GSCN NEWS LETTER No.48 2013. 8

Green & Sustainable Chemistry Network

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

GSCN Green & Sustainable Chemistry Network

JACI

Working Together to Solve Global Issues

Chemical Engineering Society, a Public Service Corporation
Keisuke Takeuchi, Chair

The world of energy, which is closely related to chemical engineering, is entering an era of unprecedented transformation, as exemplified by the rapid advancement and commercialization of shale gas and other non-conventional resources, and the rise of opportunity for the widespread use and promotion of renewable energy.

Given this massive swell, recognizing the increased expectations for chemical engineering that organically integrates academic pursuits and industry, and pursuing the realization of "Vision 2023" and thereby cultivate further potential for the Chemical Engineering Society, in FY 2013 we are endeavoring to promote (1) the augmentation of personnel resource development; (2) the tackling of global issues and transmittal of the requisite information; (3) the expansion of international exchange; and (4) the invigoration of academic meetings and the continued improvement of member services. Thus we have identified these goals as top-priority policy objectives.

The activity guidelines of the GSCN, "Establishment of Chemical Technology for the Realization of a Sustainable Society and the Creation of Requisite Products," are extremely significant to the Chemical Engineering Society as well. Accordingly, the question of how to conduct business activities in a manner that minimizes the environmental load in the fields of chemistry, resources and energy industry is a pressing one. Additionally, the tasks of "Industry – Academia – Government Coordination and International Coordination" and "Information Gathering, Transmission, and Dialog with Society," which comprise the mission of the GSCN, represent the tasks that the Chemical Engineering Society must address without delay, as noted above.

Beginning with "chemistry" and based upon industry – academia – government coordination in addressing global issues, through the use of a realistic but dynamic approach, in order to achieve specific results I believe the Chemical Engineering Society and the GSCN must conduct activities through close coordination going forward, just as we have in the past.

This is also the year in which INCHEM TOKYO will commence, being held once every two years. I anticipate that there will be numerous exhibits based on the topics that share the goals of the GSCN. I invite the active participation of GSCN members and your cooperation in making the event a success.

The 12th GSC Award, Award from the Ministry of Economy, Trade and Industry

Proposal for a New Method of Laundry toward a Sustainable Society

Noriko Yamaguchi, Toshio Miyake, Kohei Nishida, Hitoshi Ishizuka and Ayako Kita; Kao Corporation

As a result of analyzing the amount of CO_2 emissions associated with laundry operations from an LCA* perspective, Kao has identified that the components associated with products (detergent materials, containers, manufacture, transportation and disposal) and the components used in homes (electricity, water supply and wastewater) exert virtually the same environmental load, and that the water used accounts for approximately 65% of the CO_2 emissions associated with the components that are consumed. While providing a consumer benefit in the form of "time savings" per rinse of the detergent, we have developed a product that is environmentally sensible. Consumers and Kao Corporation are jointly proposing "A New Style of Washing (a joint eco-proposal)" that minimizes the global environmental impact.   *LCA : Life Cycle Assessment

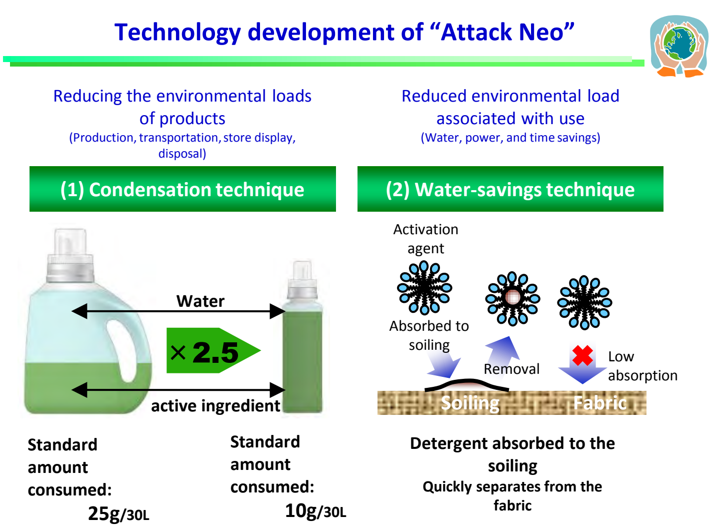
Recently, given increasing problems such as abnormal weather conditions globally and the depletion of water and energy resources, the public's awareness of environmental issues has risen. As a result of analyzing the amount of CO_2 emissions associated with laundry operations from an LCA perspective, Kao has determined that the components that are associated with home usage exert virtually the same environmental load as the products do, and that the water used accounts for approximately 65% of the CO_2 emissions associated the components related to such usage. The reason is that the processes of rinsing and water removal require a great deal of energy, suggesting that a reduction in the volume of water usage can be highly effective in minimizing the environmental load.

