brønsted acid at the metal site was studied as shown in figure 1d. The cluster model is $Zr_{36}O_{192}C_{432}H_{312}$. To represent the Lewis acid site, one BDC linker was removed [9] as shown in figure 1e. The cluster model is $Zr_{36}O_{191}C_{425}H_{310}$.

DFT has been used to study the interaction at the active region. Several DFT methods such as B3LYP and PBE cannot properly account for the dispersion interaction. [18] Recently, the M06 functional has been applied to study the adsorption and reaction mechanisms on zeolites [18] and also MOFs[20, 21, 27, 28]. It has been proved that the adsorption and activation energy resulted from M06-L functional are close to highly sophisticated calculation methods such as MP2, CCSD and also experimental data. [27] Therefore, the M06-L functional was used to study at the high level active region where the adsorption occurs.

To reduce the computational cost while preserve the accuracy of framework interaction, the calculations at the active inner region were performed using quantum cluster while the semi-empirical was used to study at the outer layer where the confinement effect inside the metal-organic-framework effected to the reaction. The six octahedral metal-oxide clusters were calculated by PM6 method. The method has been extensively used to study the structures of zeolites [29] and MOFs. The calculations were performed using ONIOM2 scheme in the Gaussian 09 program. [30] For optimization, the inner layer was treated by M06-L functional while the outer layer was calculated by PM6 method. The calculation approach can be denoted as ONIOM(M06-L:PM6). The 6-31G(d,p) basis set was employed for the H, C, O and S while the Zr atoms were treated with the LANL2DZ pseudopotential basis sets. To improve the adsorption energies, single point energy calculations with the M06-L/6-311+G(2df,2p)+LANL2DZ at the inner layer and M06-L/LANL2DZ at the outerlayer was used and be denoted as ONIOM(M06-L/6-311+G(2df,2p)+LANL2DZ:M06-L/LANL2DZ) // ONIOM(M06-L/6-31G(d,p)+LANL2DZ:PM6). The Natural Bond Orbital (NBO) [31] were analyzed to get deep details of the adsorption properties.


(a) (b)

(c) (d) (e)

FIGURE 1. The optimized structure of (a,b) UiO-66-SO_3H metal organic framework with ONIOM(M06-L:PM6) approach. The inner layer of (c) Brønsted acid at sulfonic group, (d) Brønsted acid at metal site and (e) Lewis acid on the defect UiO-66. The color of carbon, oxygen, hydrogen, sulfur and zirconium atoms are blue, red, white, yellow and gray, respectively.

Results and Discussion

The adsorption of dihydroxybenzene molecules on UiO-66, UiO-66-SO_3H and defected-UiO-66 have been studied. We started our consideration of the M06-L calculations by comparing with the results from benchmarking MP2 method. The isolated benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol molecules with several possible structures have been optimized with M06-L functional as shown in Figure 2. The benzene-1,2-diol has C_1 (figure 2a) and C_{2v} (figure 2b) symmetry, the benzene-1,3-diol has C_1 (figure 2c) and two C_{2v} (figure 2d and 2e) symmetry and the benzene-1,4-diol has C_{2h} (figure 2f) and C_{2v} (figure 2g) symmetry. The relative energies were calculated with M06-L/6-311+G(2df,2p)//M06-L/6-31G(d,p) to be 0.0 and 3.64 kcal/mol for benzene-1,2-diol; 0.17, 0.20 and 0.86 kcal/mol for benzene-1,3-diol; and 2.66 and 2.76 kcal/mol for benzene-1,4-diol, respectively. These energies compared well with the MP2/6-311+G(2df,2p) level of theory. The relative energies from MP2/6-311+G(2df,2p) were 0.0 and 4.00 kcal/mol for benzene-1,2-diol; 0.95, 1.00, and 2.86 kcal/mol for benzene-1,3-diol, and 2.57 and 2.68 kcal/mol for benzene-1,4-diol, respectively. The M06-L geometries compared with the geometries calculated from MP2 are presented in Table 1. The different of the calculated geometries were found to be only 0.03 Å. The relative energies were in the order; benzene-1,2-diol > benzene-1,3-diol > benzene-1,4-diol. The results show that the inductive effect of hydroxyl group withdraw the electron about 0.24-0.26 $| e |$ per hydroxyl group.

