

Project Title:

**Computational Studies on the Electronic Structures and the Reaction Mechanisms of
Rare-Earth- and Transition-Metal Complexes**

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**1. Background and purpose of the project,
relationship of the project with other projects**

The design of more efficient and selective catalyst is of fundamental importance in modern chemistry, therefore, numerous efforts have been made by chemists in recent decades. In this area, Rare-earth- and transition-metal have been intensively studied to design new catalyst due to its unique chemical and physical properties. Generally, the chemical reactivity and selectivity of those metal complexes are intrinsically related with their geometry structures and electronic characters. Although the chemical products catalyzed by some novel metal complexes have been widely used in industry and our daily life, the development of new catalysts featuring high selectivity and efficiency has constantly been a hot topic of researchers.

Full understanding of the reaction mechanism is an important aspect of chemistry, which is essential for improving the reaction reactivity and selectivity, as well as for further design of new catalyst. However, it is difficult for traditional experimental technique to provide the complete information about the exact reaction mechanism and the specific role of catalyst during the chemical reaction, because the technical limitation of detection for reactive intermediate and transition state featuring very short lifetime in some chemical reactions. Without the information of above key species, the full understanding of the reaction mechanism and especially the electronic structure of the catalyst could not be attained, which would hinder the development of new catalyst. The computational

chemistry is a powerful tool to handle these issues, the reaction mechanism and key electronic structure of intermediate could be clarified through quantum chemistry method. Therefore, based on the experimental results, the computational jobs should be performed for better understanding of the reaction at the molecular level, which would be helpful for development of new catalysis systems.

**2. Specific usage status of the system and
calculation method**

During the FY2018, a great quantity of specified computational resources was consumed for performing the theoretical calculation. The geometry structure and reaction mechanism are investigating at the DFT level using the Gaussian 09 and Gaussian 16 software. The detailed interaction of metal center and ligand was obtained utilizing the ADF software. Besides, a serial of high level ab-initio calculation including CCSD(T), CASSCF, and NEVPT2 were carried out to get the accurate the electronic structure and energies of the rare-earth and transition-metal complexes.

The B3PW91, TPSS/PSS, M06 functionals were utilized. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping (GD3BJ) as well. The QM/MM ONIOM Method was also used for exploring larger systems, such as the third monomer insertion reaction, multinuclear transition metal catalyzed reaction and the interaction between the counter-anion and cationic active species.

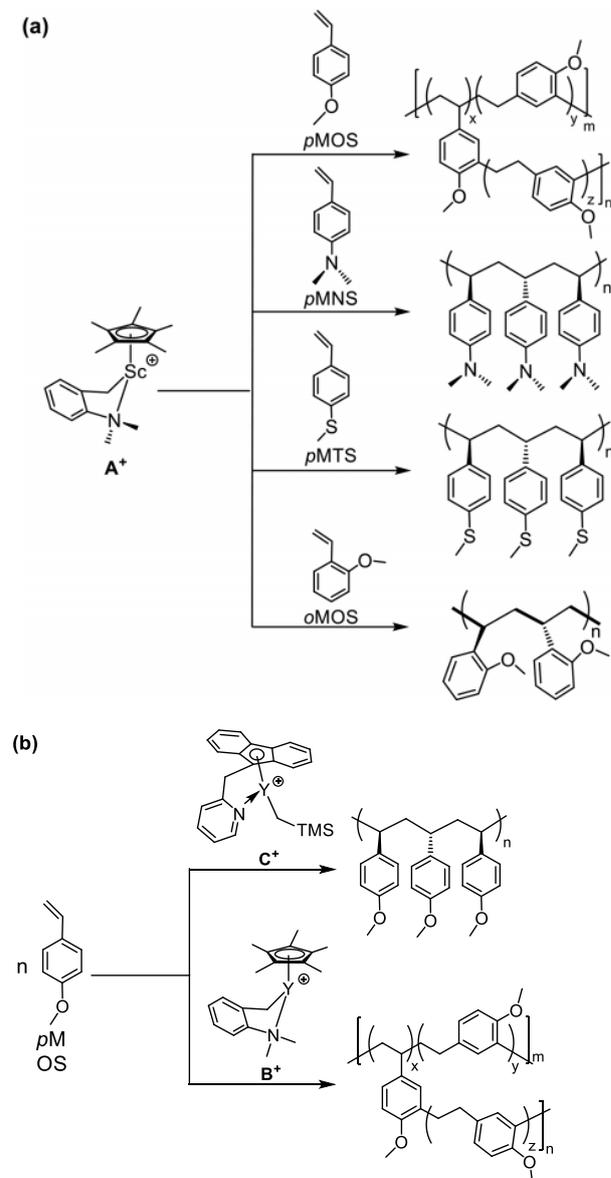
3. Result

(a) DFT Studies on the Polymerization of Functionalized Styrenes Catalyzed by Rare-Earth-Metal Complexes: Factors Affecting C–H Activation Relevant to Step-Growth Polymerization

