



GSCN was established in 2000 to promote research and development for the Environment and Human Health and Safety, through the innovation of Chemistry .

### Is the development of substitute materials hampered by a narrow interpretation of GSC?

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The development of substitute materials is one of the first things that needs to be considered as part of the strategy for addressing problems of environmental damage caused by some materials. This ought to be the central issue of green sustainable chemistry (GSC). But somehow the GSC concept doesn't appear to be working effectively for the development of substitute materials. For example, commercial advertising and even academic publications often claim that products are green and environmentally safe because they use no halogens or lead.

Fluorocarbons are non-toxic and non-flammable. They were once thought to be the ideal refrigerant materials, but were banned because they caused depletion of the ozone layer in the stratosphere. They also have a high global warming potential. Tetrafluoroethane (HFC-134a) has been developed as a substitute refrigerant for car air conditioners, but although this material has a zero ozone layer depletion coefficient, it still has a high global warming potential (GWP) of 1300, and it is essential that it should be replaced with a material that has a lower GWP. This search for substitute materials is being driven by a growing belief that fluorine-free materials are kinder to the environment. Combined with strict effluent regulations, this has brought the development of substitute materials containing fluorine to a virtual standstill in Japan. However, since the beginning of last year, a number of businesses in the United States have proposed low-GWP refrigerants that contain fluorine. In terms of CO<sub>2</sub> emissions the life cycle climate performance (LCCP) of these materials is also said to be lower than that of current refrigerants. Although no final decision can yet be made as to whether this material is good or not, the narrow concept of GSC that is prevalent in Japan is liable to impede the development of good substitute materials.

In the future, fuel cell technology will probably become an area of increasingly fierce competition in the development of solar cells. I only hope that Japan's businesses and researchers are not too late in abandoning this narrow, misguided concept of GSC.

7Th GSC Award

## Development of advanced molecular transformation of alkenes by low-valent ruthenium catalysts

**Teruyuki Kondo**

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The advanced use of materials will play an important role in the continuing development of human society in the 21st century. For this purpose, it is essential to construct environmentally friendly catalytic organic synthesis processes that can produce new substances and new materials without impacting on the environment. Teruyuki Kondo has made important advances in this field by successfully developing novel codimerization and cotrimerization reactions of different alkenes that are characteristic of low-valent ruthenium complex catalysts. These reactions have remarkably low environmental impact and high synthesis efficiency, and will contribute significantly to green sustainable chemistry (GSC) which is the aim of organic synthesis in the 21st century.

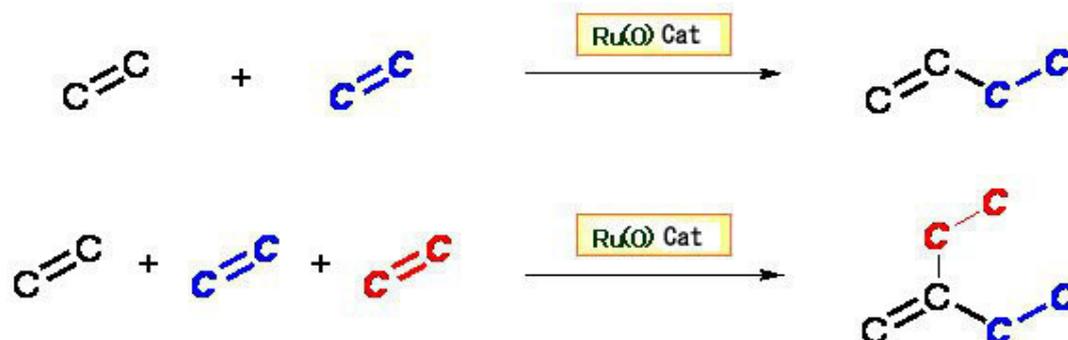
For the continuing development of society in the 21st century, it is essential to confront environmental and resource issues by developing selective production methods that can synthesize the desired substance with high atomic efficiency without forming any by-products, and by creating new substances and materials by subjecting organic resources to advanced molecular transformations. One such example is the co-oligomerization (codimerization or cotrimerization) of different alkenes, which is a form of advanced molecular transformation reaction involving alkenes (an important organic resource). Scheme 1) is an ideal environmentally friendly reaction involving the synthesis of carbon-carbon bonds and the formation of a carbon backbone which proceeds with high atomic efficiency under neutral conditions without forming any waste by-products such as inorganic salts which have caused problems in other reactions such as cross-coupling.

