

Adsorption structure and reaction path of heterocyclic sulfur compounds and the effect of methyl group on their reactivity: Ab initio study

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Abstract

Adsorption structures of benzothiophene and 7-methylbenzothiophene on MoS_2 catalysts were studied by ab initio molecular orbital (Becke3LYP) method. The π -bonded parallel configuration was more favored than the perpendicular adsorption through S, and the adsorption energies of both compounds were almost equal, i.e. the methyl group does not retard the adsorption. Also, the reaction pathways of hydrogenation supposed to be the first step of the desulfurization were studied in vacuo, and the insertion of H_2 to S was found to be hindered by the methyl group. From the analyses of the molecular orbitals as well as the experimental facts that the methyl group(s) drastically lower the reactivity of heterocyclic sulfur compounds, we suggest that the function of catalysts is the promotion of the hydrogenation on S, and this step is hampered by the methyl group. © 1997 Elsevier Science B.V.

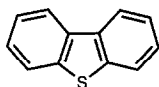
Keywords: Hydrodesulfurization; Benzothiophene; 7-methylbenzothiophene; Molybdenum sulfide; Molecular orbital

1. Introduction

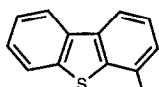
Deep desulfurization of light oil is an urgent subject from the environmental concern because the combustion of sulfur compounds contained in the fuel oil produces SO_x which is one of the major reasons for air pollution. Even under the deep desulfurization conditions, heterocyclic sulfur compounds such as dibenzothiophene (DBT) **1**, and particularly those substituted by alkyl group(s), e.g. 4-methyldibenzothiophene (4-MDBT) **2** and 4,6-dimethyldibenzothiophene (4,6-DMDBT) **3**, are hardly decomposed, thus the elimination of these refractory compounds is

a present key issue in the petroleum industry. In the case of DBT, methyl substitutions at position 4 and/or 6 drastically lower the hydrodesulfurization reactivity, but the roll of the methyl group is still controversial. Occasionally compounds in the thiophene family were postulated to be adsorbed at the coordinatively unsaturated site of the catalyst perpendicularly through their sulfur atom [1,2]. And the low desulfurization reactivity of these compounds was explained by the difficulty in the adsorption due to the steric hindrance of methyl groups. Recent studies, however, suggested that the flat coordination via their π electrons of the conju-

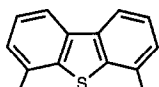
gate ring is favored and that the adsorption is not hindered or even strengthened by methyl groups, which contradicts the explanation above.



1



2



3

Kabe and Ishihara [3] calculated the reaction rate constant and adsorption equilibrium constant of DBT, 4-MDBT, and 4,6-DMDBT based on the Langmuir–Hinshelwood equation, and from the temperature dependence of these constants they determined the activation energy and the adsorption energy, respectively. The activation energies were inversely proportional to the reactivity as expected, i.e. $\text{DBT} < 4\text{-MDBT} < 4,6\text{-DMDBT}$, while the adsorption energy of the latter two was higher than that of the first. This result suggests that the low reactivity of methyl-substituted DBTs is not due to the difficulty in the adsorption on the catalyst. They inferred that DBTs are adsorbed on the catalyst through their π electrons because the sulfur bonded mode should be sterically hindered by the methyl substitutions.

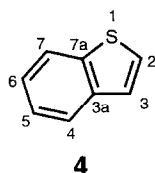
Meille et al. [4] applied the competitive catalytic reaction kinetics to study the adsorption equilibrium constant of DBT and 4-MDBT. From the reactivity ratio of the mixture, which is defined by the ratio of the adsorption rate and of the surface reaction rate, and the reaction rate constants of individual compound determined separately, the ratio of the adsorption equilibrium constant was estimated. Their results

demonstrated that the adsorption equilibrium constants of these two compounds are equal, and suggested that the molecules are adsorbed flat on the catalyst surface. The difference in reactivity is therefore due to the variations in the surface reaction rate probably caused by the steric hindrance of the methyl group during the approach of hydrogen.

