様　式　Ｃ－１９、Ｆ－１９－１、Ｚ－１９　（共通）

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研究課題名（和文）Large range functionalization of h-BN monolayer by Carbon doping

研究課題名（英文）Large range functionalization of h-BN monolayer by Carbon doping

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研究成果の概要（和文）：本研究では、実験の系に近い、複数の炭素原子をドープしたh-BNのバンド構造と酸素分子の活性化について検討した。触媒のバンド構造と活性が深く関連しているルールを利用し、複数の炭素原子をドープしたC@h-BNの安定性、バンド構造と触媒活性について理論計算にもとづき検討した。1割から5割の炭素原子を様々な形を考慮して、ドープする形や割合とエネルギー差、活性領域の関係を明らかにした。また、複数の酸素分子の同時での活性化とその時の吸着エネルギーの変化を明らかにした。

研究成果の学術的意義や社会的意義
The factors that are responsible for oxygen activation activation is elucidated. The relationship between doped atoms and properties of h-BN surface will be clarified. This research plan will provide a theoretical direction for the experimental design of material for reaction involving O2 molecule.

研究成果の概要（英文）：By controlling the energy difference between the highest occupied defect level of the doped atoms and the bottom of the conduction band of h-BN, the catalytic activity and active area of surface can be tuned. In the present research, the system closed to the experimental ones with multiple carbon atoms was investigated. The influence of, concentration, edge effect, the geometry of doped carbon atoms on the electronic properties and the stability of C@h-BN surface was clarified. The catalytic activity of C@h-BN surface for O2 molecule activation can be predicted by the electronic structure of the surface. The computational time is high decreased. The C@h-BN surface with high catalytic activity of O2 molecule activation was proposed theoretically.

研究分野：計算化学　触媒化学

キーワード：DFT　h-BN　表面　ドープ　酸素分子　触媒活性

## １．研究開始当初の背景

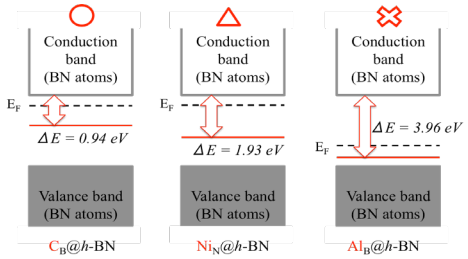


**Fig.1** Scheme of the band structure of *h*-BN surface with doped atoms

The activation and dissociation of molecular oxygen on two-dimensional (2D) surface is a topic of interests due to its wide industrial applications, such as oxidation of carbon dioxide, and oxygen reduction reaction (ORR) in fuel cells and many others. Until now, the catalysis with metal, especially with noble metals such as Pt, Au, Pd, are the best catalyst for various reactions including $O_2$ molecule. While those noble metals are expensive and difficult to be used commercially. To solve this problem, many works has been done to design efficient catalyst without metal. Graphene is one of the examples, it becomes very catalytic active with introducing heteroatoms, such as B or N atoms. However, to my best knowledge, most of the theoretical works are only focus the active sites near by the doped atoms. *h*-BN is very stable material and has very similar geometrical structure with grapheme, but rarely be considered as a catalyst. Because it has a very large band gap, and hardly interact with reactants. *h*-BN surface can become functionalized to be catalytic active and can be applied to catalyze various of reactions. We have done a series of work to show that it can also be modified to be catalytic active by introducing other atom, vacancy or metal support. We found that C atom doping in the B position of *h*-BN ($C_B$@*h*-BN) produces *n*-type semiconductor BN material with noticeable catalytic activity for $O_2$ activation in the large area. It is shown that the activation area for oxygen molecule on *h*-BN surface with impurity highly depends on the energy gap ($\Delta E$) between the highest occupied defect level of doped atom (red line) and the bottom of the conduction band of BN atoms as the example shown in Fig.1. However, the synthesis of one atom doped *h*-BN surface is still a challenge for experiments.

