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研究課題名(和文) 豊富元素を活用した新規ナノ触媒の理論設計

研究課題名(英文) Theoretical design of novel nanocatalysts using abundant elements

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研究成果の概要(和文)：本研究では構造と担持基板の効果に着目して、豊富元素新規ナノ触媒の理論設計を行った。構造が柔軟な金属クラスターの最安定および準安定構造の二原子分子吸着解離反応の触媒経路を、反応経路自動探索法を用いて系統的探索して構造異性体がより高い触媒活性を持ちうることを初めて明らかにした。酸化物基板担持によって機能修飾されたNiクラスター触媒のH₂脱離反応に加えて、単層の窒化ホウ素、あるいはそのNあるいはCによる部分置換体が酸素還元反応や水素精製反応などにおける新規電極触媒として有望であることを明らかにした。以上、豊富元素化合物を活性化して貴金属を代替する新規触媒材料開発に向けた設計指針を十分明らかにできた。

研究成果の学術的意義や社会的意義

Strategy for a systematic analysis and prediction of reactivity of small metal clusters accounting for structural fluxionality has been developed. It is demonstrated the ability to functionalize inert materials and design effective nanocatalysts using materials had never been considered as catalyst.

研究成果の概要(英文)：The proposal has been devoted to theoretical design of novel nanocatalysts based on abundant elements with the primary focus on elucidation of the structural and support effects. We have performed systematic investigation on reactivity of metal clusters in the regime of structural fluxionality by adopting the global reaction route mapping (GRRM) technique for the processes of H₂, O₂, and NO adsorption and dissociation. We have revealed the important role of the support effects for functionalization of Ni clusters for hydrogen elimination reactions; performed theoretical design of a number of new and effective electrocatalysts for the oxygen reduction reaction (ORR) and the hydrogen evolution reaction (HER) based on the hexagonal boron nitride, nitrated carbon and carbon nitride. Our calculations demonstrate the principal ability to functionalize inert materials opening new way to design effective Pt-free catalysts for fuel cell technology. The research plan has been fully completed.

研究分野：化学

キーワード：クラスター 理論化学 触媒反応 表面・界面

様式 C - 19、F - 19 - 1、Z - 19、CK - 19 (共通)

1 . 研究開始当初の背景

Nanocatalysts possess unique properties that significantly depend on the size, structure, morphology of nanoparticles, type of the support, etc. and hence can be controlled by these factors. This feature opens up new possibilities for atom-by-atom design of nanocatalysts with tailored chemical activity and selectivity. Moreover, it can be possible to functionalize even inert nanomaterials to work as active catalysts (*J. Am. Chem. Soc.* **136**, 6542, (2014)). Unfortunately, our lack of understanding of the fundamental processes at the nanoscale creates barriers to develop nanocatalysts with predicted and desired properties. There are several factors that can affect catalytic properties of nanoparticles. Among them the size, the geometry structure and morphology, the charge state of nanoparticle, the support effects, etc. To create new catalytic materials by design at the nano-level it is necessary to predict how these factors affect the catalytic properties of nanoparticles.

The support effect is one of the most important factors in nanocatalysis. Currently there are quite a number of theoretical works devoted to investigation of catalytic activity of the supported nanoparticles. However, there is no systematic understanding how the one or another type of support affects the catalytic properties of metal clusters and how to control and tune catalytic properties of nanoparticles by the support design. There is no clear understanding what type of support (if any) can be considered as an inert one for metal nanoparticles. Thus, recently we have demonstrated that the hexagonal boron nitride (h-BN) commonly believed to be an inert support can dramatically affect catalytic properties of small gold particles (*J. Chem. Phys.* **138**, 034701 (2013); *J. Phys. Chem. C* **116**, 9054 (2012); *Int. J. Quantum Chem.* **113**, 443 (2013)). Moreover, inert h-BN monolayer can be functionalized by nitrogen doping or a metal support and become catalytically active for the oxygen reduction reaction (*PCCP* **15**, 2809 (2013); *J. Phys. Chem. C* **117**, 21359 (2013); *J. Am. Chem. Soc.* **136**, 6542, (2014)). These our findings open new way to design effective precious metal free catalysts based on materials never been considered as catalysts before.