It is well known that the desulfurization of DBTs follows one of two reaction pathways: one is hydrogenation of the neighboring aromatic ring followed by hydrogenolysis (hydrodesulfurization route: HDS) and the other is direct hydrogenolysis (direct desulfurization route: DDS). The products of (4-M) DBT desulfurization via respective routes are (methyl substituted) cyclohexylbenzene and biphenyl. Kabe and Ishihara [3] analyzed the desulfurized products of 4-MDBT and observed that the activation energy of the DDS route is close to that of total conversion of 4-MDBT, or higher than that of DBT decomposition. The reaction barrier in the HDS route was, on the other hand, close to that of DBT conversion. Meille et al. [4] also noticed that HDS product selectivity increases markedly in the case of 4-MDBT as compared to DBT.

Angelici [5] reviewed the coordination modes of thiophene in the organometallic complexes. In all determined coordination structures through sulfur (η^1 mode), the thiophene ring is not oriented perpendicular to the surface but is rather tilted. Binding by C–C π bond (η^2 mode) is preferred to η^1 when strong π backdonation from the metal to the π^* orbital of the ligand is expected. The most common mode is, however, the parallel adsorption via the entire thiophene ring (η^5 mode) found in the complexes of Cr, Mn, Fe, Ru, Rh, and Ir. Also, two electron reduction of the η^5 -complex gives the η^4 -complex, where the thiophene ring puckers and the sulfur atom moves away from the metal. The most common coordination mode of benzothiophene (BT) **4** and DBT is through their phenyl ring (η^6 mode) and no η^5 -complexes of them were reported. Furthermore, they also measured

the equilibrium binding constants for thiophenes in Ru complexes, where the tilted η^1 coordination was confirmed by X-ray diffraction. It was found that increasing the number of methyl groups on the thiophene increases its ability to bind to the ruthenium. Therefore the trend appears to be controlled by the electron-donating ability of the methyl groups, and the methyl groups at positions 2 and 5 show no steric effects.



In this study the following questions are concerned. (1) What is the adsorption structure of heterocyclic sulfur compounds on the catalyst surface? (2) What is the role that methyl groups play to lower the reactivity, whether interfering with the adsorption or with the following reactions? Experimental determination of the adsorption structures or the intermediates of reaction is prohibitively difficult because of their short life time. Computational chemistry has become a powerful tool to analyze the target from the atomic level. Hydrodesulfurization catalysts, however, have not been subjected to the quantitative calculations because they usually consist of transition metals which make the calculations formidable because the electron correlation must be taken into account, hence only qualitative discussions have been made so far (vide infra). The latest development of new theory together with fast computers has made this kind of calculations affordable.

Rong et al. [6] assumed that the active site is made of the coordinatively unsaturated Mo with 3 unsaturations and two SH. They used Mo_5S_9 clusters with or without surface SH groups as the active site models, and calculated the bond order of lying-flat adsorbed thiophene and β -dihydrothiophene by means of the DV-X α method. When no SH groups exist on the cata-

lyst surface, the C–S bond order of thiophene and β -dihydrothiophene increased upon the adsorption compared to that of the free thiophene. The presence of surface SH groups activates the C–S bond of adsorbed β -dihydrothiophene due to the interaction between H of SH and a carbon as well as some other interactions.