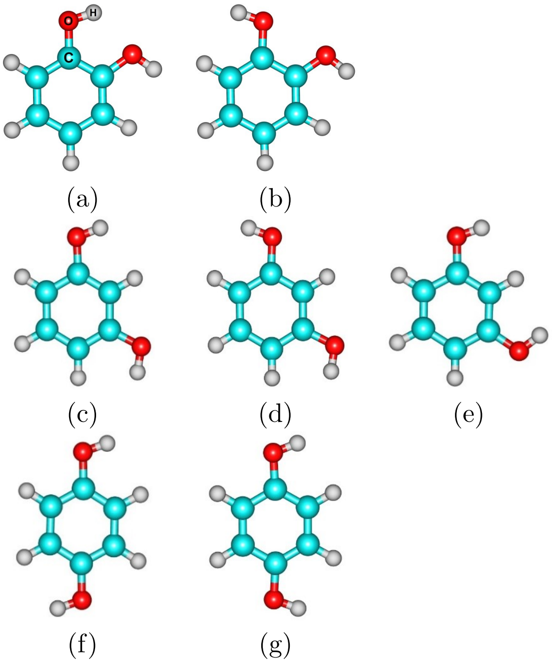


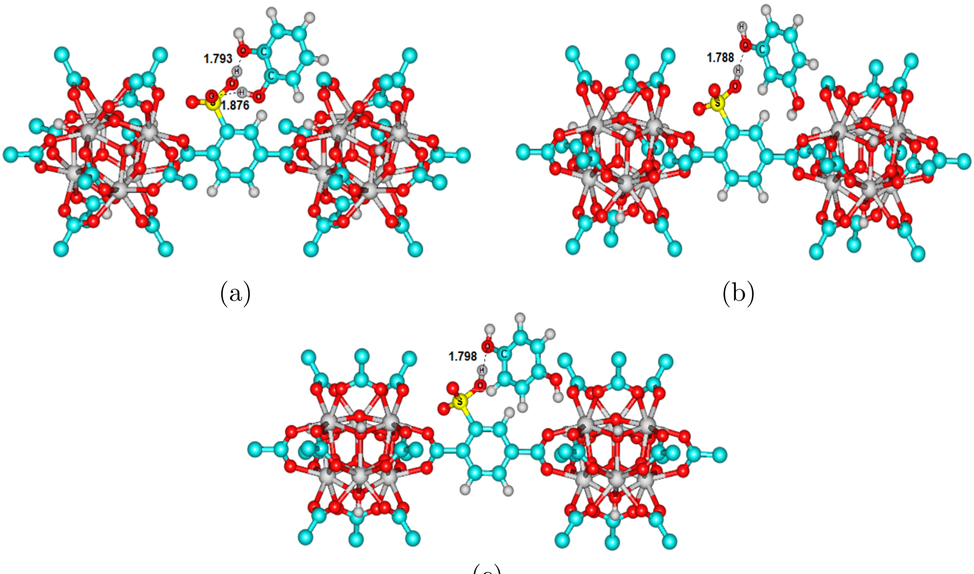
Figure 2. The optimized structures of benzene-1,2-diol (a,b), benzene-1,3-diol (c,d,e) and benzene-1,4-diol (f,g) calculated with M06-L/6-31G(d,p). The color of carbon, oxygen and hydrogen atoms are blue, red and white, respectively.

TABLE 1. The bond distance (Å) and relative energy (kcal/mol) of the benzene-1,2-diol (C_1), benzene-1,3-diol (C_1) and benzene-1,4-diol (C_{2h}) obtained from M06-L and MP2 method.

