

## Project Title:

## Computational Study on Rare Earth Metal Complexes and Their Catalytic Reactions

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RIKEN Advanced Science Institute, RIKEN Wako Institute**Background and purpose of the project**

Chemical conversions driven by catalysts are essential to modern society. The ability to predict and modify the reaction route and rate-determining steps in chemical reactions would be a boon in designing better catalysts. Technical innovations in computer simulations bring that goal closer. Our research is focused on the fundamental study of molecular design for rare earth metal catalysts. As a powerful tool, quantum chemical theory planted into available programs was used to investigate the relationship between electronic structure and properties and hence predict and design new molecules. Since it is hard for experiment to do the same, static quantum chemical calculation and molecular dynamics simulation play an important role in this field.

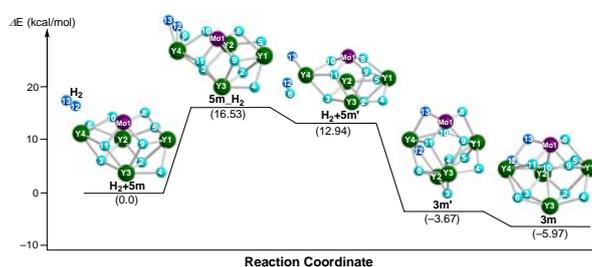
**Specific usage status of the system and calculation method**

Part of specified computational resources was used. The DFT method planted in Gaussian and ADF programs were used.

**Result**

To gain further insight into the hydrogenation process from  $Y_4MoH_9$  (**5-Y**) to  $Y_4MoH_{11}$  (**3a**), density functional theory (DFT) computations<sup>i</sup> were performed on model compounds of **3a** and **5-Y**, viz.,  $[Cp_5Y_4MoH_{11}]$  (**3m**, a model of **3a**) and  $[Cp_5Y_4MoH_9]$  (**5m**, a model of **5-Y**) (Figure 1). It was found that an  $H_2$  molecule first approaches to the Y4–H6 bond in **5m** to induce the cleavage of the H6–Y2 bridging bond and

yield an  $\square^3$ -(H13--H12--H6)–Y4 unit (**5m\_H2**). The H13--H12 bond is then dissociated to give a new  $H_2$  molecule (H12–H6) and **5m'** (**H2+5m'**). The resulting terminal H13 ligand in **5m'** then rapidly bridges Y4 and Mo1, and at the same time, the H12–H6 bond is dissociated to connect the Y4, Y3 and Y2 atoms with one H atom (H6) and bridge the Y4 and Y2 atoms with the other H atom (H12). This process is accompanied by cleavage of the Y4–H3 bond and formation of the Y1–H10 bond to yield **3m'**. Further rearrangement of the H ligands within the metal framework in **3m'** gives the more stable product **3m**. Apparently, the whole  $H_2$  addition process is cooperatively assisted by the heteromultimetallic sites. Without the Mo atom, only hydrogen exchange would be possible.



**Figure 1.** DFT calculated energy profile for the  $H_2$  addition reaction to **5m** (a model of **5-Y**). The Cp units have been omitted for clarity.

In addition, 1-hexene polymerization catalyzed by dicationic rare earth metal alkyl species  $[Ln(\textit{i}Pr\text{-trisox})(CH_2SiMe_3)]^{2+}$  ( $Ln = Sc$  and  $Y$ , trisox = trisoxazoline) has been

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computationally studied by using QM/MM approach. It has been found that the initiation of 1-hexene polymerization kinetically prefers 1,2-insertion (free energy barrier of 17.23 kcal/mol) to 2,1-insertion (free energy barrier of 20.05 kcal/mol). Such a preference of 1,2-insertion has been also found for chain propagation stage. The isotactic polymerization was computed to be more kinetically preferable in comparison with syndiotactic manner, and the dicationic system resulted in lower insertion free energy barrier and more stable insertion product in comparison with the monocationic system. The stereoselectivity was found to follow chain-end mechanism, and the isospecific insertion of 1-hexene is mainly controlled by kinetics. In addition, the current computational results, for the first time, indicate that the higher activity of Sc species toward 1-hexene polymerization in comparison with the Y analogue could be ascribed to lower insertion barrier, easier generation of the active species, and its larger chemical hardness.

### **Conclusion**

The usage of RICC has provided scientific insights to the mechanism of conversion from  $Y_4MoH_9$  to  $Y_4MoH_{11}$  in the presence of  $H_2$ . The mechanism of olefin polymerization catalyzed by mononuclear rare earth complex has been also elucidated with the help of RICC system.

In the future, the mechanisms of C-H activations catalyzed mononuclear rare earth metal complex and olefin polymerization catalyzed binuclear metal complex will be studied.

We wish to continue to use RICC system for the current long-term project. At this stage,

only primary results were obtained. More systematic results on the mechanism of newly discovered reactions catalyzed by rare earth metal complex are expected.

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**Fiscal Year 2011 List of Publications Resulting from the Use of RICC**

**[Publication]**

1. **Yi Luo\***, Yang Li, Hang Yu, Jinfeng Zhao, Yanhui Chen, Zhaomin Hou, Jingping Qu\* “DFT Studies on Reduction of Dinitrogen to Ammonia by a Thiolate-bridged Diiron Complex as Nitrogenase Mimic” *Organometallics* **2012**, *31*, 335–344.
2. Xiaohui Kang, Yuming Song, **Yi Luo,\*** Gang Li, Zhaomin Hou,\* Jingping Qu\* “Computational Studies on Isospecific Polymerization of 1-Hexene Catalyzed by Cationic Rare Earth Metal Alkyl Complex Bearing a C<sub>3</sub> *i*Pr-trisox Ligand” *Macromolecules* **2012**, *45*, 640–651.
3. Takanori Shima, **Yi Luo**, Timothy Stewart, Robert Bau, Garry J. McIntyre, Sax A. Mason, Zhaomin Hou\* “Molecular heterometallic hydride clusters composed of rare-earth and d-transition metals” *Nature Chemistry* **2011**, *3*, 814–820.
4. **Yi Luo,\*** Yunjie Luo, Jingping Qu, Zhaomin Hou\* “QM/MM Studies on Scandium-Catalyzed Syndiospecific Copolymerization of Styrene and Ethylene”, *Organometallics* **2011**, *30*, 2908–2919.