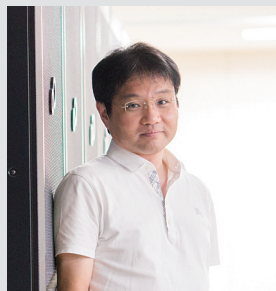


Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

Department of Theoretical and Computational Molecular Science
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Education

1988 B.E. Kyoto University
1990 M.E. Kyoto University
1993 Ph.D. Kyoto University

Professional Employment

1993 Postdoctoral Fellow, Institute for Fundamental Chemistry
1994 JSPS Postdoctoral Fellow
1994 Visiting Researcher, Heidelberg University (–1995)
1995 Assistant Professor, Kyoto University
2002 Associate Professor, Kyoto University
2006 Theoretical Research Division Supervisor, Kyoto University (–2008)
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2012 Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009 APATCC Pople Medal
2009 QSCP Prize CMOA

Member

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ZHAO, Pei
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Keywords

Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at hetero-junction of Ag nanocluster supported by alumina surface in terms of H₂ activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy

Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, “SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution,” *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, “Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser,” *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, “CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions,” *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, “Cooperative H₂ Activation at Ag Cluster/θ-Al₂O₃ Dual Perimeter Sites: A DFT Study,” *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Mechanistic Studies on Photoinduced Catalytic Olefin Migration Reactions at the Pd(II) Centers of a Porous Crystal, Metal-Macrocyclic Framework¹⁾

Porous crystals with well-defined active metal centers on the pore surface have high potential as heterogeneous metal catalysts. We have recently demonstrated that a porous molecular crystal, metal-macrocyclic framework (MMF), catalyzes olefin migration reactions by photoactivation of its Pd^{II}Cl₂ moieties exposed on the crystalline channel surface. Herein we report a mechanistic study of the photoinduced olefin migration reactions at the Pd^{II} active centers of MMF. Several experiments, including a deuterium scrambling study, revealed that olefin migration is catalyzed *via* an alkyl mechanism by *in situ* generated Pd-H species on the channel surface during photoirradiation. This proposed mechanism was further supported by DFT and ONIOM calculations.

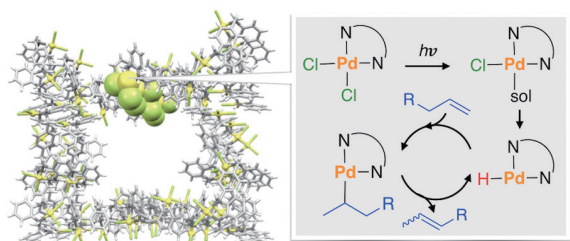


Figure 1. Porous Crystal Metal-Macrocyclic Framework show characteristic photoinduced olefin migration reaction at the Pd^{II} active centers.

2. Selective Catalytic Reduction of NO with NH₃ over Cu-Exchanged CHA, GME, and AFX Zeolites: A Density Functional Theory Study²⁾

Density functional theory calculations have been applied to study the selective catalytic reduction of NO by NH₃ over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages. The Cu^I, Cu^{II}, and [Cu^{II}(OH)]⁺ ions are considered as the active sites to study both the reduction and oxidation processes during the catalytic cycle. In the case of the reduction process, the NH₂NO formation at the [Cu^{II}(OH)]⁺ site possesses high barriers in the three frameworks, while the lower barriers are found at the Cu^{II} site. Importantly, it is found that the barriers are largely decreased at the solvated [Cu^{II}(NH₃)₄]²⁺ site for the *cha* and *aft* frameworks, while the barrier is only slightly decreased for the *gme* cage. As for the oxidation, the nitrate formation has similar reaction barriers at the Cu^I site of the three frameworks, which are lower than the following nitrite formation. In particular, the smallest *gme* cage possesses the highest barrier for the nitrite formation. Calculations on the O₂ activation by the NH₃-solvated Cu dimer revealed that the *cha* and *aft* cages have better performance than the *gme* cage, and the much smaller adsorption energy of O₂ in the *gme* cage indicates the unfavorable O₂ insertion. Therefore, the selectivity caused by the cage size is identified during the reaction process, and the *cha* and *aft* cages are more favorable.

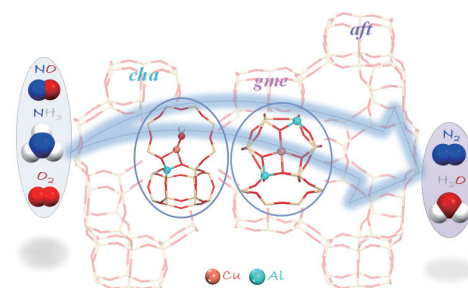


Figure 2. Density functional theory calculations on selective catalytic reduction of NO by NH₃ over the Cu-exchanged zeolites with *cha*, *gme*, and *aft* cages revealed the selectivity caused by the cage size during the reaction process.

3. Facet-Dependent Catalytic Activity of Anatase TiO₂ for the Selective Catalytic Reduction of NO with NH₃: A Dispersion-Corrected Density Functional Theory Study³⁾

Recently, the facet-dependent catalytic activity of anatase TiO₂ for the selective catalytic reduction of NO with NH₃ (NH₃-SCR) has been observed experimentally. In this study, the NH₃-SCR of NO on the TiO₂ (001) and (101) surfaces was systematically investigated using dispersion-corrected density functional theory. We propose that the surface-assisted mechanism is predominant on the (001) surface, which involves the oxygen active sites playing a crucial role in facilitating the reaction. The NH₃ dissociation step reveals the largest activation energy barrier (E_a) of 61 kJ/mol on the (001) surface, whereas the NH₂NO decomposition step has the largest barrier, $E_a \approx 156$ kJ/mol, on the (101) surface. The results obtained by calculation are consistent with the experimental results, which have shown that a TiO₂ nanosheet with a dominant (001) facet shows superior catalytic performance in NH₃-SCR of NO compared to TiO₂ nanoparticles with dominant (101) facet.

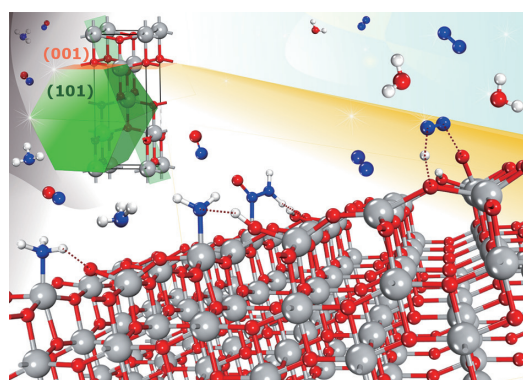


Figure 3. NH₃-SCR of NO on the (001) facet of anatase TiO₂.

References

- 1) H. Yonezawa, T. Shiraogawa, M. Han, S. Tashiro, M. Ehara and M. Shionoya, *Chem. –Asian J.* **16**, 202–206 (2021).
- 2) P. Zhao, B. Boekfa, K. Shimizu, M. Ogura and M. Ehara, *Catal. Sci. Technol.* **11**, 1780–1790 (2021).
- 3) A. Junkaew, M. Ehara, L. Huang and S. Namuangruk, *Appl. Catal., A* **623**, 118250 (2021).