	Method	benzene-1,2-diol	benzene-1,3-diol	benzene-1,4-diol
r(C-C)	MP2[a]	1.391	1.391	1.391
	M06-L[b]	1.393	1.362	1.393
r(C-O)	MP2[a]	1.367	1.367	1.369
	M06-L[b]	1.366	1.394	1.367
r(O-H)	MP2[a]	0.963	0.962	0.962
	M06-L[b]	0.964	0.963	0.962
Relative Energy	MP2[a]	0.00	0.95	2.57
	M06-L[b]	0.00	0.17	2.66

[a] MP2/6-311+G(2df,2p)
[b] M06-L/6-311+G(2df,2p)//M06L/6-31G(d,p)

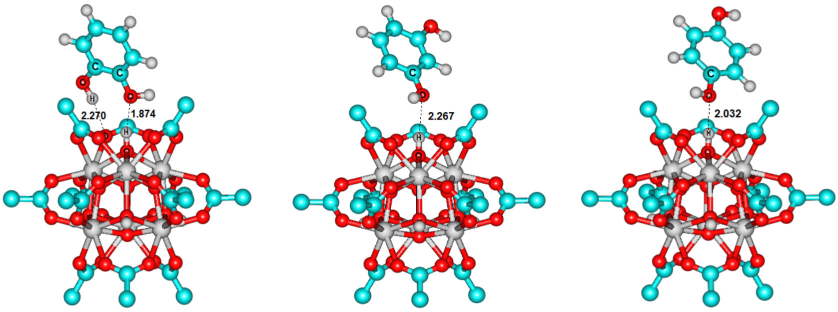
Next, the UiO-66-SO_3H, UiO-66 and defected-UiO-66 structures were calculated with ONIOM(M06-L/6-311+G (2df,2p+LANL2DZ:M06-L/LANL2DZ) // ONIOM(M06-L/6-31G(d,p) +LANL2DZ:PM6) approach. The optimized structure of these 3 MOFs were shown in figure 1c-e. To ensure the correction of geometries from the previous optimization step, it should be noted that the prior step ONIOM (M06-L:PM6) method provided the structures which closely related to experimental data.[20] At this point, several possible adsorption positions of dihyroxybenzenes over UiO-66-SO_3H, UiO-66 and defect-UiO-66 were calculated. For UiO-66-SO_3H, the benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol, they were located inside the main pore, over the active Brønsted acid of the sulfonic group as shown in figure 3. One hydrogen bond was found during the adsorption of benzene-1,3-diol and benzene-1,4-diol on the MOF. Due to the steric effect from the hydroxyl group at para position, the hydrogen bond occurred from hydroxyl group to the oxygen of sulfonic group as shown in figure 3c. For benzene-1,2-diol, double hydrogen bond interactions were found with strong interaction. The intermolecular distances between the Brønsted acid and dihydroxybenzene were 1.793 and 1.876 Å as shown in figure 3a. This implies that the hydroxyl group at ortho position of the aromatic ring improves the adsorption interactions via hydrogen bond interaction. The adsorption of dihydroxybenzene on UiO-66 were shown in figure 4 (a-c). The benzene-1,2-diol interacted with a Brønsted at the metal site with two hydrogen bond length around 1.874 and 2.270 Å. The benzene-1,3-diol and benzene-1,4-diol interacted each other via hydrogen bond. The intermolecular distances were 2.267 and 2.032 Å, respectively.



(a) (b)

(c)

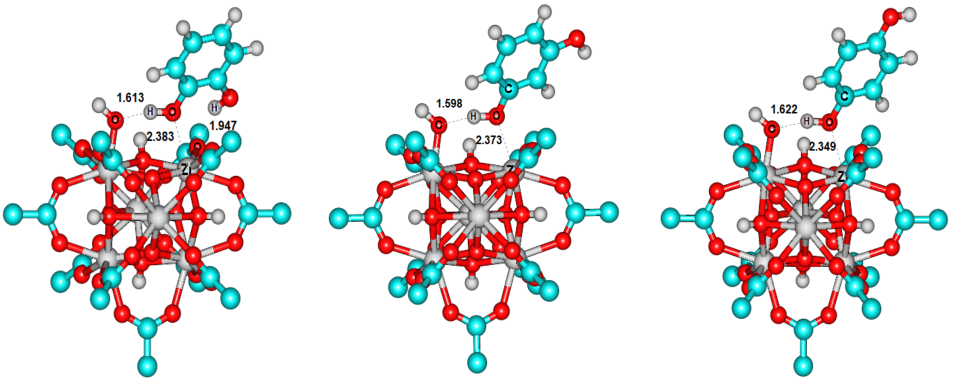
Figure 3. The optimized structures of benzene-1,2-diol (a), benzene-1,3-diol (b) and benzene-1,4-diol (c) on UiO-66-SO_3H optimized with ONIOM approach. Distances are in Å.