Smit and Johnson [2] investigated the interaction between the model cluster RuS_5^{6-} , which was obtained by the omission of one sulfur atom from the octahedrally coordinated metal, and thiophene standing on it perpendicularly by means of the scattered wave density functional method. It had been believed that the metal d-thiophene sulfur p interaction is dominant in this binding, but they pointed out the importance of the interaction between the π orbital on thiophene S and p orbitals directing toward thiophene on four S atoms. Furthermore, the same authors examined the Ni promoted MoS_2 catalyst using the model based on the structure determined by EXAFS [7]. When thiophene is adsorbed on the exposed Ni, catalyst sulfur p-thiophene π interactions are responsible for binding rather than metal d-(thiophene) sulfur p interactions, being consistent with the results derived from the previous simplified models. When thiophene approaches the catalyst surface sulfur, thiophene S-surface S bonding is established and the heat of adsorption in this mechanism was of a similar magnitude as that of the former case. The sulfur–sulfur mechanism does not require an S vacancy site for the adsorption and is therefore consistent with the Ni coordination number of 5–6 determined by EXAFS, which suggests the existence of surface sulfur [8]. Their models are, however, based on the assumption that thiophenes are adsorbed on the catalyst perpendicularly and the inability to calculate accurately the total energy with this computational method is well known.

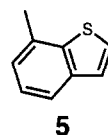
Ruette et al. [9] carried out the semi empirical CNDO calculations to study two molybdenum carbonyl–thiophene complexes: $\text{Mo}(\text{CO})_5$ (η^1 -thiophene) and $\text{Mo}(\text{CO})_3$ (η^5 -thiophene). Potential energy curves obtained by optimizing only

the thiophene–metal fragment distance while the other parameters were fixed revealed that thiophene is more strongly bound in the latter complex. From the analyses of the molecular orbitals they found that LUMO of the η^5 -complex is located on the thiophene ring, mainly on the C–S bond, and has an antibonding character. They suggested that a nucleophilic attack on C2 or C5 would result in C–S bond scission. In case of the η^1 -complex, LUMO is located on CO bonds, hence the activation of thiophene bonds toward a nucleophilic attack is not expected.

Ma et al. [10] calculated the electronic parameters of heterocyclic sulfur compounds by semi empirical PM3 method and found good correlations between the DDS reactivity and the electron density on the sulfur atom, and between the HDS reactivity and the bond order of the unsaturated bond. Furthermore, 4-MDBT and 4,6-DMDBT were found out of the DDS reactivity–sulfur electron density correlation, which they explained that methyl groups at 4 and/or 6 of DBT sterically retard the DDS because they prevent the S atom from interacting with the catalyst surface.

In an attempt to answer the questions mentioned above, we employed BT and 7-methylbenzothiophene (7-MBT) **5** as the model compounds of DBT and 4-MDBT, because the effect of methyl substitution occurring at the neighboring phenyl ring is expected to be similar and the computational cost is saved for their smaller sizes. The adsorption structures and binding energies of these compounds on the MoS_2 catalyst in three adsorption modes, namely η^1 , η^5 , and η^6 , were investigated by means of the HF-DFT hybrid Becke3LYP method whose quantitative reproducibility of various molecular properties has been noticed by many computational chemists. From the comparison between the adsorption modes, η^5 was found to be the most stable. In this mode as well as others, the differences of the adsorption energy between BT and 7-MBT were found negligible, which defies the hypothesis that hin-

dered adsorption by the steric effect of methyl groups is the reason for the low reactivity. Furthermore, because the DDS route is most markedly hampered by methyl groups, the reaction pathways supposed to be the first step of DDS, i.e. H_2 insertion to S atom, C–S bond, and two C's neighboring S, were investigated in vacuo. Among these hydrogenation steps, the barrier height for the H_2 insertion to S atom was found to be influenced by methyl substitution, and thus the role of the methyl was suggested to be the interference with this step. The possible function of the catalyst was also proposed from the analyses of the molecular orbitals.