One of the most interesting and mysterious materials in nanocatalysis is gold. Gold possesses absolutely unique and unusual properties emerging at nanoscale. Until 25 years ago, gold was believed to be catalytically inactive, inert metal. However, revolutionary experiments performed in Japan by M. Haruta and co-authors (*Chem. Lett.* **16**, 405, (1987)) demonstrated that gold nanoparticles were able to catalyze the oxidation of carbon monoxide (CO) at mild conditions. Since then interest to gold nanocatalysis has increased dramatically, due to the fact that nanoparticles of gold demonstrate extraordinary catalytic activity and selectivity even at room temperatures.

Based on this background we planned to investigate properties of nanocatalysts and learn how to functionalize inactive or even completely inert nanomaterials to work as active catalysts.

2 . 研究の目的

The proposed research is devoted to the theoretical design of a novel class of effective sustainable catalytic nanomaterials (nanocatalysts) for environmental applications with the main focus on investigation of possibility to control and tune catalytic properties (activity, selectivity) of metal nanoparticles via support design and cluster structure/morphology. The priority task is elucidation of the key mechanisms of chemical reactions at the contact area nanoparticle – support. A large number of experimental evidences pointing out that the perimeter interface between the nanoparticle and the support acts as an active site for catalytic reactions (see, e.g., M. Haruta, Role of perimeter interfaces in catalysis by gold nanoparticles, *Faraday Discuss.* **152**, 11 (2011)). In the present proposal we primarily focus on the reactions of activation of molecular oxygen and hydrogen, hydrogenation/dehydrogenation processes, oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER).

3 . 研究の方法

In our research we use the fully automated reaction path search techniques, i.e., anharmonic downward distortion following (ADDF) and artificial force induced reaction (AFIR) methods, implemented in the global reaction route mapping (GRRM) program coupled with the standard methods of Density Functional Theory (DFT) as implemented in GAUSSIAN, PWSCF, SIESTA, and VASP packages. We also use the standard nudge elastic band (NEB) method for search of reactions barriers, considering chemical reactions not only on the most stable cluster isomers, but also on the several energetically low lying isomers, to ensure correct accounting of morphology effects on the cluster reactivity.

4 . 研究成果

The proposed research is devoted to the theoretical design of a novel class of effective sustainable catalytic nanomaterials (nanocatalysts) for environmental applications with the primary focus on

elucidation of the structural and support effects in nanocatalysis. The research plan for the whole duration of the project has been fully completed:

(1) We have performed systematic investigation on reactivity of metal clusters in the regime of structural fluxionality – an important phenomenon accounting for the change in cluster structure during the reaction process. For this purpose we have successfully adopted the fully automated reaction path search methods within the global reaction route mapping (GRRM) technique for metal clusters. A number of processes such as H_2 , O_2 , NO and CO_2 adsorption and dissociation on metal (Au, Cu) and metal oxide ($Ti_2O_3^-$, $Ti_3O_6^-$) clusters have been considered [2,3,11,13]. We have demonstrated that the most stable structures of catalytic nanoparticles are not always highly reactive and an ensemble of isomeric structures must be taken into account for adequate description of the reaction rates. The predictive power of our theoretical approach has been confirmed experimentally in the group of Prof. Dr. Knut R. Asmis (Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, University of Leipzig, Germany) using methods of infrared photodissociation spectroscopy [3,13]. The developed strategy presents a promising tool for a systematic analysis and prediction of reactivity of small atomic clusters. We have also investigated clustering of Si atoms in lithium matrix for the different concentration of lithium using methods of molecular dynamics (MD) and X-ray spectroscopy. Si clusters with different structure and morphology exhibit different spectral dependencies reflecting the process of lithiation/delithiation. We have demonstrated that such technique can be used as a powerful tool for analysis of the electronic and structural properties of electrode materials in lithium-ion batteries (LIBs) upon multi-phase electrochemical lithiation/delithiation processes [1,7].

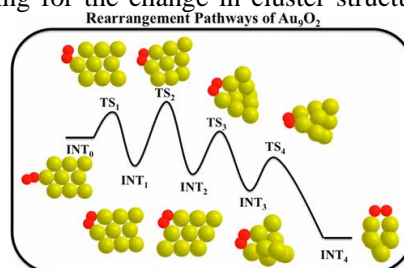


Fig. 1 Structural transformations of gold cluster induced by O_2 adsorption [11].