(a) (b) (c)

Figure 4. The optimized structures of benzene-1,2-diol (a), benzene-1,3-diol (b) and benzene-1,4-diol (c) on UiO-66 optimized with ONIOM approach. Distances are in Å.

The defect-UiO-66 contains the Lewis acid site as shown in figure 1e. The benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol interacted by adsorption at Zr atom as shown in figure 5 (a-c). The strong bond Zr$\cdots$O was generated with the bond distances of 2.383, 2.373 and 2.349 Å, for benzene-1,2-diol, benzene-1,3-diol, and benzene-1,4-diol, respectively. The strong hydrogen bond were found between the hydroxyl group of dihydroxybenzene and the hydroxyl group of metal cluster with distances of 1.613, 1.598 and 1.622 Å, respectively.



(a) (b) (c)

FIGURE 5. The optimized structures of benzene-1,2-diol (a), benzene-1,3-diol (b) and benzene-1,4-diol (c) on defect-UiO-66 optimized with ONIOM approach. Distances are in Å.

The adsorption energies calculated from the ONIOM and the high level M06-L were shown in table 2. The adsorption energies for benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on UiO-66-SO_3H MOF were -14.9, -15.9 and -13.9 kcal/mol, respectively. The adsorption energies from high level were -10.6, -12.3 and -12.1 kcal/mol, respectively. We found that the framework accelerated the increase in adsorption energies to be 4.3 kcal/mol. The adsorption energies on the Brønsted acid at metal site of UiO-66 were -23.6, -19.5 and -24.6 kcal/mol for the benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol, respectively. For the defect-UiO-66, the strong interactions were found. The adsorption energies were -40.8, -36.5 and -36.5 kcal/mol, respectively. Dihydroxybenzene can form strong bond with the metal atom. A hydrogen bond were also occurred in this site. The most strongest interaction was benzene-1,2-diol which was arised from the double hydrogen bond interaction. Available experimental energies can be compared with zeolite. The adsorption energies of ethanol on H-zeolite was reported to be -31.0 kcal/mol [32].

TABLE 2. The adsorption energies (kcal/mol) of the benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on the UiO-66-SO_3H, UiO-66 and defect-UiO-66 obtained from ONIOM approach.

	Method	benzene-1,2-diol	benzene-1,3-diol	benzene-1,4-diol
UiO-66-SO_3H	ONIOM[a]	-12.8	-13.1	-10.7
	ONIOM[b]	-14.9	-15.9	-13.9
	M06-L[c]	-10.6	-12.3	-12.1
UiO-66	ONIOM[a]	-18.2	-16.5	-20.5
	ONIOM[b]	-23.6	-19.5	-24.6
	M06-L[c]	-16.5	-15.0	-19.4
defect-UiO-66	ONIOM[a]	-40.3	-36.5	-37.8
	ONIOM[b]	-40.8	-36.5	-36.5
	M06-L[c]	-37.8	-36.1	-37.0

[a] ONIOM(M06-L(6-31G(d,p)+LANL2DZ):PM6)

[b] ONIOM(M06-L(6-311+G(2df,2p)+LANL2DZ):M06-L(LANL2DZ)) // ONIOM(M06-L(6-31G(d,p)+LANL2DZ):PM6)

[c] high level energy M06-L(6-311+G(2df,2p)+LANL2DZ)