Teruyuki Kondo has taken on the challenge of this research topic by adopting low-valent ruthenium complexes as environmentally friendly catalysts. In 1999, Kondo and his team were the first to synthesize the zero-valent ruthenium complex  $\text{Ru}(\eta^6\text{-COT})(\eta^2\text{-DMFM})_2$ , where COT = 1,3,5-cyclooctatriene and DMFM = dimethyl fumarate (Fig. 1). Using this as a raw material, they successfully produced a large number of new zero-valent and divalent ruthenium mononuclear and multinuclear complex groups by reacting it with phosphine, amines, arenes, quinines and water. Next, as a result of developing catalyst functions that are characteristic of these new complexes, they found that a highly site-selective and stereo-selective codimerization reaction first takes place between 2-norbornene compounds and acrylic acid derivatives, and that the corresponding *exo-trans* type codimer is obtained with a high yield. Using a  $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$  complex catalyst in the presence of a primary alcohol, they discovered that a specific *head-to-head* dimerization reaction of styrenes and a chainlike codimerization of styrenes and ethylene take place. They were also the first to show that  $\text{Ru}(\eta^6\text{-cot})(\eta^2\text{-dmfm})_2$  is highly discriminating between three

types of alkene — electron-rich *N*-vinylamide, electron-deficient acrylic acid esters, and electronically neutral ethylene — and acts as an effective catalyst for regioselective and stereoselective bonding to these materials. In the field of organic synthetic chemicals, this enamide synthesis reaction is likely to be useful for the synthesis of enamide derivatives such as the macrolide-based anticancer agent lobatamide C, and in the field of polymer chemistry, it could well lead to the development of ternary alternating copolymerization reactions.

The co-oligomerization of different alkenes using transition metal complex catalysts may seem a very simple and basic reaction on paper, but given that most of the world's prominent chemists have struggled with this theme, it is still an important reaction with a high degree of difficulty even in this age of advanced organic chemistry and organometallic chemistry. Professor Kondo's research achievements have made a significant breakthrough by allowing energy savings and raw material savings to be made by eliminating by-products, effluents and waste products, and by placing the highest priority on the health and safety of humans and the environment.

Professor Kondo's research achievements have made a large contribution to green sustainable chemistry (GSC) which is the aim of synthetic organic chemistry in the 21st century, and have been widely lauded not just in Japan but around the world. In recognition of his achievements, he has therefore been awarded the Green Sustainable Chemistry Award.



Scheme 1. Codimerization and cotrimerization reactions of different alkenes using a Ru(0) catalyst