2. Computational details

As the model of MoS_2 catalyst, the Mo_3S_6 cluster shown in Fig. 1 was extracted from the crystal data. This model satisfies the MoS_2 stoichiometry, thus it is electronically balanced, which is a crucial requirement to obtain the realistic adsorption chemistry. Furthermore, each Mo site is coordinated by four S atoms while the coordination number of bulk Mo in MoS_2 is six, thus Mo of our model can be regarded as the coordinatively unsaturated edge site. BT and 7-MBT were then placed on one of Mo sites in three modes corresponding to η^1 , η^5 , and η^6 , respectively (Fig. 2), and only

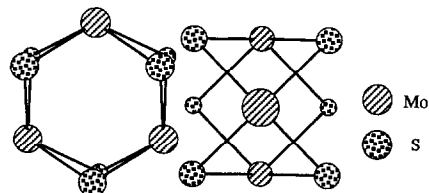


Fig. 1. Mo_3S_6 model (left: side view, right: top view).

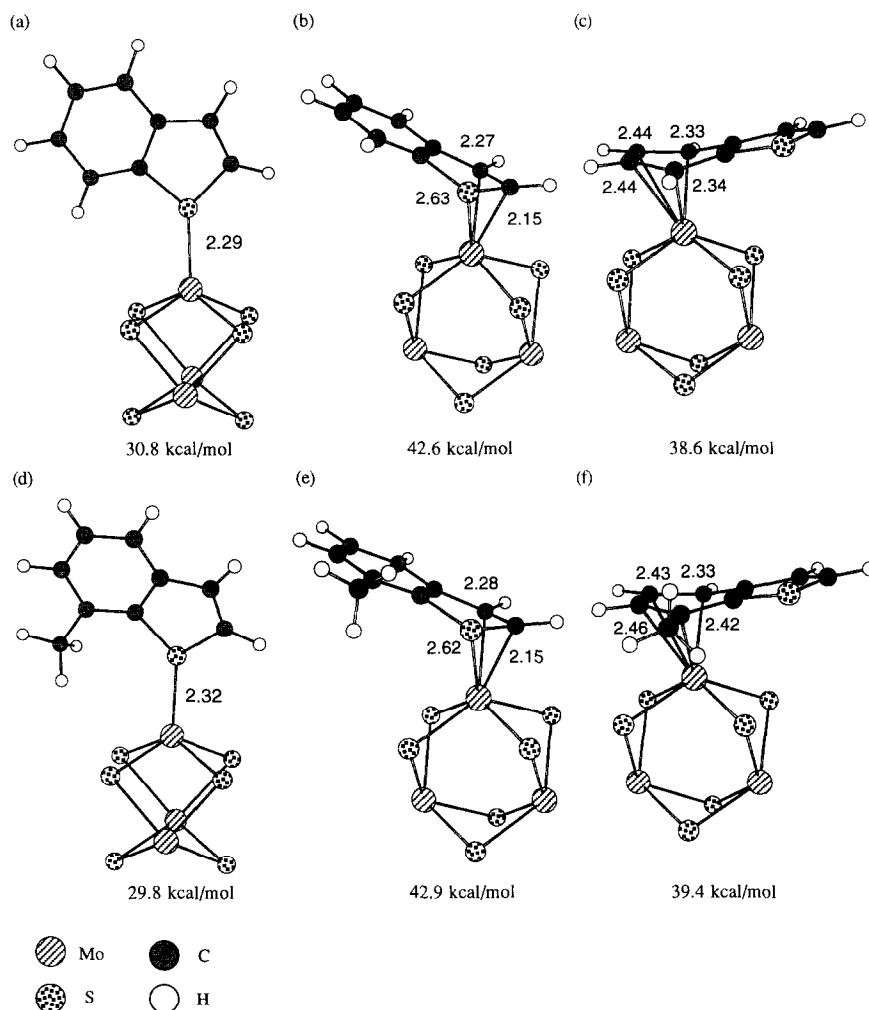


Fig. 2. Adsorption structures and energies of BT (a–c) and 7-MBT (d–f) in mode η^1 (a, d), η^5 (b, e), η^6 (c, f).

sulfur compounds were geometry optimized while the catalyst part was held fixed.