## ２．研究の目的

The purpose of this research is to design a surface with high catalytic activity and activation area based on h-BN material. As the synthesis of one atom doped *h*-BN surface is still a challenge for experiments, in this plan, the *h*-BN surface with introducing multiple C atoms, which has been obtained in experiment. [1] was investigated for $O_2$ molecule activation. The target of the research is to clarify the edge effect, geometrical effect and stability of the doped C atoms in *h*-BN surface on the catalytic activity and area for oxygen activation; To investigate the concentration effect of doped C atoms on the electronic properties of C doped *h*-BN surface; To propose a theory to tune the electronic structure and catalytic activity of C doped *h*-BN surface will be proposed; To investigate catalytic activities and active area of multiple C doped *h*-BN surface for oxygen molecule adsorption.

## ３．研究の方法

The calculations are carried out using density functional theory (DFT) with the gradient-corrected exchange-correlation functional of Wu and Cohen (WC) as implemented in the SIESTA code. All calculations are performed accounting for spin polarization. Periodic boundary conditions are used for all systems including free molecules.

４．研究成果

Firstly, the effect of concentration effect of doped C atom on $\Delta E$ of C@h-BN was investigated. It is shown that there are three factors related to the $\Delta E$ of C@h-BN: the number of doped C atoms and doped position; for each given sized C atoms, the area of C atoms formed; and the edge (zizag and armchair edge) C formed in the *h*-BN surface.

Secondly, the concentration effect of doped C atoms on the stability of C@h-BN was studied. The stability of C@h-BN was calculated by eq. 1. $E_{tot}$ is the electronic energy of total system, N indicated the number of atoms in the system, and $\mu_i$ indicates the chemical potential of B, C and N atoms. It is shown that the stability of C@h-BN surface is different in the B-rich or N-rich experimental condition. It is possible to control the geometry of C@h-BN surface with tuning the ratio of B or N source.

$$E_{form} = (E_{tot} - \sum_i n_i \mu_i)/N \quad (1)$$

Thirdly, the catalytic activity of C@h-BN surface for $O_2$ molecule activation was proved. The C@h-BN with small $\Delta$E was chosen to investigate catalytic activity for $O_2$ activation. The relationship between the number of doping C atoms, doping position and the activation energy of $O_2$ molecule was clarified. It is also found that activation area and the number of activated $O_2$ molecule highly depend on the spin multiplicity of C@h-BN.

According to these investigations, the influence factors of the chemical and physical properties of C@h-BN were investigated. The catalytic activity of C@h-BN surface for $O_2$ molecule activation can be predicted by the electronic structure of the surface. The computational time is high decreased. The C@h-BN surface with high catalytic activity of $O_2$ molecule activation was proposed theoretically. However, there is still big gap with experimental system. Therefore, the investigation of catalytic activity of h-BN surface supported metal cluster was chosen as the first try. Experimental results and theoretical calculations indicate that surface engineering on defects of Ni/h-BN catalyst favor the adsorption and catalytic activation of $CH_4$ and $CO_2$ via electron donor/acceptor mechanisms of metal-support interaction.

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Theoretical study on geometry effect on the catalytic activity of gold clusters

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(2) 高 敏
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2018 年 10 月 29~30 日統合物質創製化学研究推進機構第 4 回国内シンポジウム, 福岡
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h-BN/Au(111)に担持した金クラスターの水素発生反応に対する触媒活性に関する理論的研究
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2017 年 5 月 10 ~ 12 日 第 15 回ナノ学会　(札幌)

〔図書〕（計 0 件）

〔産業財産権〕
○出願状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
出願年：
国内外の別：

○取得状況（計 0 件）

名称：
発明者：
権利者：
種類：
番号：
取得年：
国内外の別：

〔その他〕
ホームページ等
http://theory.cat.hokudai.ac.jp/?page_id=979

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