(2) Role of support and interface effects in nanocatalysis has been investigated on the example of hydrogen elimination reaction from isopropanol by Ni_{13} cluster on $\theta-Al_2O_3(010)$ surface [10]. It is demonstrated that dehydrogenation of C_3H_8O on the free Ni_{13} cluster is a two-step process with the first hydrogen elimination from the alcohol hydroxyl group, followed by C–H bond cleavage. Our calculations show that H elimination from OH group of C_3H_8O to Ni_{13} cluster is the rate-determining step with the barrier of 0.95 eV, while the C–H bond cleavage requires overcoming the barrier of 0.41 eV. In the case of Ni_{13} cluster supported on $\theta-Al_2O_3(010)$ the isopropanol molecule adsorbs on top of the surface Al atom in the close vicinity of the nickel cluster, which results in considerable decrease in barrier for H elimination due to formation of the complementary adsorption sites at the metal/support interface. It is demonstrated that intermediate formation of the Ni–C bond considerably promotes C–H bond cleavage. Our research provides fundamental understanding of the process of the oxidant-free catalytic hydrogen elimination from alcohols on supported nickel clusters and can serve as a tool for rational design of novel type of nanocatalysts based on abundant noble-metal-free materials. We have also investigated the crucial role of the support structure on the growth dynamics of carbon graphene nanoribbons and organometallic intermediates on various metal surfaces [6,18].

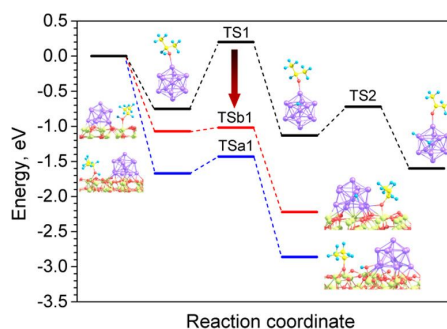


Fig. 2 Interface effect for H elimination from isopropanol at $Ni_{13}/\theta-Al_2O_3(010)$ [10].

(3) Considerable efforts have been devoted to theoretical design of novel effective electrocatalysts for energy conversion. Functionalization of boron nitride nanosheets (BNNS) for hydrogen evolution reaction (HER), oxygen reduction reaction (ORR) and water dissociation has been systematically explored [5,12,14,15,16]. We have succeeded in showing an extremely promising direction for the rational design of new catalytic materials, through the combination of theoretical calculations and experiments [15]. A key role of the interface area between boron nitride nanosheets (BNNS) or graphitic carbon nitride (g- C_3N_4) layers and metal support has been discovered [5,14,16]. Thus we proposed a simple concept for obtaining catalysts from inert and

hence stable materials by forming their heterojunctions, namely, covering inert Au with corrugated carbon–nitrogen-based two-dimensional porous frameworks [9]. We have demonstrated that gold nanoparticle decoration of insulating boron nitride nanosheet on inert gold electrode results in formation of an efficient electrocatalyst for the reduction of oxygen to water [5,16]. We have demonstrated that electrochemical HER proceeds very efficiently at Au electrode, an inert substrate for HER, modified with BNNS, an insulator [14]. Theoretical evaluation suggests that some of edge atoms provide energetically favored sites for adsorbed hydrogen, i.e., the intermediate state of HER. This study opens a new route to develop HER electrocatalysts [14]. Influence of doping effects on the catalytic activity of inert materials such as hexagonal boron nitride or carbon has been investigated [4,17]. It has been revealed that the N-doping at very small concentrations sensitively affects the catalytic activity of carbon materials for the ORR. Our calculations demonstrate the principal ability to functionalize inert materials open new way to design effective Pt-free catalysts for fuel cell technology. We have achieved breakthrough in fundamental understanding of the mechanism of ORR by accounting for a quantum tunneling effect in a proton-transfer during potential induced transformation of dioxygen on a platinum electrode in a low overpotential region at room temperature [8]. This quantum process is converted to the classical proton-transfer scheme at high overpotentials.

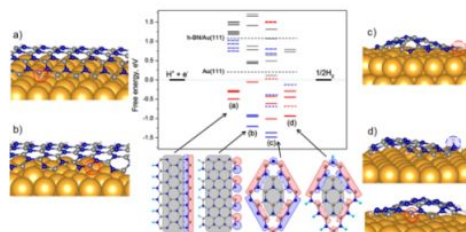


Fig. 3 Rational design of the active sites for HER on BNNS/Au system [14].

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〔図書〕(計 0 件)

〔産業財産権〕

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