In order to examine the reaction pathway of the DDS route, which is most significantly hampered by methyl substitution, products of the H_2 insertion to the S atom, C–S bond, and two C's neighboring S, i.e. 1,1-, 1,2-, 1,7a-, and 2,7a-dihydrobenzothiophene, as well as the transition states leading to them were computed in vacuo. Geometry was completely relaxed and it was confirmed that the transition states have only one negative eigenvalue of Hessian and that descending from them along the intrinsic reaction coordinate leads to the reactants and the products. In case of the 1,1-form, where H_2 was

found to approach S from the side, two transition states corresponding to the insertion of H_2 from the phenyl side and from the other side were located.

All the calculations were performed by the HF-DFT hybrid Becke3LYP method which takes into account the electron correlation effect with the reasonable computational cost. The valence double zeta basis set with the effective core potential (LANL2DZ) augmented by the polarization function on only sulfur of thiophene was employed (no polarization function was placed on S of MoS₂). The reason for this additional basis function is to ensure the adsorption via η^1 mode and the insertion of H_2 to S,

where S becomes hyper valent and the d orbital on S is indispensable in such cases. Gaussian 94 [11] was employed for all the calculations.

3. Results

Calculated adsorption structures and binding energies are shown in Fig. 2. Among three adsorption modes, the flat coordination through the thiophene ring, η^5 , was found to be the most stable for both BT and 7-MBT. Adsorption through the phenyl ring, η^6 , was slightly less favored than η^5 , by 4 and 3.5 kcal/mol for BT and 7-MBT, respectively. Adsorption through thiophene S (η^1) was far unstable compared to the other two, and the adsorption energies in this mode were more than 10 kcal/mol lower than those in η^5 for both compounds. The η^1 adsorption structure of BT was perpendicular, while that of 7-MBT was tilted probably due to the steric effect of the methyl group. The adsorption energy of 7-MBT in the η^1 mode was, however, only 1 kcal/mol lower than that of BT. The bending motion of the thiophene ring adsorbed via S is therefore considerably soft and the sorbates must be fluctuating between perpendicular and tilted structures at elevated temperatures. Methyl groups hence do not retard the adsorption even in this mode. In modes η^5 and η^6 , which are more favorable than η^1 , 7-MBT binds stronger than BT by 0.3 and 0.8 kcal/mol, respectively. In all cases, the effects of the methyl substitution on the adsorption energies are negligible at the working temperature, hence it may be concluded that the effect of methyl groups which is responsible for the low reactivity of methyl substituted compounds is not hindrance of the adsorption on catalysts. Further discussions on the adsorption structure will be made below.

The structures of the dihydro products (right side of each row in Fig. 3, i.e. b, d, g, j, l, and n) and the transition states (left side and center of each row in Fig. 3, i.e. a, c, e, f, h, i, k, and m) of the hydrogenation supposed to be the first

step of DDS were calculated in vacuo. The relative energies of each state compared with the reactants (BT or 7-MBT + H_2) are also given under each structure in Fig. 3. In all cases the energy is higher than that of the reactant, thus their life time is expectedly short and the detection of these intermediates would be difficult. The lowest energy reaction path among these is the hydrogenation route to two carbons 2 and 7a (Fig. 3a–d). But the activation energies in this route are nearly the same for BT and 7-MBT. In case of the hydrogenation on S (1,1), H_2 was found to approach from the side as a result of the geometry search, and two transition states corresponding to the insertion of H_2 from the phenyl side and from the other side were obtained (Fig. 3e, f, or h, i). In the route where H_2 approaches from the phenyl side (Fig. 3f, i), the activation energy increased by 7.6 kcal/mol as a consequence of the methyl substitution. Therefore this route is hampered by the methyl group probably due to its steric effect. In the case of 7-MBT, the alternative route from the other side to attack the sulfur is available. But 4,6-DMDBT possesses methyl groups at both sides and thus H_2 insertion to S is expected to be strongly inhibited. 4-MDBT has only one methyl group, like 7-MBT, and H_2 may approach from the side of phenyl without the methyl group. But if H_2 insertion is a stochastic step, then the chance of H_2 approaching from the favorable side becomes half, which may be the reason for the lower reactivity of 4-MDBT than DBT, but not as low as 4,6-DMDBT. Finally, the hydrogenation of the C–S bond was considered. No significant difference was observed between the activation energies of the H_2 insertion to the positions 1 and 2 of BT and of 7-MBT (Fig. 3k, m). Many trials were devoted to identify the reaction path for the H_2 insertion to the positions 1 and 7a, and it was found that in this route the phenyl ring is forced to take a puckered structure that makes the intermediate in this route extremely unstable. Although we were unable to locate the transition state of this path, this route can safely be excluded from the

