Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

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Education

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

Professional Employment

1993	Postdoctral 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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Secretary
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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 H_2 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 H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Theoretical Design of Photofunctional Molecular Aggregates for Optical Properties: An Inverse Design Approach1)

Properties of molecular aggregates are defined by their composition and structure. It is becoming possible to control these elements via advances in experimental techniques, and therefore the design guidelines are demanded for developing efficient optical materials. Here we propose a theoretical design approach for photofunctional molecular aggregates using an inverse design framework, the linear combination of atomic potentials (LCAP). The Frenkel exciton model coupled with the LCAP is introduced for designing systems with desired optical properties by gradient-guided optimization searches in terms of constituent molecules in chemical space of molecular aggregates. We have applied this approach to design one-dimensional molecular aggregates having locally maximized absorption and/or circular dichroism (CD) intensities as an example. By exploring a small fraction of the vast chemical space of 10^{26} possible systems varying in composition and structure, we successfully obtained the optimal aggregates. The optimal structure–photofunction relationships were investigated from the designed systems. The present method is useful to design photofunctional molecular aggregates and accelerate optical material discoveries.

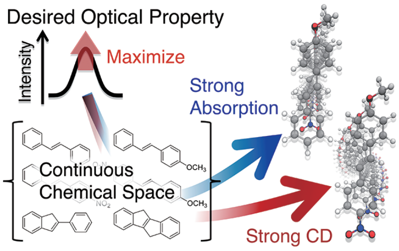

Figure 1. Schematic representation of the inverse design of photofunctional molecular aggregates with desired optical properties.

2. Importance of the Pd and Surrounding Site in Hydrosilylation of Internal Alkynes by Pd-Au Alloy Catalyst2)

Hydrosilylation is one of the key reactions in the formation of carbon−silicon bonds, where the addition of Si−H bonds occurs across the unsaturated bond in organic compounds. The Pd−Au alloy catalyst has been developed for the hydrosilylation of internal alkynes as well as α, β-unsaturated ketones under mild conditions. Herein, density functional theory calculations were utilized to study the mechanism of the hydrosilylation reaction of internal alkynes on the Pd−Au catalyst. The calculated energy profiles show that the reaction follows the Chalk–Harrod mechanism. The Pd site acts as the adsorption site and the reactive center as observed in experiments. The surrounding Pd−Au bridge and Au sites are also relevant for the bond activation and accepting the substrates or intermediates during the reaction, which is characteristic in the Pd−Au alloy catalysts and not available in the homogeneous catalyst. The present picture of the relevance of the Pd atomic site and its surrounding Pd−Au bridge or Au sites will be useful for developing the alloy catalysts for the related catalytic reactions.

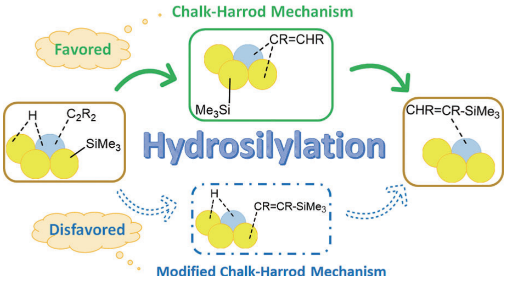

Figure 2. Hydrosilylation on the Pd-Au Alloy Catalyst.

3. Theoretical Study on ^{31}P NMR Chemical Shifts of P-Modified CHA Zeolites3)

The modification of zeolites with phosphorus is a widely adopted method to tune the acidity and consequently the catalytic properties in terms of activity, shape selectivity, and hydrothermal stability. The ^{31}P MAS NMR spectra of phosphorus-modified chabazite (P-CHA) zeolites have been observed during the hydrothermal treatment to probe the structural changes of phosphorus species in zeolites. Theoretical calculations on the ^{31}P and ^{27}Al NMR chemical shifts have been systematically performed to disclose the possible phosphorus species of intra- and extra-framework and the structural changes during the hydrothermal treatment. The present theoretical results provide useful information regarding the ^{31}P NMR chemical shifts in P-CHA, which will significantly improve the ^{31}P NMR assignments in future experiments.

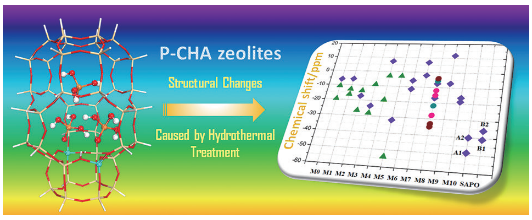

Figure 3. ^{31}P NMR chemical shifts of P-CHA zeolites.

References

1) T. Shiraogawa and M. Ehara, *J. Phys. Chem. C* **124**, 13329–13337 (2020). (Supplemental Cover)
2) T. Sadhukhan, A. Junkaew, P. Zhao, H. Miura, T. Shishido and M. Ehara, *Organometallics* **39**, 528–537 (2020). (Supplemental Cover)
3) P. Zhao, B. Boekfa, T. Nishitoba, N. Tsunoji, T. Sano, T. Yokoi, M. Ogura and M. Ehara, *Microporous Mesoporous Mater.* **294**, 109908 (2020).

Award

SHIRAOGAWA, Takafumi; Poster Award, The 13th Annual Meeting of Japan Society for Molecular Science (2019).