学 位 論 文 題 名

Theoretical study of catalytic activity of gold clusters on the h-BN substrate

（h-BN 基板に担持した金クラスターの触媒活性に関する理論的研究）

学位論文内容の要旨

The present work is focused on the theoretical investigation of catalytic properties of small gold clusters supported on the hexagonal boron nitride (h-BN) substrate. In particular, I have performed systematic investigation how support affects physical and chemical properties of gold. Currently, an extensive research is devoted to understanding the catalytic properties of gold. Such an interest is stipulated by the fact that gold nanoparticles are active even at room temperatures [1] that makes them unique catalysts for many industrial applications. One of the most important factors in gold nanocatalysis is a support effect. It was demonstrated that metal oxide supports [2,3] (such as, MgO, TiO_2, Al_2O_3, Fe_2O_3, etc.) can considerably influence the catalytic properties of the supported gold nanoparticles and modify (enhance or suppress) their reactivity. On the other hand it is commonly believed that inert supports, such as h-BN, do not affect the electronic and geometrical structures of the supported nanoparticles, and hence, such nanoparticles can be considered as pseudo-free. In spite of intensive theoretical and experimental studies the origin of catalytic activity of supported gold nanoparticles remains highly debated and poorly understood, because it depends on many factors [3,4] (size, geometry and electronic structure of nanoparticles, charge transfer from/to the surface, interface effects, presence of defects, etc.). Surprisingly, catalytic activity of gold clusters supported on h-BN surface has never been studied theoretically, in spite of the fact that experiments demonstrate high catalytic activity of gold clusters supported on h-BN [4]. Thus, there is an urgent need to elucidate activity of small gold clusters supported on the inert h-BN surface. In the present work, I clarify whether the origin of catalytic activity of small gold clusters supported on h-BN derives from the gold itself, or the 'inert' h-BN support is not inert for gold and can modify its catalytic properties. In order to answer this question, I have studied theoretically the structural, electronic, and catalytic properties of Au and Au_2 supported on the pristine and defected h-BN surface.

In **Chapter 1**, a detailed research history of nanocatalyst and the objectives of the present research are presented as general introduction. In **Chapter 2**, an overview of the basic theoretical methods used for calculations is given, while in **Chapter 3**, the methodology on how to choose various important parameters and approaches used for calculations is described. In **Chapter 4**, the adsorption, activation, and dissociation of O_2 on Au atoms supported by h-BN are discussed. It is demonstrated that adsorption and catalytic activation of O_2 on Au and

Au_2 supported by h-BN can be affected by the interaction with the h-BN support via electron pushing and donor/acceptor mechanisms. It is shown that even weak interaction of Au and Au_2 with the defect-free "inert" h-BN surface can have an unusually strong influence on the binding and catalytic activation of the molecular oxygen. This effect occurs due to the mixing of the 5d orbitals of the supported Au and Au_2 with the N-p_z orbitals. Although the defect-free h-BN surface does not act as a good electron donor for the supported O_2-Au, it promotes an electron transfer from the Au to O_2, pushing electrons from the gold to the adsorbed oxygen (**Fig**). In the case of defected h-BN surface Au and Au_2 can be trapped effectively by N or B vacancy and impurity point defects. Strong adsorption on the surface defects is accompanied by the large charge transfer to/from the adsorbate. The excess of the positive or negative charge on the supported Au and Au_2 can considerably promote their catalytic activity. Such a phenomenon can be particularly important for understanding the mechanisms of the catalytic activity of the supported small gold particles in oxidation reactions employing molecular oxygen.
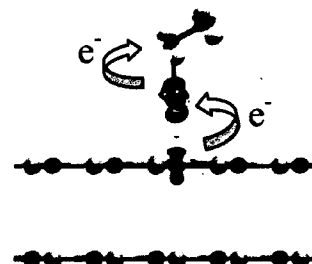
Fig. Isosurfaces of the electron density difference in O_2-Au induced by the interaction of Au with the h-BN surface.