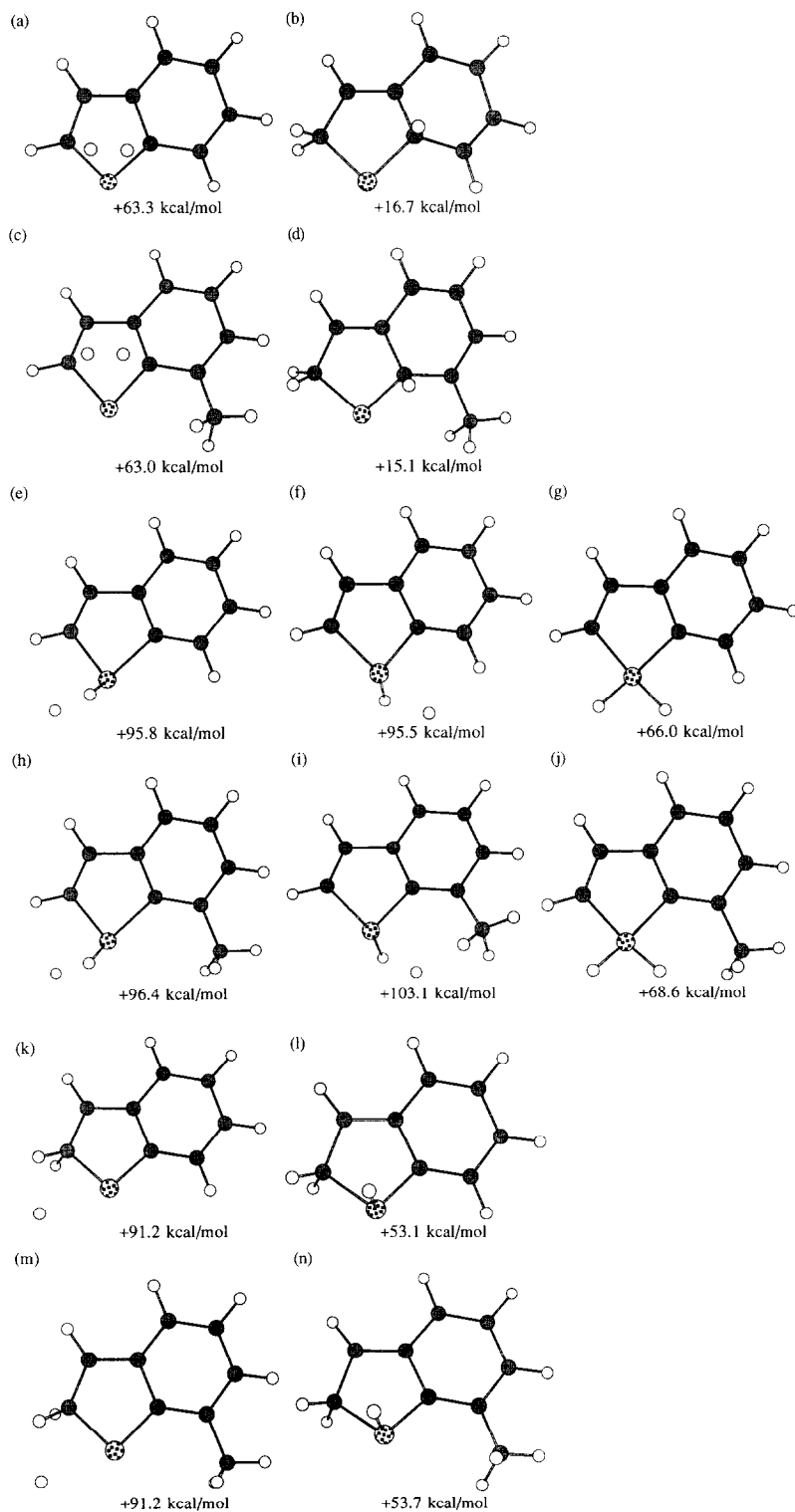


Fig. 3. Dihydro products (b, d, g, j, l, n) and transition states (a, c, e, f, h, i, k, m) of hydrogenation supposed to be the first step of DDS. Energies are differences from the reactants (BT or 7-MBT H_2). (a–d) H_2 insertion to 2, 7a. (e–j) H_2 insertion to 1,1. (k–n) H_2 insertion to 1,2. (a, b, e–g, k, l) Hydrogenation of BT. (c, d, h–j, m, n) Hydrogenation of 7-MBT.

consideration for its inhibitive high activation barrier.

4. Discussion

First we will discuss the adsorption mode of DBTs. The nature of the adsorption in the η^6 mode is expected to be similar for BT and DBT because they are adsorbed from the edge phenyl ring and the effect of the extra phenyl ring at the other side appears to be small. No strong interaction between the phenyl ring and the catalyst is expected in the η^1 mode, hence the adsorption energy of BT and DBT in this mode should also be similar. Therefore at least the adsorption via η^6 should be preferred to η^1 in the case of DBT. In the η^5 coordination BT is slightly out of the horizontal plane with its free C2–C3 bond downward. In the case of BT one side of the thiophene ring is open while DBT has phenyl rings at both sides. Therefore the η^5 mode is expected to be less favored by DBT. Preference of the η^6 mode was also suggested by the studies on the organometallic complexes [5].

The adsorption energy of BT through the phenyl ring (η^6) is expected to be strengthened by the methyl group for its electron donation effect. Calculated binding energies of BT and 7-MBT in this mode were, however, almost equal. The insensitivity of the adsorption energies to the methyl substitution is