The NBO analysis of dihydroxybenzene adsorption on the Brønsted acid site at sulfonic group of UiO-66-SO_3H was performed to understand changes in electronic properties in more details. We found that electrons transfer from the donor orbitals (the hydroxyl group of adsorbate) to the Brønsted acid acceptor orbitals as shown in Figure 6. For benzene-1,2-diol, ion pair electrons of oxygen in hydroxyl group (O atom: p 100%) transfer to the antibonding of the O-H of the Brønsted acid of sulfonic group (O atom 21% : s 28% p 72% and H atom 79% s 100%) has E(2) energy of 10.1 kcal/mol. For benzene-1,3-diol and benzene-1,4-diol, the electrons from ion pair of oxygen in hydroxyl group transfer to the antibonding orbital of the O-H in the sulfonic group, yielding E(2) energies of 14.8 and 17.1 kcal/mol, respectively. The adsorption of dihydroxybenzene on the Brønsted at metal cluster of UiO-66 was analyzed with NBO as shown in figure 7. The electrons transfer the ion pair electrons of oxygen of dihydroxybenzene transfer to the antibonding of the O-H of the Brønsted acid at metal cluster (O atom 21% : s 14% p 86% and H atom 79% s 100%) of UiO-66, yielding E(2) energy of 7.5, 3.4 and 3.6 kcal/mol, respectively.

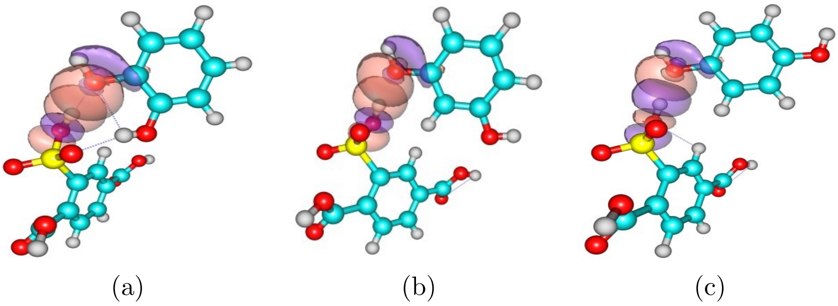

(a) (b) (c)

Figure 6. The NBO orbital (LP O to $\sigma*$ (O-H)) for the interaction of (a) benzene-1,2-diol, (b) benzene-1,3-diol and (c) benzene-1,4-diol on the Brønsted at sulfonic group of UiO-66-SO$_3$H.

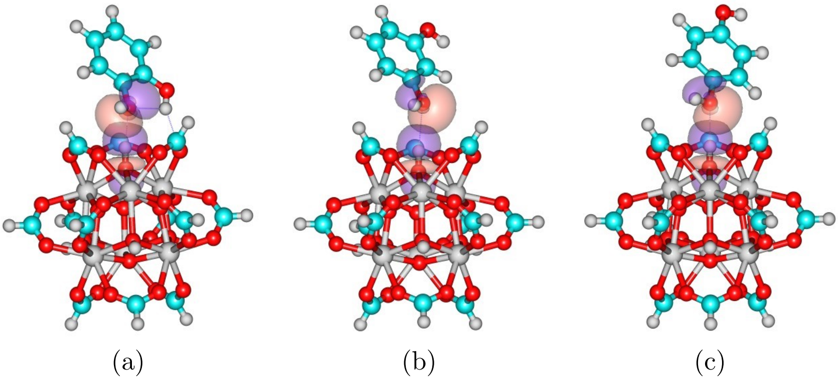

(a) (b) (c)

Figure 7. The NBO orbital (LP O to $\sigma*$ (O-H)) for the interaction of (a) benzene-1,2-diol, (b) benzene-1,3-diol and (c) benzene-1,4-diol on Brønsted at metal site of UiO-66.

Finally, we analyzed the NBO in the adsorption of dihydroxybenzene on defect-UiO-66, as shown in Figure 8. The chemical bond between the O of hydroxyl group of benzene-1,2-diol and Zr atom of defect-UiO-66 was found to have the electron from 94% O (s 35% p 65%) and 6% Zr (s 10% p 44% d 46%). We found that the electron transferred from the bonding of Zr-O bond to the antibonding orbital of O-H bond of hydroxyl group of benzene-1,2-diol as shown in Figure 8a. This bonding orbital is also presented on the interaction of benzene-1,3-diol and benzene-1,4-diol on defect-UiO-66 MOF, as shown in Figure 8b and 8c. The E(2) energy at this stage were 33.9, 35.5 and 32.4 kcal/mol, respectively. These energies are higher than those of the interactions at the Brønsted acid correspond with the adsorption energies. This data is able to reflect tendency in diffusion coefficients which corresponded to chemical reactions for dihydroxybenzene and its derivatives.

