RESEARCH ACTIVITIES

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

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 heterojunction 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


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-macrocycle framework (MMF), catalyzes olefin migration reactions by photoactivation of its Pd$^{II}$Cl$_2$ 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-Macroyclic Framework show characteristic photoinduced olefin migration reaction at the Pd$^{II}$ active centers.](image1)

2. Selective Catalytic Reduction of NO with NH$_3$ over Cu-Exchanged CHA, GME, and AFX Zeolites: A Density Functional Theory Study$^2$

Density functional theory calculations have been applied to study the selective catalytic reduction of NO by NH$_3$ over the Cu-exchanged zeolites with cha, gme, and aft cages. The Cu$^0$, 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 NH$_3$NO 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$^{II}$(NH$_3$)$_2$]$^{2+}$ 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$^{II}$ 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 O$_2$ activation by the NH$_3$-solvated Cu dimer revealed that the cha and aft cages have better performance than the gme cage, and the much smaller adsorption energy of O$_2$ in the gme cage indicates the unfavorable O$_2$ 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 NH$_3$ over the Cu-exchanged zeolites with cha, gme, and aft cages revealed the selectivity caused by the cage size during the reaction process.](image2)

3. Facet-Dependent Catalytic Activity of Anatase TiO$_2$ for the Selective Catalytic Reduction of NO with NH$_3$: A Dispersion-Corrected Density Functional Theory Study$^3$

Recently, the facet-dependent catalytic activity of anatase TiO$_2$ for the selective catalytic reduction of NO with NH$_3$ (NH$_3$-SCR) has been observed experimentally. In this study, the NH$_3$-SCR of NO on the TiO$_2$ (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 NH$_3$ dissociation step reveals the largest activation energy barrier ($E_a$) of 61 kJ/mol on the (001) surface, whereas the NH$_3$NO 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 TiO$_2$ nanosheet with a dominant (001) facet shows superior catalytic performance in NH$_3$-SCR of NO compared to TiO$_2$ nanoparticles with dominant (101) facet.

![Figure 3. NH$_3$-SCR of NO on the (001) facet of anatase TiO$_2$.](image3)

References