MOF-5의 Zn의 배위결합상태 변화가 수소저장거동에 미치는 영향 : DFT 전산모사를 이용한 분석

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Hydrogen Storage on Hetero-atom Substituted CNTs : Computer Simulation using Density Functional Theory

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1. Introduction

Metal-organic frameworks (MOFs) are thought to be a set of promising hydrogen storage materials,[1][2] and various MOFs have been synthesized and characterized for their hydrogen storage capacities.[3][4] However, although in the early stages of development, the material MOF-5 is already able to adsorb hydrogen up to 4.5 wt% at 78 K, but they only can adsorb H2 less than 2.0 wt% at room temperature and ambient pressure. Zinc atoms as a constituent of core part of MOF-5 are fully coordinated with neighboring four oxygen atoms. It may result in the weak interaction with molecular hydrogen or in the un-activation of H2 for effective adsorption.

In this study, With the aim of finding the effect of coordination state of zinc atoms in MOF-5 for high storage capacity, we calculated the hydrogen adsorption characteristics using both density functional theory and montecarlo method

2. Methodology

The calculation is practically performed with the local density approximation (LDA) by Perdew et al.[5] The implementation of DFT employed here combines a double numerical plus polarization basis set (DNP) embodied in the Dmo13 code. Materials Studio (Accelrys, USA). The set is equivalent to 6-31G++ which is an analytic basis set. And we set the orbital cut-off distance as 3.9 Å and the energy convergence as 10-5 Ha

1) Noro, S.; Kitagawa, S.; Kondo, M.; Seki, K. Angew. Chem., Int. Ed. 2000, 39, 2082-2084.
2) Rowsell, J. L. C.; Yaghi, O. M. Microporous Mesoporous Mater 2004, 73, 3-14
3) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O'Keeffe, M.; Yaghi, O. M. Science 2003, 300, 1127-1129
4) Rowsell, J. L. C.; Millward, A. R.; Park, K. S.; Yaghi, O. M. J. Am. Chem. Soc. 2004, 126, 5666-5667
5) Perdew, J. p.; Wang. Y. J. Phys. Rev. B 1992, 45, 13244-13255

3. Results and Discussion

Pristine MOF-5 show stable structure in which one zinc atom is interconnected with four oxygen atoms, tetrahedral structure, and core part consist of four zinc atom, one central oxygen atom, and twelve oxygen atoms in BDC organic ligands. And also, they have adsorption potential of 1.66~2.88 kcalmol. In a meanwhile, after removal of a few BDC ligands, it is appeared the different structure of symmetric and asymmetric geometrically. Now. the coordination number of zinc atoms on each stage is followed by,

	Zn_1	Zn_2	Zn_3	Zn_4	avg.		Zn_1	Zn_2	Zn_3	Zn_4	avg.
0	4	4	4	4	4.0	A2	4	3	3	2	3.0
1	4	4	3	3	3.5	S3	3	3	2	2	2.5
S2	3	3	3	3	3.0	A3	4	2	2	2	2.5

Table 1. coordination number of zinc atoms and average coordination number after removal of a few organic ligand

As the number of removed organic ligands is higher, in other words, as the average coordination number of zinc atoms is decreased, adsorption potential energy of molecular hydrogen to MOF-5 core metal part is increased step by step. We can not find the difference between symmetric structure and asymmetric structure. (table 2)

	adsorption energy (kcal/mol)		adsorption energy (kcal/mol)
0	-1.66~-2.88	A2	-4.30~-5.83
1	-2.66~-3.96	S3	-1.99~-4.66
S2	-4.11~-7.35	A3	-2.46~-3.19

Table 2. adsorption potential energy after removal of a few organic ligand

In case of S3 and A3, whose avg. coordination number is 2.5, the adsorption energy is rather bounced back. It may be reason why those structures are very unstable due to breakdown of tetrahedral structure.

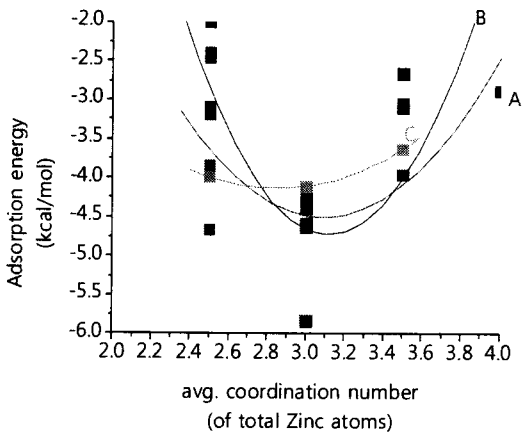

Figure 1. adsorption energy as a function of average coordination number of zinc atom of core part in MOF-5