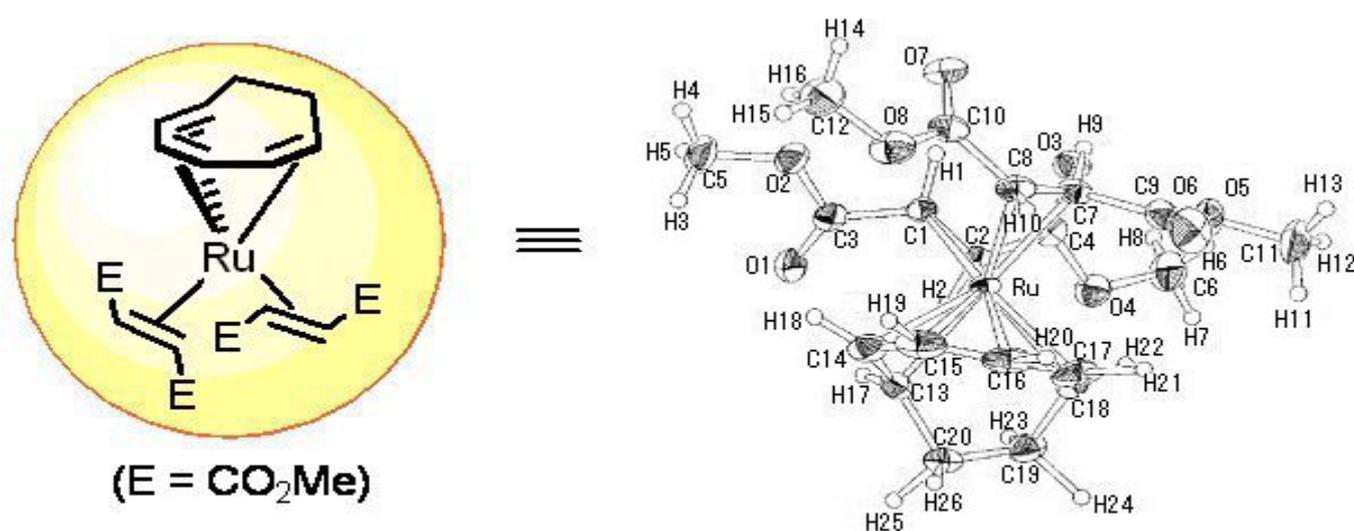


Fig 1 A zero-valent ruthenium complex with advanced functionality

## Development of Green Oxidation Systems by Fine Control of Metal Oxide Cluster Catalysts

Noritaka Mizuno

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(1) We elucidated the relationship among structures, functions, and catalytic properties for selective oxidation of hydrocarbons with solid polyoxometalate compounds, of which the structures of the active sites can be controlled at atomic levels, including the roles of additives at atomic levels. In addition, (2) we succeeded in the developments of highly atom-efficient catalytic systems for selective oxidations of alkanes, alkenes, and alcohols with hydrogen peroxide or molecular oxygen by fine design and synthesis of novel polyoxometalates with the basic knowledge of (1). (3) As easily separable, collectable, and recyclable catalysts, (a) the immobilized polyoxometalates or polyoxometalate complexes and (b) metal hydroxides supported on appropriate supports for the selective oxidation with molecular oxygen without solvents or in water, have been developed.

Oxidation reactions are very important in chemical industry and related to the 70% processes. The developments of highly atom-efficient catalytic selective oxidation processes for the syntheses of epoxides, alcohols, aldehydes, and ketones with environmentally friendly molecular oxygen or hydrogen peroxide have extensively been demanded because the byproduct is water.

The catalytic function of polyoxometalates (POMs) has attracted much attention because their acidic and redox properties can be controlled at atomic or molecular levels. The strong acidity or oxidizing property of POMs has induced a lot of studies on the heterogeneous and homogeneous catalysis. Additional attractive and technologically significant aspects of POMs in catalysis are their inherent stability towards oxygen donors such as molecular oxygen and hydrogen peroxide. Therefore, POMs are useful catalysts for liquid-phase oxidation of various organic substrates with hydrogen peroxide or molecular oxygen as described below (1)-(4).

**(1) Efficient epoxidation catalysts with hydrogen peroxide.** (a) **Lacunary silicotungstate.** The epoxidation with  $\text{H}_2\text{O}_2$  catalyzed by lacunary silicotungstate ( $[\gamma\text{-SiW}_{10}\text{O}_{34}(\text{H}_2\text{O})_2]^{4-}$ ) proceeded with  $\geq 99\%$  selectivity to epoxide,  $\geq 99\%$  efficiency of  $\text{H}_2\text{O}_2$  utilization, high stereospecificity, and the easy recovery of the catalyst. (b) **Di-vanadium-substituted silicotungstate.**  $[\gamma\text{-1,2-H}_2\text{SiV}_2\text{W}_{10}\text{O}_{40}]^{4-}$  with the  $\{\text{VO}-(\mu\text{-OH})_2\text{-VO}\}$  core could catalyze epoxidation of olefins using only one equivalent  $\text{H}_2\text{O}_2$  with the high epoxide yield and high efficiency of  $\text{H}_2\text{O}_2$  utilization. Notably, this system showed unique stereospecificity, diastereoselectivity, and regioselectivity.