Functionalized polystyrenes with improved surface properties are highly desired materials for industrial applications. The simultaneous chain-growth and step-growth polymerizations can provide the unique microstructure of polymers, but the few suitable organometallic catalysts limit the development of this field. Therefore, the quest for efficient catalyst systems for such extraordinary transformations remains challenging, and mechanistic studies are of substantial importance. Hou and Cui reported that the microstructures of the polymerization product of four styrene derivatives is different (Scheme 1). For the polymerization of *p*MOS, the A^+ , B^+ mediate the step-growth process, while C^+ mediate the chain-growth process. For the remaining *p*MNS, *p*MTS, *o*MOS, all three catalysts promote the chain-growth polymerization. The DFT calculation was performed to elucidate the origin of different polymerization manners.

The results show that (1) Smaller steric hindrance and greater average charge distribution in the four-center transition state are beneficial for C–H activation relevant to step-growth polymerization; (2) The C–H activation reaction can hardly occur in ortho-substituted styrene mainly because of the large steric hindrance of the substituted functional group next to the vinyl group. Instead, the coordination of the heteroatom of the functional group could facilitate the insertion of its neighboring vinyl group, resulting in a relatively detrimental effect on C–H activation. (3) The catalyst with a coordinative side arm is adverse to C–H activation. This is due to the steric hindrance around the metal center and electron-donating nature of the side arm, which destabilized the C–H activation transition state. The current theoretical results provide useful information for the development of a C–H activation

based polymerization system of polar group substituted styrene and the control of polymer microstructure. (Published in *Organometallics*, 2018, 37, 3210.)

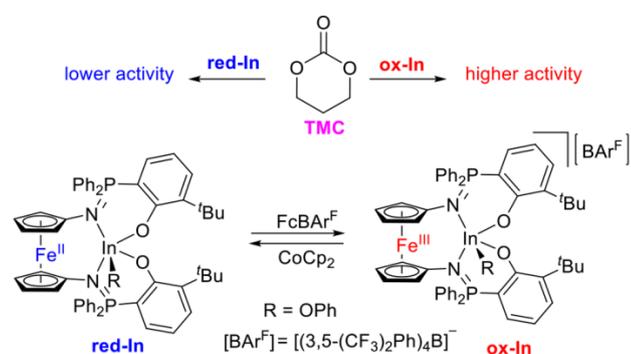


Scheme 1. Polymerizations of Various Functionalized Styrene Derivatives by Cationic Species A^+ , B^+ , and C^+ : (a) Monomer-Dependent Polymerization; (b) Catalyst-Dependent Polymerization

(b) Theoretical Mechanistic Studies on Redox-Switchable Polymerization of Trimethylene Carbonate Catalyzed by an Indium Complex Bearing a Ferrocene-Based Ligand

Redox-switchable catalysis, being capable of serving as an effective polymerization methodology, has attracted considerable attention because it can not

only modulate polymerization process and polymer microstructure but provide biodegradable polymers from biomass-derived monomers. The mechanism behind the redox-switch is complicated, and the related knowledge is very limited. The reported indium complex showed the opposite switchable behavior in TMC polymerization where the activity of oxidized indium complex was higher than its reduced state (Scheme 2). However, the related switchable mechanism needs to be further investigated. In the present work, DFT method has been applied to investigate the mechanism of TMC polymerization catalyzed by the indium alkoxide phosphine complex.



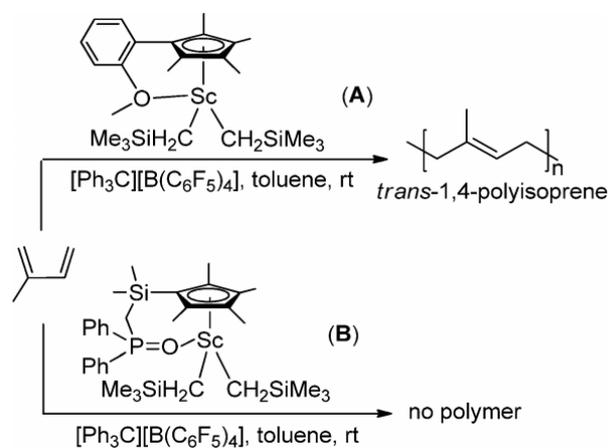
Scheme 2. Polymerization of Trimethylene Carbonate Catalyzed by Indium Complexes.