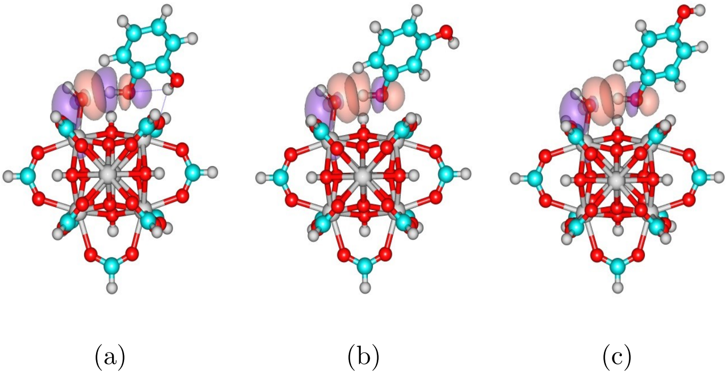


FIGURE 8. The NBO orbital (σ (Zr-O) to $\sigma *$ (O-H)) for the interaction of (a) benzene-1,2-diol, (b) benzene-1,3-diol and (c) benzene-1,4-diol on Lewis acid at metal site of defect-UiO-66.

CONCLUSIONS

The adsorption of benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on the UiO-66-SO_3H, UiO-66 and defected-UiO-66 MOF has been investigated by the ONIOM approach. For pre-calculation, the dihydroxybenzene conformers were calculated using M06-L functional and were compared with the ones calculated by MP2 method. The most stable conformer is benzene-1,2-diol. Their relative energies were found in the order of; benzene-1,2-diol> benzene-1,3-diol > benzene-1,4-diol. The results are in agreement with the ones from MP2 method, showing a performance of the selected ONIOM approach used in this study. The calculations on adsorption properties on UiO-66 MOF were performed by ONIOM(M06-L/6-311+G(2df,2p)+LANL2DZ:M06-L/LANL2DZ) // ONIOM(M06-L/6-31G(d,p)+LANL2DZ:PM6). During the adsorption, benzene-1,2-diol was strongly interacted with UiO-66 via double hydrogen bond interactions. The adsorption energies for benzene-1,2-diol, benzene-1,3-diol and benzene-1,4-diol on UiO-66-SO_3H MOF were -14.9, -15.9 and -13.9 kcal/mol, respectively. The adsorption on Brønsted acid at metal site of UiO-66 were -23.6, -19.5 and -24.6 kcal/mol, respectively. For the defected-UiO-66, the adsorption energies were -40.8, -36.5 and -36.5 kcal/mol, respectively. The NBO analysis shows that electrons from ion pair of hydroxyl group transfer to the antibonding orbital of the Brønsted acid while electrons from Lewis site Zr-O bond transfer to the hydroxyl group of dihydroxybenzene. These calculated data will be useful for further studies in the diffusion coefficient and chemical reaction for dihydroxybenzene.

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References

[1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O.M. Yaghi, Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage, Science. 295 (2002) 469–472.

[2] J. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Metal-organic framework materials as catalysts, Chem. Soc. Rev. 38 (2009) 1450–1459.

[3] H.C.J. Zhou, S. Kitagawa, Metal-Organic Frameworks (MOFs), Chem. Soc. Rev. 43 (2014) 5415–5418.

[4] M. Kandiah, M.H. Nilsen, S. Usseglio, S. Jakobsen, U. Olsbye, M. Tilset, C. Larabi, E.A. Quadrelli, F. Bonino, K.P. Lillerud, Synthesis and stability of tagged UiO-66 Zr-MOFs, Chem. Mater. 22 (2010) 6632–6640.

