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## 論 文 内 容 要 旨

In this dissertation, a variety of periodic calculation methods are introduced and successfully applied for accurate calculations of physicochemical properties of some organic molecules on different metallic nascent surfaces. Moreover, the analysis method is developed and introduced. The periodic density functional calculations combined the plane-wave basis and the pseudopotential method are found to be an useful tools for accurate estimation of the adsorption properties of organic molecules on metal surfaces at relatively low computational cost and also for prediction of a new lubricant which can be used in tribology field. The Quantum Chemical Molecular Dynamics method was adopted to investigate the dynamical adsorption properties and gave the reasonable results for applying to large-scale systems.

In chapter 3, the first principle density functional theory (DFT) calculations have been carried out in order to investigate the adsorption properties of various organic molecules on the clean Al surfaces. We have calculated the adsorption energies for methanol, ethylene, ketone, and dimethyl ether molecules, which are widely used in the lubrication field. It has been found that the calculated adsorption energies are in good agreement with the experimental data. The adsorption energy order of the organic compounds can be presented

as follows: methanol > ketone > dimethyl ether > ethylene. Furthermore, the molecular adsorption of ethylene, methanol and methanethiol on Fe (100) surface is reported in chapter 2. It has been observed that the molecular adsorption of methanethiol on the Fe (100) surface occurs more easily than that of ethylene and methanol. The abridge adsorption site for methanethiol and ethylene are more stable than other sites, in case of methanol adsorption, the on-top site is favorable.

In chapter 4, the nature of S-Au bond forming was studied through methanethiol molecule adsorbed on Au (111) surface. In order to take into account the influence of initial structure to adsorption system, two different initial structures as 4-fold and bridge initial structure were considered. After optimization calculation, we got the almost similar structure as on-top site geometry. Further insight into the association of S-Au bound comes from the density of states (DOS) were accounted for adsorption of methanethiol on Au (111) surface. On the basis of the atomic density of states analysis, the p orbital of S atom contributes most to this state (89%) in the adsorption system. This indicates the strong interaction occurred between the S atoms and the surface Au atoms. In chapter 4, the prediction of the adsorption property for large organic molecules on several metallic surfaces was also carried out. We found that the component of orbital for all three surfaces (Fe, Cu and Au) are mainly from d states, it is also certified d orbital play an crucial role in transition metallic surface, this standpoint is in agreement with several previous research. It is suggested that iron surface should show the strongest activity than that of copper and gold surface. On the basis of analysis from electron transfer direction, it was showed that there is the same tendency:  $C_2H_5SC_2H_5$  has highest adsorption activity on iron surface compared to copper and gold surface; iron has high adsorption activity for  $C_2H_5SC_2H_5$  and  $C_2H_5OC_2H_5$  than copper and gold surface; after iron surface, copper surface should has higher activity than gold surface.  $C_2H_5SC_2H_5$  has higher adsorption activity than  $C_2H_5OC_2H_5$  molecule.

In chapter 5, firstly, structure parameters for benzene molecule are reported. Secondly, the computed adsorption energies and geometries at the different high symmetry sites are presented. Hollow-hcp and hollow-fcc adsorption site are observed as activity adsorption sites. Thirdly, we analyze the change of the orbital energies upon adsorption in order to gain insight in the site preference of benzene. In the case of iron surface, d orbital of iron plays a crucial role in adsorption system. In the case of benzene molecule, the analysis of partial density of states confirms the assumption of bonding via the  $\pi$  states: the  $\pi$  states are broadened and shifted to lower energies. This chemical shift stresses the important role of the  $\pi$  states in the adsorption. In addition, the donation of electrons from the substrate to the adsorbed molecule leads to a partial occupation of an additional antibonding

$\pi$  state for adsorption. Thus C atom bonded to an iron atom, and Fe-C bond came into being. In the final section, the molecular dynamics behavior is elucidated for benzene adsorbed on iron surface. Corresponding to the adsorption sites that we mentioned before, we found the frequency of hollow-hcp sites arised about 60% and hollow-fcc sites took place around 20% among 2000 steps. This tendency is in agreement with quantum calculation in this chapter. From the simulation, C-H bond distorted from aromatic ring, and the H atoms are tilted away from the iron surface. In this chapter, even though this study did not give the concrete value for entropy, the effect of entropy has already been reflected during calculation by colors.