In **Chapter 5**, the mechanism of CO oxidation by O_2 ($2CO + O_2 \rightarrow 2CO_2$) on Au atoms supported on the pristine and defected h-BN surface has been studied. CO oxidation occurs on Au atom supported by pure h-BN and V_B@h-BN, and at interface boundary for Au-V_N@h-BN, where V_B and V_N denote vacancy defects for B and N atoms, respectively. It is shown that catalytic reaction of CO on free and supported gold atom proceeds via two different pathways for CO oxidation: a two-step pathway where two CO_2 molecules are formed independently and self-promotion pathway where oxidation of the first CO molecule is promoted by the second CO molecule. Interaction of Au with the defect-free and defected h-BN surface considerably affects the CO oxidation reaction pathways and barriers. The influence of h-BN support on the supported Au atom results in decrease of the CO oxidation barrier.

On the basis of my theoretical studies, I have made an important conclusion that pristine and defected h-BN support cannot be considered as an inert support for small gold clusters. General conclusion and future perspective are presented in **Chapter 6**.

Reference
[1] M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.* **16**, 405 (1987).
[2] M. Haruta, *Catalysis Today* **36**, 153 (1997).
[3] M. Haruta, *Faraday Discussion* **152**, 11 (2011).
[4] M. Turner *et al., Nature* **454**, 981 (2008).

学位論文審査の要旨

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博士学位論文審査等の結果について（報告）

　金は、バルクでは反応活性を示さない一方、微粒子にしてサイズを小さくしていくと触媒活性が急激に増大することが知られており、常温条件下でも触媒活性を示すため工業的重要度も高く、近年多くの実験研究・理論研究の対象となっている。金微粒子の反応の選択性については、担持基板の性質も関与していることが実験研究により示唆されているが、その役割については十分に理解されているとは言い難い。特に不活性な基板に担持した場合、金微粒子の触媒活性への影響はほとんど無いものと考えられているが、理論研究も皆無であり、実際の影響の有無についてはよくわかっていなかった。

　本論文では、不活性な基板が金クラスターの触媒活性に影響を及ぼす可能性の有無に焦点をあて、基板として実験に用いられている六方晶窒化ホウ素（h-BN）を題材として、欠陥をもたない完全な h-BN 基板と、異なるタイプの欠陥を導入した 4 種の h-BN 基板に金クラスターを担持して、金クラスターへの酸素分子の吸着や金クラスター上における酸素分子の解離について系統的な理論計算を実施し、金クラスターの触媒活性への基板効果を議論している。理論計算には周期境界条件を考慮した既存の密度汎関数法プログラム SIESTA を利用しているが、信頼性の高い計算を実現するため、酸素分子、金クラスター、BN を同時に計算する際に必要となるパラメーターの最適化を行うなど、慎重な予備計算を行った上で理論計算を実施し、精緻な議論を展開している。本計算により、ホウ素原子の1つを窒素原子に置換した窒素不純物欠陥の導入が金クラスターの触媒活性を上げる上で最も有効なこと、基板に欠陥がある場合には基板と金クラスターの間に強い電子移動があり、金クラスターと吸着酸素の相互作用に大きく影響すること、さらに欠陥がない基板で金クラスターとの相互作用が弱い場合でさえ、基板の影響で金から酸素への電子移動が助長され、酸素分子がより活性化されることを明らかにしている。特に、不活性基板が金クラスターと吸着酸素分子との相互作用に及ぼす効果を「electron pushing 効果」と名付け、不活性基板の特異的効果として新しい概念を提案し、当該分野の実験研究に重要な知見を与えている点は高く評価される。

　これを要するに、著者は、不活性と考えられている基板であっても金クラスターの触媒活性に強く影響を及ぼしていることを理論計算に基づき初めて解明したものと評価でき、金クラスターの触媒機構の微視的理解に対して貢献するところ大なるものがある。

　よって著者は、北海道大学博士（理学）の学位を授与される資格があるものと認める。