consistent with Meille's report [4]. But the studies on the organometallic complexes by Angelici revealed that methyl substitution on the thiophene increases the binding energy [5], and also Kabe and Ishihara concluded that 4,6-DMDBT is adsorbed more strongly on the catalyst than DBT does [3]. Further studies with more possible adsorption species may be required to clarify this point.

H_2 insertion to S was found to be retarded by the methyl group from the calculations in vacuo, probably due to the steric effect. But the lowest energy path is the hydrogenation to two car-

bons, which is not affected by methyl substitution. The function of the catalysts is to lower the activation energy of a certain reaction route, hence the reaction pathway on the catalyst is not always the same as that in vacuo. Actually our calculations based on the same computational models used here in vacuo (not presented here) revealed that the activation energy of the H_2 insertion to the phenyl ring is lower than any of the hydrogenation routes considered here. Hydrogenation on the phenyl ring, however, leads to the HDS instead of DDS, which contradicts the experimental findings that DDS is favored over HDS at least in the case of DBT when decomposed by conventional catalysts [3,4]. Therefore, in order to investigate the reaction path on the catalyst, although they are qualitative, HOMOs of the adsorbed compounds were analyzed (Fig. 4). Because HOMO of the BT-catalyst system is localized on the MoS_2 part and is not involved in the reaction, the highest occupied molecular orbital among those localized on the adsorbate are drawn in this figure. While HOMOs of isolated BT, η^1 -, and η^5 -

