Optimal Adsorption Site of Periodical Metal Surface Based on Global Search of Genetic Algorithm

Jingjing Zhang[1, a]

[1] Department of Chemical Engineering and Technology, China University of Petroleum-Beijing, Beijing, China, 102249

[a] email

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Abstract. When using the chemical calculation method to study the adsorption, we should firstly find the preferential adsorption site of the catalyst surface. But at present, we often place the reactants in the typical adsorption sites, such as bridge position, vacancy and vertex position, to find the minimum energy point of the system according to the DFT structure optimization. The lack of study on atypical adsorption sites leads to the lack of other preferential adsorption sites. Therefore, we need to explore the potential adsorption sites on the periodic metal surfaces using global search method. The calculation operation of this paper involves the single point energy and structure optimization. The single point energy measures the size of the total energy of the system. The low the total energy of the system, the more stable adsorption is. The structural optimization is to change the structure to the most stable point by adjusting the coordinates of the atoms. In other words, the structural optimization is to find the most stable geometry. Structural optimization is used to calculate the configuration, which is the lowest energy structure and corresponds to the position of the optimal adsorption site. In addition, this paper also introduces the orbital analysis to verify the molecular structure of thiophene. We use the HOMO-LOMO Channel analysis to confirm whether there is π conjugate in thiophene. Conjugate is a criterion for judging whether thiophene molecules are dissociated or adsorbed.

Method

We choose the super unit cell model to study the adsorption of thiophene molecules on Ni (100) surface. The thiophene and the two layer of the metal top are allowed to relax.

Table 1 Methods and parameters in calculating energy

Theory	DFT
Software	Materials Studio 8.0
Module	Dmol3
Functional	GGA/PBE
Basis Set	DNP
Density mixing charge	0.03
SCF tolerance	1.0×10^{-3}
Smearing	0.02 Ha

Table 2 Methods and parameters in calculating geometry optimization

Theory	DFT
Software	Materials Studio 8.0
Module	$Dmol^3$
Functional	GGA/PBE
Basis Set	DNP
Density mixing charge	0.03
SCF tolerance	1.0×10^{-3}
Smearing	0.02 Ha
Convergence tolerance of energy	2×10^{-5}
Convergence tolerance of Max.force	Hatree/Å
Convergence tolerance of Max.displacement	0.005 Å

Results

After 50 iterations, the twelve adsorption configurations of the lowest energy in the population are in the stable state. We consider the population has lost the evolutionary, that is to say the population is convergent.

Table 3 The rank of single energy of adsorption structure and the coordinates of the sulfur atom in the thiophene

number	Single Point Energy(Ha)	X(Å)	Y(Å)	Z(Å)
1	-11503.347	4.2824	2.8519	7.2833
2	-11503.347	6.4087	5.2966	7.1240
3	-11503.345	4.6802	2.9578	7.3379
4	-11503.344	6.4014	4.9455	7.0582
5	-11503.343	4.1755	2.8202	7.3130
6	-11503.342	6.4089	5.2984	7.1259
7	-11503.342	4.3019	2.7640	7.2154
8	-11503.342	1.6642	2.7526	7.2251
9	-11503.342	4.7666	2.0180	7.5835
10	-11503.339	2.1433	3.3708	7.3136
11	-11503.339	4.2731	2.8527	7.2816
12	-11503.339	4.1641	2.8206	7.3132

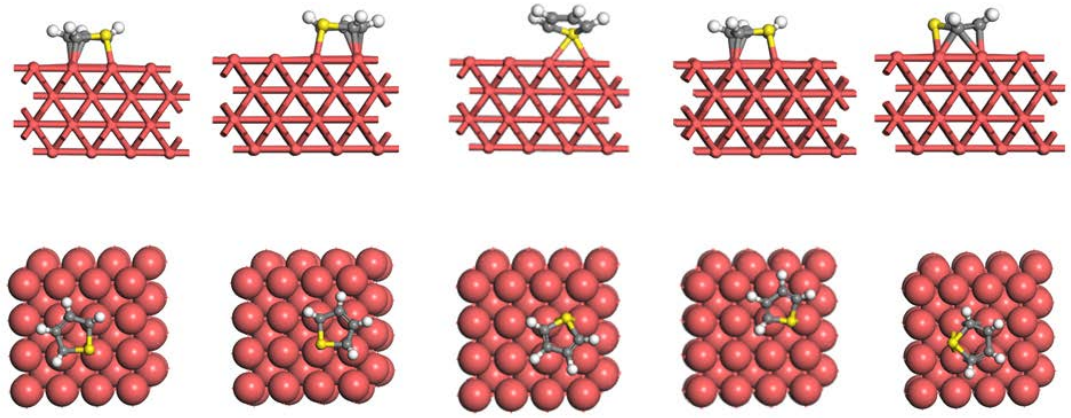

Figure 1 Front view and vertical view of adsorption structure

Table 4 The rank of single energy of adsorption structure and the coordinates (Å) of the sulfur atom in the thiophene