The computational results indicate that the oxidized state of the indium complex has higher activity than the reduced analogue, being in agreement with experimental observations. The detailed structure and energy analyses revealed the origin of the redoxswitch behavior of the indium complex catalyst. Our studies have revealed that although the redox occurred at the fc unit, the electronic effect induced longer coordinative $\text{In} \cdots \text{N}$ (ligand) bonds upon the oxidation and thus increased the coordination ability of the indium center, which makes the monomer unit bind to the indium center stronger and thus stabilized the oxidized species. This could account for the higher reactivity of oxidized indium complex compared with its reduced state. Such knowledge could be helpful for further development of highly efficient redox-switchable

polymerization catalysts. (Published in *Organometallics*, 2018, 37, 4599.)

(c) Theoretical Investigations of Isoprene Polymerization Catalyzed by Cationic Half-Sandwich Scandium Complexes Bearing a Coordinative Side Arm

The stereospecific polymerization of conjugated dienes is an attractive research subject and has drawn much attention from both academic and industrial researchers since the 1950s because of the limited supply of natural rubber and the increasing demands for high-performance synthetic materials. In particular, polyisoprenes with versatile microstructures show different chemical, physical, and mechanical properties. Hou and co-workers reported that the halfsandwich complex $[(\text{C}_5\text{Me}_4\text{C}_6\text{H}_4\text{OMe-o})\text{Sc}(\text{CH}_2\text{SiMe}_3)_2]$ (**A**) with a coordinative ether side arm, in combination with an equivalent of $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, was effective for the *trans*-1,4-polymerization of isoprene, but its analogue $[(\text{C}_5\text{Me}_4\text{SiMe}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2)\text{Sc}(\text{CH}_2\text{SiMe}_3)_2]$ (**B**) having a phosphine oxide side arm was inert toward isoprene polymerization under the same conditions (Scheme 3). Encouraged by previous theoretical results, we became interested in clarification of the mechanism of the **A**-mediated *trans*-1,4-specific polymerization of isoprene and the origin of inertness of the **B**-involved system.



Scheme 3. Performance of Scandium Complexes (**A** or **B**) with Different Coordinative Side Arms for Isoprene Polymerization

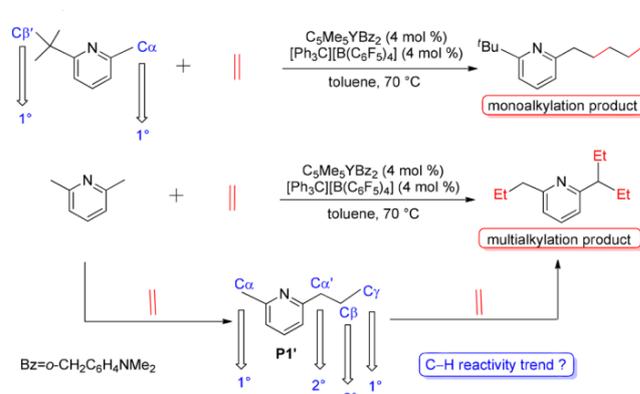
It is found that the *trans*-1,4-specific polymerization of isoprene favorably follows an insertion–isomerization mechanism, and both steric and electronic factors govern the stereoselectivity. The bulky sterics could account for the inertness of B. We hope that the current results could add better understanding to the selective polymerization mediated by the catalysts with a coordinative side arm and hopefully offer some hints for design of more efficient homogeneous rare-earth-metal polymerization catalysts. (Published in *Organometallics*, 2018, 37, 551.)

(d) Origin of Product Selectivity in Yttrium-Catalyzed Benzylic C–H Alkylations of Alkylpyridines with Olefins: A DFT Study

The development of efficient processes for the synthesis of pyridine-containing compounds has received intense attention because the pyridine moieties are among the most important heterocyclic structural motifs and exist widely in natural products, pharmaceuticals, and functional materials. The direct catalytic C–H functionalization of pyridines with olefins is a desirable method for the synthesis of alkylated pyridine derivatives, which meets the most straightforward and atom economical requirements. In this context, catalytic aromatic C(sp²)–H alkylation of pyridines with olefins has been extensively reported previously, while the direct benzylic C(sp³)–H addition of pyridines to olefins remain scarce, possibly because of its low activity and inert nature. In 2013, Hou and co-workers first reported the catalytic addition of benzylic C–H bond of alkylpyridines to simple ethylene by using half-sandwich yttrium alkyl catalysts to give monoalkylation or multialkylation products, respectively (Scheme 4). The reactivity of the different C–H bonds in the current reaction is of interest to be clarified by theoretical method.