**(2) Bis ( $\gamma$ -oxo) bridged di-iron site on the lacunary POM as an efficient epoxidation catalyst with molecular oxygen.** Bis ( $\mu$ -oxo) bridged di-iron site on the lacunary POM has been used as catalysts for the oxygenation of alkenes in homogeneous reaction media using molecular oxygen as an oxygen donor. The selectivity to cyclooctene oxide and turnover number reached up to 98% and 10000, respectively, for the oxygenation of cyclooctene.

**(3) Immobilization of POMs.** The active POMs could be immobilized onto the ionic liquid-modified  $\text{SiO}_2$  with maintenance of the catalytic performance of the corresponding homogeneous analogues. This catalyst was recyclable and reusable.

**(4) Application of the information on the catalytically active sites to the design of supported catalysts.**

The easily prepared, recyclable, and reusable supported ruthenium hydroxide catalyst  $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$  acted as an effective heterogeneous catalyst for the aerobic oxidations of alcohols, amines, naphthols, phenols, and aromatic compounds with molecular oxygen (or air) as an sole oxidant. In addition, the other supported metal hydroxide catalysts have been developed and applied to various kinds of transformations of functional groups.

As above described, we succeeded in the developments of catalytic systems for the environmentally friendly selective oxidation with control of structures and functions of catalytically active sites, and significantly contributed to the green chemistry.