In chapter 6, the nature of benzene/cyclohexane adsorbed on variety gold nascent surfaces is investigated by using accelerated quantum chemical molecular dynamics method that is developed by our group. From orbital shapes for clean gold surface, point defect surface and step defect surface, the high reaction orbitals are appeared on defect surfaces. We found that both benzene and cyclohexane molecules are easily adsorbed in point defect and step defect nascent gold surfaces. Step defect surfaces showed high activity than that of point defect surface, cyclohexane systems were obtained high adsorption energies than that of benzene adsorption energies. The nature of such adsorption systems was investigated from charge information and HOMO-LUMO analysis. The sequence is in agreement with adsorption energy.

In the present dissertation, the theoretical investigations about adsorption system are proved to be reasonable and reliable for both DFT and QCMD methods. At the same time, the applicability and effectiveness of these two methodologies are justified, since the various experimental justifications are reproduced very well. On the basis of these periodic models and methodologies, some essential issue especially regarding the active site of molecule on nascent surfaces have been elucidated by means of a series of adsorption studies. Although adsorption energy cannot reflect all the factors like friction coefficient, friction velocity, viscosity coefficient and so on, it is still the important factor for reflecting the strength of coating in lubricants. Furthermore, some properties have been predicted and revealed for deeply understanding the adsorption systems and contributing towards design and development of lubricant in tribology fields.

# 論文審査結果の要旨

近年、機械の高性能化が進むに連れて、トライボロジー特性の向上という潤滑剤に対する一層の厳しい要求があるとともに、省資源・省エネルギーを実現するための潤滑剤など、従来の潤滑剤の改良や新しい潤滑剤の開発への期待が高まっている。

通常、金属材料の表面は金属酸化物や有機汚染物質に覆われているが、これらが境界潤滑条件下で摩擦など機械的作用により除去されると金属新生面が露出する。潤滑剤を開発する際に、露出する新生面における潤滑剤分子の挙動が重要なファクターとして認識されつつある。しかし、実験的試行錯誤に基づく従来の開発手法は、膨大な費用と時間を要し、効率的な潤滑剤の開発手法とは言えない。そこで、本論文では、計算手法を用い、金属新生面における潤滑剤分子の吸着挙動に関する理論研究を行っている。本論文ではその理論研究をまとめ、潤滑剤の開発に役立つ理論根拠を示したので、全7章よりなる。

第1章は緒論であり、本研究の背景、目的、概要を述べている。

第2章は本研究に用いた計算手法である電子密度汎関数法 (DFT) と高速化量子分子動力学法 (QCMD) について述べている。

第3章はトライボロジー分野において広く使われている Fe と Al 新生面をそれぞれ用い、有機分子との吸着特性を検討している。Al 新生面において、methanol > ketone > dimethyl ether > ethylene という吸着活性の序列が得られている。Fe 新生面において、メタンチオールが一番吸着エネルギーが高く、続いてエチレン、メタノールの順番であることが明らかにされている。これらに関する詳細的な解析について述べている。

第4章は硫化添加剤の金新生面への吸着特性について述べている。硫黄と金の間に結合が生成されていることが理論計算から明らかにしている。更に、実験結果を再現するだけでなく DFT 手法を用いて特性の予測を試みている。ジエチルモノスルフィードがジエチルエーテルより金、鉄、銅新生面に吸着しやすいとの予測を得ている。各種金属新生面の吸着強さについても検討を行い、鉄 > 銅 > 金という序列の予測が得られている。

第5章は当研究室で開発した高速化量子分子動力学法 (QCMD) を用い、ベンゼン分子の鉄新生面上での動的な挙動について検討した結果を述べている。ベンゼンの平面構造が崩れ、水素が解離するという結果が得られている。

第6章は欠陥を持つ金新生面におけるベンゼンとシクロヘキサンの吸着特性に関して述べている。欠陥を持つ金新生面の吸着活性が高く、更に、ポイント欠陥表面よりステップ欠陥表面の方が吸着力の強いことが明らかにしている。また、シクロヘキサンがベンゼンより吸着しやすい傾向が確認されている。

第7章は本研究で得られた結果の総括である。

以上要するに本論文は、金属新生面における潤滑剤の吸着挙動について理論的に検討・機構の解明に成功したものであり、新規潤滑剤の開発およびその為の理論設計手法の発展に対して寄与するところが少なくない。

よって、本論文は博士 (工学) の学位論文として合格と認める。