The mechanism of benzylic C(sp³)–H alkylation of alkylpyridines (2,6-lutidine and 2-*tert*-butyl-6-methylpyridine) with olefins

(norbornene and ethylene) catalyzed by yttrium complexes has been investigated by using density functional theory. On the basis of C–H alkylation of 2,6-lutidine with norbornene, the reaction mechanism has been computationally demonstrated as two steps: (a) the generation of active species and (b) olefin insertion and subsequent C–H activation of the pyridine substrate. In the case of C–H addition of 2-*tert*-butyl-6-methylpyridine to ethylene, a kinetic priority was observed for successive ethylene insertion achieving butylation, and the C–H activation is kinetically unfavorable due to the steric repulsion between the *tert*-butyl groups of two 2-*tert*-butyl-6-methylpyridine moieties in the C–H activation transition states. However, hexylation via continuous insertion of the third ethylene was unfavorable both kinetically and thermodynamically in comparison with C–H activation. (Published in *Organometallics*, 2018, 37, 2741.)



Scheme 4. Yttrium-Catalyzed Benzylic C–H Addition of Alkylpyridines to Ethylene and Reactivity of C–H Bonds

4. Conclusion

In summary, with the aid of RIKEN's supercomputer system, a series of works, including the mechanism of the polymerization of functionalized styrenes catalyzed by rare-earth metal complexes, redox-switchable polymerization of trimethylene carbonate catalyzed by an indium complex bearing a ferrocene-based ligand, isoprene polymerization catalyzed by cationic half-sandwich scandium

complexes bearing a coordinative side arm, and the origin of product selectivity in yttrium-catalyzed benzylic C–H alkylations of alkylpyridines with olefins, were carried out by DFT calculations. These results could not only add deep understanding of the chemical reactions at the molecular level but also be helpful for development of new catalysis systems.

5. Schedule and prospect for the future

In the future, the mechanism of a series of chemical reactions concerning the activation of σ -bond and unsaturated bond mediated by rare-earth and transition-metal complexes will continue to be studied. We will focus on the activation of small molecules by mononuclear or multinuclear transition-metal complexes. Besides, we will concentrate on the polar-monomer/olefin copolymerization catalyzed by rare-earth- and transition-metal complexes.

We wish to continue to use HOKUSAI system for the current long-term project. Although some primary results have been obtained, more systematic studies on the mechanism of newly discovered reactions mediated by rare-earth and transition-metal complexes are obviously necessary.

Fiscal Year 2018 List of Publications Resulting from the Use of the supercomputer

- (1) Yanan Zhao, Gen Luo, Xingbao Wang, Xiaohui Kang*, Dongmei Cui, **Zhaomin Hou, Yi Luo***. "DFT Studies on the Polymerization of Functionalized Styrenes Catalyzed by Rare-Earth-Metal Complexes: Factors Affecting C–H Activation Relevant to Step-Growth Polymerization" *Organometallics* **2018**, *37*, 3210–3218. (SCI, Impact Factor: 4.051)
- (2) Xiaowei Xu, Gen Luo, Andleeb Mehmood, Yanan Zhao, Guangli Zhou, **Zhaomin Hou***, **Yi Luo***. "Theoretical Mechanistic Studies on Redox-Switchable Polymerization of Trimethylene Carbonate Catalyzed by an Indium Complex Bearing a Ferrocene-Based Ligand" *Organometallics* **2018**, *37*, 4599–4607. (SCI, Impact Factor: 4.051)
- (3) Guangli Zhou, Gen Luo, Xiaohui Kang, **Zhaomin Hou***, **Yi Luo***. "Origin of Product Selectivity in Yttrium-Catalyzed Benzylic C–H Alkylations of Alkylpyridines with Olefins: A DFT Study" *Organometallics* **2018**, *37*, 2741–2748. (SCI, Impact Factor: 4.051)
- (4) Guangli Zhou, Xiaohui Kang, Xingbao Wang, **Zhaomin Hou***, **Yi Luo***. "Theoretical Investigations of Isoprene Polymerization Catalyzed by Cationic Half-Sandwich Scandium Complexes Bearing a Coordinative Side Arm" *Organometallics* **2018**, *37*, 551–558 (SCI, Impact Factor: 4.051)
- (5) Yuanhong Ma, Shao-Jie Lou, Gen Luo*, Yong Luo, Gu Zhan, Masayoshi Nishiura, **Yi Luo, Zhaomin Hou***. "B(C₆F₅)₃/Amine-Catalyzed C(sp)–H Silylation of Terminal Alkynes with Hydrosilanes: Experimental and Theoretical Studies" *Angew. Chem. Int. Ed.* **2018**, *57*, 15222–15226. (SCI, Impact Factor: 12.102)