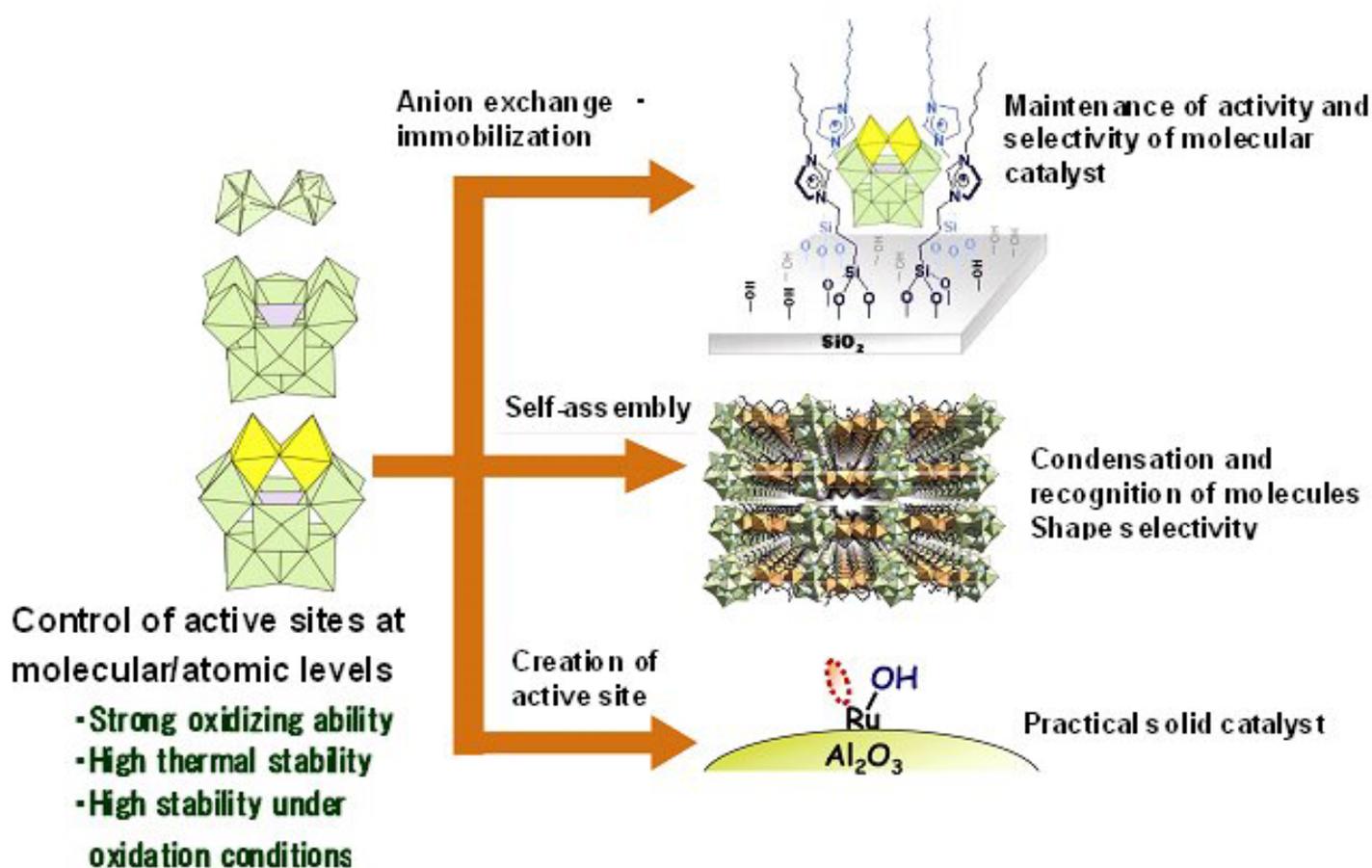


Figure 1. Strategy for the development of green oxidation reactions catalyzed by metal oxide cluster catalysts.

## The 3rd GSC Student Travel Grant Awards Call for Candidates

Since its launch in March 2000, the Green & Sustainable Chemistry (GSC) Network has been promoting GSC activities with the aim of achieving “human and environment health and safety” and a sustainable society through innovative chemical technologies.

As part of its activities, a GSC symposium is held annually in Japan to promulgate and promote GSC practices. And as an international endeavor, the 1st International Conference on Green and Sustainable Chemistry was held in Tokyo in March 2003. At this conference, international participants were exposed to the high level of GSC activities that are carried out in an integrated manner by industry, academia, and national institutions in Japan. After this gathering, the GSC International Conference moved on to the United States and Europe. The 2nd International Conference on Green and Sustainable Chemistry was held in the U.S. in June 2005, and the 3rd International Conference on Green and Sustainable Chemistry was held in The Netherlands in July 2007. The 4th International Conference (GCS-4) is schedule to be held in China in August 2009 marking the return of the conference to Asia.

Recruitment for the 3rd GSC Student Travel Grant Awards is now taking place in the GSC network. These awards are given to Japanese graduate students that are performing outstanding research in the field of GSC to help deepen their knowledge by attending the 4th International Conference on Green and Sustainable Chemistry. The awards will assist with the expenses involved in attending the conference. We encourage those interested to apply for these awards.

### Details on Call for Candidates

#### 1. Candidate qualifications

- (1) Must has been a graduate student enrolled at a Japanese university on September 1, 2008, and must be a graduate student on August 1, 2009 with the intention of attending the 4th International Conference on Green and Sustainable Chemistry and giving a presentation.
- (2) Must have received a recommendation from one’s supervising instructor.

#### 2. Number of award recipients

Approximately six.

#### 3. Please visit the following Web site for more information.

<http://www.gscn.net/awards/index.html>

### Information on the 9th GSC Symposium

—GSC Practices and Outlook toward a Sustainable Society—

Dates: March 9-10, 2009 (Monday-Tuesday)

Venue: Hitotsubashi Memorial Hall, National Center of Sciences (Tokyo)

Host: Green & Sustainable Chemistry Network

Poster Presentation Submission Deadline: December 12, 2008 (Friday)

Early Registration Discount: until January 31, 2009 (Saturday)

Contact: GSC Network Secretariat (inside Japan Chemical Innovation Institute)

TEL: 03-5282-7272, e-mail: [gscn@jcii.or.jp](mailto:gscn@jcii.or.jp)

For more information, please visit the GSCN Web site (<http://www.gscn.net/>).