

平成23年度北海道大学情報基盤センター共同研究成果報告書

1. 研究領域番号 A 1 大規模計算機シミュレーション

2. 研究課題名 *Tuning the catalytic activity of metal nanoparticles via support design*

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4. 研究代表者

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6. 共同研究の成果

In accordance with the research plan we have investigated support effects on catalytic activity of gold clusters.

Thus, we have demonstrated that the interface between the gold nanoparticles and the rutile TiO_2 (110) support plays a crucial role in H_2 dissociation [1]. Our theoretical results explain recent experimental findings reported by M. Haruta *et al* on the important role of the perimeter interface in H_2 dissociation on supported gold nanoparticles.

We made an important conclusion that Au and Au_2 supported on the h-BN surface (pristine or defected) cannot be considered as pseudo-free particles. We have demonstrated that the support effects have to be taking into account, even when the interaction of the gold atoms with the support is weak. Thus, even inert support can count. The study contains three parts: (1) Adsorption of Au and Au_2 on pristine and defected h-BN surface; (2) Adsorption and activation of O_2 on Au/h-BN and Au_2 /h-BN; (3) Dissociation of O_2 on supported Au and Au_2 .

(1) In recent works [2-4] we have studied the structural, electronic and catalytic properties of gold atoms and dimers supported on the pristine and defected hexagonal boron nitride (h-BN) surface. We have demonstrated that Au and Au_2 interact weakly with the pristine h-BN surface.

However, interaction of Au and Au_2 with the support becomes considerably stronger when h-BN surface contains point defects, such as nitrogen and boron vacancies (V_N , V_B) and impurities (N_B , B_N). Strong adsorption on vacancy defects is accompanied by the large charge transfer to/from the gold particles. We demonstrated that the charge localized on the adsorbed gold particles strongly depends on type of defects, and can possess either negative or positive values. Thus, V_N , N_B and B_N donate electrons to the adsorbed Au and Au_2 ; while V_B acts as an electron acceptor. Hence, it is possible to modify considerably the electron donor-acceptor capacity of the supported gold particles and hence tune their catalytic properties by the support design.

(研究成果のつづき)

2) We have studied adsorption and activation of O₂ on Au atoms supported on the regular and defected hexagonal boron nitride (h-BN) surface [4]. We have demonstrated that adsorption and catalytic activation of O₂ on the h-BN supported Au and Au₂ can be affected by the interaction with the support via electron pushing and donor/acceptor mechanisms. We have shown that even weak interaction of Au with the defect-free h-BN support has 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 Au₂ with the N-p_z orbitals. Although the defect-free h-BN surface does not act as a good electron donor for the supported O₂-Au, it promotes electron transfer from the Au to O₂, pushing electrons from the gold to the adsorbed oxygen. The strong interaction of Au with vacancy point defects on the h-BN surface is accompanied by the large charge transfer from the gold considerably affecting the activation of the adsorbed O₂.

(3) We have performed systematic investigation of oxygen dissociation on Au atom supported on pristine h-BN surface, as well as the h-BN surface with point defects [3]. The optimized structures of the adsorbed O₂ and dissociation pathways have been studied. In the case of dissociation of the adsorbed O₂ both oxygen atoms bind to the Au atom supported on a defect-free h-BN surface; however, only one oxygen atom binds to Au, whereas another O binds to the B atom located nearby the V_B defect in the case of Au/V_B@h-BN adsorption center. After O₂ dissociation on Au/V_N@h-BN both O atoms bridge the supported Au and the surface B atoms located nearby the V_N vacancy. We found strong structural relaxations of the h-BN surface on dissociative adsorption of O₂ on the Au/V_N@h-BN center and dissociative adsorption of O₂ on the Au/V_B@h-BN center. Interaction of Au with the defect-free support does not affect the dissociated configuration of the adsorbed O₂, however, interaction of Au with the V_B defect strongly suppress O₂ dissociations resulting in formation of the metastable configuration of the dissociation oxygen. Indeed, Au atom adsorbed on V_B@h-BN gains a positive charge making dissociation of O₂ very unfavorable. However, Au adsorbed on the V_N@h-BN center possesses a negative charge which strongly promotes O₂ dissociation. Dissociative adsorption of O₂ becomes energetically favorable in comparison with the molecular on in the case of V_N@h-BN adsorption center. The dissociation barriers calculated for O₂ adsorbed on Au/h-BN are affected by the interaction of Au with the support. Thus, we have explicitly demonstrated that the h-BN surface (pristine or defected) cannot be considered as an "inert" support for Au.

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4. M. Gao, A. Lyalin, and T. Taketsugu, Catalytic activity of Au clusters supported on h-BN surface: Adsorption and activation of O₂, *J. Phys. Chem. C* **116**, 9054–9062 (2012).