[5] A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke, P. Behrens, Modulated synthesis of Zr-based metal-organic frameworks: From nano to single crystals, Chem. Eur. J. 17 (2011) 6643–6651.

[6] L. Valenzano, B. Civalleri, S. Chavan, S. Bordiga, M.H. Nilsen, S. Jakobsen, K.P. Lillerud, C. Lamberti, Disclosing the complex structure of UiO-66 metal organic framework: A synergic combination of experiment and theory, Chem. Mater. 23 (2011) 1700–1718.

[7] A.J. Howarth, Y. Liu, P. Li, Z. Li, T.C. Wang, J.T. Hupp, O.K. Farha, Chemical, thermal and mechanical stabilities of metal-organic frameworks, Nat. Rev. Mater. 1 (2016) 15018.

[8] C.A. Trickett, T.M. Osborn Popp, J. Su, C. Yan, J. Weisberg, A. Huq, P. Urban, J. Jiang, M.J. Kalmutzki, Q. Liu, J. Baek, M.P. Head-Gordon, G.A. Somorjai, J.A. Reimer, O.M. Yaghi, Identification of the strong Brønsted acid site in a metal-organic framework solid acid catalyst, Nat. Chem. 11 (2019) 170–176.

[9] K. Yang, J. Jiang, Computational design of a metal-based frustrated Lewis pair on defective UiO-66 for CO_2 hydrogenation to methanol, J. Mater. Chem. A, 8 (2020) 22802–22815.

[10] S. Pornsatitworakul, B. Boekfa, T. Maihom, P. Treesukol, S. Namuangruk, S. Jarussophon, N. Jarussophon, J. Limtrakul, The coumarin synthesis: a combined experimental and theoretical study, Monatsh. Chem. 148 (2017) 1245–1250.

[11] C. Loarueng, B. Boekfa, S. Jarussophon, P. Pongwan, N. Kaewchangwat, K. Suttisintong, N. Jarussophon, Theoretical and experimental investigation of NMR, IR and UV-visible spectra of hydroxyl-substituted-4-chloromethylcoumarin derivatives, Arkivoc. (2019) 116–127.

[12] S. Klinyod, B. Boekfa, S. Pornsatitworakul, T. Maihom, N. Jarussophon, P. Treesukol, C. Wattanakit, J. Limtrakul, Theoretical and Experimental Study on

the 7-Hydroxy-4-Methylcoumarin Synthesis with H-Beta Zeolite, ChemistrySelect. 4 (2019) 10660–10667.

[13] M. Opanasenko, M. Shamzhy, J. Čejka, Solid Acid Catalysts for Coumarin Synthesis by the Pechmann Reaction: MOFs versus Zeolites, ChemCatChem. 5 (2013) 1024–1031.

[14] J.C. Kim, R. Ryoo, M.V. Opanasenko, M.V. Shamzhy, J. Čejka, Mesoporous MFI Zeolite Nanosponge as a High-Performance Catalyst in the Pechmann Condensation Reaction, ACS Catal. 5 (2015) 2596–2604.

[15] A. Hegedüs, Z.Hell, Zeolite-catalyzed Pechmann synthesis of coumarins, Catal. Lett. 112 (2006) 105–108.

[16] J. Hajek, M. Vandichel, B. Van De Voorde, B. Bueken, D. De Vos, M. Waroquier, V. Van Speybroeck, Mechanistic studies of aldol condensations in UiO-66 and UiO-66-NH_2 metal organic frameworks, J. Catal. 331 (2015) 1–12.

[17] Y. Zhao, D.G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals, Theor. Chem. Acc. 120 (2008) 215–241.

[18] B. Boekfa, S. Choomwattana, P. Khongpracha, J. Limtrakul, Effects of the zeolite framework on the adsorptions and hydrogen-exchange reactions of unsaturated aliphatic, aromatic, and heterocyclic compounds in ZSM-5 zeolite: A combination of perturbation theory (MP2) and a newly developed density functional theory (M06-2X) in ONIOM scheme, Langmuir. 25 (2009) 12990–12999.