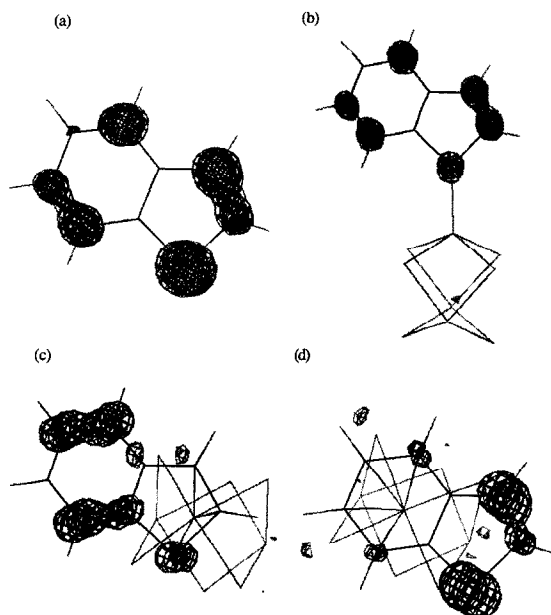


Fig. 4. HOMO of isolated BT (a) and the highest occupied molecular orbital among those localized on BT of complexes in η^1 (b), η^5 (c) and η^6 (d).

complexes have a considerable contribution from the phenyl ring, it is localized only on the thiophene ring with a large contribution from the sulfur in case of the η^6 -complex. Therefore when BT is adsorbed in the η^6 mode, the electrophilic attack of H (or proton) on S is expected to be promoted. The importance of the electrophilic attack on S in the DDS route is consistent with the good correlation between the DDS reactivity and the electron density on sulfur [10]. Furthermore, Mulliken population analysis of the transition state of H_2 insertion to S revealed that the hydrogen atom closer to sulfur is positively charged while the one which is far from S bears a negative charge. This indicates that the insertion of H_2 proceeds from the first H^+ attack on S followed by H^- induction. In this study we considered the H_2 insertion but the proton source may be SH species present on the catalyst surface. The importance of surface SH groups was pointed out previously [6], and should thus be studied further. Adsorption in the η^5 mode increases the contribution from the unsaturated bond of the phenyl ring in HOMO, thus this mode may promote the HDS route.

According to the above considerations we propose the adsorption structure, reaction mechanism, the function of catalyst, and the role of methyl groups as follows. DBT favors to be adsorbed on the catalyst in the η^6 mode. This results in the enhancement of the S contribution in HOMO of DBT, which promotes the electrophilic attack of hydrogen (or proton) on sulfur. In the case of 4-MDBT and 4,6-DMDBT, however, the methyl group(s) retard this hydrogenation step, which is responsible for the low reactivity of these compounds.

5. Conclusion

Our calculation revealed that BT and 7-MBT are not adsorbed vertically on MoS_2 vacant sites through S (η^1), but horizontally through their π electrons of the conjugate ring (η^5 or η^6), with a slight favor of the adsorption from the thio-

phene ring (η^5). In all adsorption modes, the binding energies were found insensitive to the methyl substitutions, and the hindered adsorption by the steric effect of methyl groups was thus ruled out as the reason for the low reactivity.

Calculated reaction pathways supposed to be the first step of DDS revealed that the lowest energy path is the H_2 insertion to two carbons neighboring S (2 and 7a) in vacuo. However, the activation energy of this route is not affected by the methyl group. For the insertion of H_2 to S, when hydrogen approaches from the phenyl ring side, the activation energy increased as a result of the methyl substitution. Also, from the analysis of HOMO of the adsorbate, it was found that the η^6 mode makes HOMO to localize on the thiophene ring with a significant contribution from sulfur, and thus promotes the electrophilic attack of hydrogen on S. This route is, however, hampered by the methyl groups at 4 and/or 6 position of DBT.

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