	X（Å）	Y（Å）	Z（Å）	E_{ad}(eV)	d(S-Ni)/Å	d(C-S)/Å
1	4.554579000	2.907568000	7.460874000	-3.462023496	2.161	1.845
7	4.555998586	2.918952850	7.458956847	-3.461952745	2.160	1.841
11	4.561080000	2.914930000	7.461874000	-3.461443883	2.160	1.842
12	4.558490552	2.921046173	7.456357887	-3.461288790	2.160	1.847
3	5.414490645	2.909085388	7.459262527	-3.461280612	2.164	1.846
9	5.406217757	2.913769893	7.460485246	-3.460907810	2.164	1.845
2	7.057716244	5.405918923	7.465070895	-3.459962140	2.161	1.846
4	7.053928836	5.415587360	7.463389430	-3.459710489	2.160	1.844
6	6.463459653	5.261291601	7.334681452	-3.430851992	2.477,2.208	1.841
10	2.257416732	3.709267990	7.279651831	-3.421693540	2.265,2.291	1.879
8*	1.257586752	2.976564533	7.183961353	-3.490310202	2.492,2.304,2.302,2.433	2.968,1.923
5*	3.798675785	3.646174515	6.934493979	-0.675972014	2.253,2.172	2.722,1.834

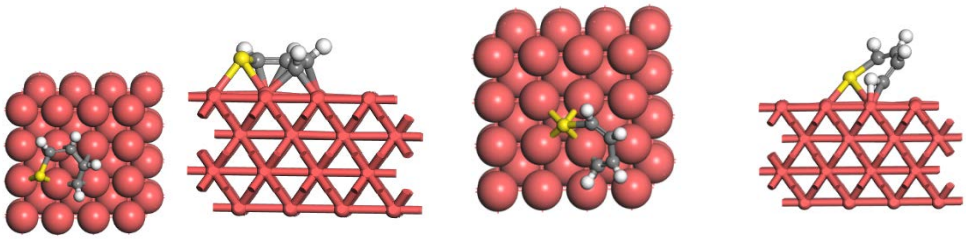

Figure 2 Front view and vertical view of adsorption structure 5 and 7

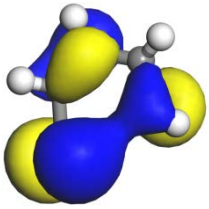

Figure 3 HOMO orbital analysis of thiophene in configuration5

The C-S bond in the adsorption configuration lengthens from 1.728 Å to 1.845Å after the DFT structure optimization. The C-S bonds in all the configurations have increased and the growth rate ranges from 6% to 9%; the C2-C3 bonds have increased by 6%~7%; the C3-C4 bonds have decreased 0.2% averagely; the Ni-S bonds have decreased from 2.268 Å to 2.160 Å compared to the literature situation and the average decreasing rate is about 4.7%~5%. It shows that the Ni atom and the S atom have bonding tendency after the reaction of thiophene and Ni (100) adsorbent. The carbon atom in the middle of thiophene is more close to the Ni surface. And all the C-H bonds are tilted up, far away from the Ni (100) plane.

Conclusion

This paper combines the genetic algorithm with the adsorption system successfully, adopts the genetic algorithm and DFT method and finds the adsorption sites of periodical metal surface successfully. We use the genetic algorithm and DFT single point energy to search the existing adsorption sites on the surface of Ni (100). Most of the adsorption sites concentrate in the region of (3.5, 4.5) and (2, 4). Only a few adsorption sites are discrete. The distribution of relatively low energy configurations of thiophene is also retained. The change situation of C-S and S-Ni are also close to the data obtained by H Orita, which are respectively 1.845 Å and 2.160 Å. A small number of the configurations of the discrete distribution, optimized by the DFT structure, have occurred dissociation adsorption. Although the undissociated configuration doesn't have the lowest energy, its energy is close to the lowest energy configuration, which is -3.460 eV.

The dissociation adsorption configuration after the structure optimization by DFT, the C-S bond is broken and the thiophene ring opened. Other bonds have lengthened correspondingly. The bond of C3-C4 lengthens from 1.421 Å to 1.459 Å. After the HOMO orbital analysis, the conjugation of π does not exist and there is only a single bond.

The C-S bond in the adsorption configuration lengthens from 1.728 Å to 1.845Å after the DFT structure optimization. The C-S bonds in all the configurations have increased and the growth rate ranges from 6% to 9%; the C2-C3 bonds have increased by 6%~7%; the C3-C4 bonds have decreased 0.2% averagely; the Ni-S bonds have decreased from 2.268 Å to 2.160 Å compared to the literature situation and the average decreasing rate is about 4.7%~5%. It shows that the Ni atom and the S atom have bonding tendency after the reaction of thiophene and Ni (100) adsorbent. After the

analysis of HOMO and LOMO orbit configuration, the conjugation of π bond in thiophene still exist. The configuration after adsorption is the configuration of molecular adsorption.

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The implication of Zeng Ziyi's ISTP

The thesis named Research on Protection and Industrialization Development of Qiang Embroidery Culture in Globalization Context written by Zeng Ziyi who works in Art College of Southwest University for Nationalities has been published in Advances in Social Science, Education and Humanities Research（ETMHS 2016,ISSN:2352-5398） Vol.50 Part C. It is the Key Program of Humanities and Social Science of Sichuan Educational Committee in 2015 (Grant No. 15SA0212). It also is the Program of Postgraduate Degree Construction of Southwest University for Nationalities in 2015 (Grant No. 2016XWD-SO504).