[19] B. Boekfa, E. Pahl, N. Gaston, H. Sakurai, J. Limtrakul, M. Ehara, C-Cl bond activation on Au/Pd bimetallic nanocatalysts studied by density functional theory and genetic algorithm calculations, J. Phys. Chem. C. 118 (2014) 22188–22196.

[20] V.Tangsermvit, T.Pila, B.Boekfa, V.Somjit, W.Klysubun, J.Limtrakul, S.Horike, K.Kongpatpanich, Incorporation of Al^{3+} Sites on Brønsted Acid Metal-Organic Frameworks for glucose-to-Hydroxylmethylfurfural Transformation, Small. (2021) 2006541.

[21] W. Thongnuam, S. Pornsatitworakul, T. Maihom, P. Treesukol, N. Jarussophon, P. Maitarad, K. Kongpatpanich, B. Boekfa, An experimental and theoretical study on the aldol condensation on zirconium-based metal-organic framework, Key Eng. Mater. 757 (2017) 98–102.

[22] S. Dapprich, I.K.S. Byun, K. Morokuma, M.J. Frisch, A new ONIOM implementation in Gaussian98. Part I. The calculation of energies, gradients, vibrational frequencies and electric field derivatives, J. Mol. Struct. THEOCHEM. 461–462 (1999) 1–21.

[23] L.W. Chung, W.M.C. Sameera, R. Ramozzi, A.J. Page, M. Hatanaka, G.P. Petrova, T.V. Harris, X. Li, Z. Ke, F. Liu, H.B. Li, L. Ding, K. Morokuma, The ONIOM Method and Its Applications, Chem. Rev. 115 (2015) 5678–5796.

[24] E.G. Derouane, Zeolites as solid solvents, J. Mol. Catal. A Chem. 134 (1998) 29–45.

[25] X. Feng, J. Hajek, H.S. Jena, G. Wang, S.K.P. Veerapandian, R. Morent, N. De Geyter, K. Leyssens, A.E.J. Hoffman, V. Meynen, C. Marquez, D.E. De Vos, V. Van Speybroeck, K. Leus, P. Van Der Voort, Engineering a Highly Defective Stable UiO-66 with Tunable Lewis-Brønsted Acidity: The Role of the Hemilabile Linker, J.

Am. Chem. Soc. 142 (2020) 3174–3183.

[26] K. Tan, H. Pandey, H. Wang, E. Velasco, K.Y. Wang, H.C. Zhou, J. Li, T. Thonhauser, Defect Termination in the UiO-66 Family of Metal-Organic Frameworks: The Role of Water and Modulator, J. Am. Chem. Soc. 143 (2021) 6328–6332.

[27] S. Phikulthai, Y. Injongkol, T. Maihom, P. Treesukol, P. Maitarad, V. Tangsermvit, K. Kongpatpanich, B. Boekfa, Adsorption of ammonia on zirconium-based metal-organic framework: A combined experimental and theoretical study, Key Eng. Mater. 757 (2017) 93–97.

[28] W. Jumpathong, T. Pila, Y. Lekjing, P. Chirawatkul, B. Boekfa, S. Horike, K. Kongpatpanich, Exploitation of missing linker in Zr-based metal-organic framework as the catalyst support for selective oxidation of benzyl alcohol, APL Mater. 7 (2019) 111109.

[29] P. Boonyoung, T. Kasukabe, Y. Hoshikawa, A. Berenguer-Murcia, D. Cazorla-Amoros, B. Boekfa, H. Nishihara, T. Kyotani, K. Nueangnoraj, A simple ”nano-templating” method using zeolite y toward the formation of carbon schwarzites, Front. Mater. Sci. 6 (2019) 104.

[30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian, Inc., Wallingford CT, 2016. Gaussian 09. 2009.

[31] A.E. Reed, L.A. Curtiss, F. Weinhold, Intermolecular Interactions from a Natural Bond Orbital, Donor-Acceptor Viewpoint, Chem. Rev. 88 (1988) 899–926.

[32] C.C. Lee, R.J. Gorte, W.E. Farneth, Calorimetric study of alcohol and nitrile adsorption complexes in H-ZSM-5, J. Phys. Chem. B, 101 (1997) 3811–3817.