The amount of water used during washing consists of the part used during the washing cycle and the part used during the rinse cycle. In order to reduce the amount of water usage, we focused on minimizing the volume of water used during the rinse process. We developed a novel hydrophilic non-ionic (nonion) surfactant based on a new washing technology, so that it tends not to adhere to clothing but also offers a high capacity to become absorbed to the soiling for its removal.

As a result, we have accomplished the development of a detergent that, while retaining a high washing capacity, can be rinsed away in a single rinse cycle as opposed to the conventional liquid detergent that requires two rinse cycles, and thereby achieve the same cleaning performance. In the year 2009, the new product was released under the brand name "Attack Neo."

"Attack Neo" has achieved substantial reductions in CO_2 emissions, 21% in the product component (condensed) and 22% in the component related to home usage (water and electricity savings by requiring only one rinse cycle), for a total reduction of 21% (according to an assessment conducted by Kao in June 2009). By using "Attack Neo," the consumer not only reaps functional values in the form of reduced washing time and more compact equipment size but also saves water and power in an easily accessible manner, in the form of daily washing operations. The consumer also achieves societal values in the form of enhanced eco-awareness and goodwill through the creation of more spare time by reducing the amount of time spent in attending to washing chores.

Since the release of "Attack Neo," similar environmentally friendly liquid detergents have become the mainstream. We believe that we can contribute, modest as it may be in scale, toward the attainment of a sustainable society as washing that requires just one rinse cycle becomes the de-facto standard.



•Product condensation: 2.5x
•Weight of container: Approx. 45% reduced
•Transportation, store display, warehousing effect: Approx. 3x

[Reducing the amount of CO_2 emission through the use of Attack Neo]

*Surveyed by Kao, 6/2009 Fully automatic vertical washing machine (8kg capacity)
Clothing: 4kg, water volume setting: 47L
2 rinse cycles
(water volume: 130L; power reading: 67kW)
1 rinse cycle
(water volume: 102L; power reading: 52kW)

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Surveyed by Kao, 2011 Neo series
Compared with the use of conventional method (Attack Bio-Gel)
Approximate value based on 2011 sales

The 12th GSC Award, Award from the Ministry of Education, Culture, Sports, Science and Technology

Development of Innovative and Practical Catalysts toward Green & Sustainable Chemistry

Shū Kobayashi, Professor, School of Science, The University of Tokyo shu_kobayashi@chem.s.u-tokyo.ac.jp

The development of innovative, practical catalysts in organic synthesis holds the key to the attainment of GSC. The authors, in pursuing basic research that may contribute to advancements in the field of GSC, have engaged in (1) the development of organic reactions using water as a solvent; (2) the development of innovative immobilized metal catalysts based on the polymer-incarcerated method; and (3) the development of asymmetric catalysts based on original concepts. These efforts have resulted in significant advances to GSC.

Water is the representative green solvent. Accordingly, the authors have discovered that lanthanide triflates are Lewis acid catalysts that are stable in water. Using that discovery as a starting point, they have developed numerous catalytic reactions in aqueous solvent systems--a feat that was once considered difficult--and made substantial contributions to the field. The development of a Lewis acid–surfactant-combined catalyst (LASC) eliminates the need for the addition of organic solvents and this novel catalytic system was applied for aqueous catalytic asymmetric Mannich-type reactions and catalytic asymmetric ring-opening reactions. The authors have pioneered the catalytic use of metal hydroxides and zero-valent indium, which had not been previously utilized as catalysts, in water. Moreover, they achieved highly-controlled organic synthesis using ammonia and formaldehyde (which are small molecules known for the difficulty of controlling their reactivity) in aqueous solvents.

The authors have also developed polymer-immobilized catalysts, which they named "polymer-incarcerated catalysts (PI catalysts)." These easily recoverable and reusable catalysts offer the best of both worlds: high activity and ease of separation, which are advantages inherent in homogeneous catalysts and heterogeneous catalysts. Using their innovative method, the authors have accomplished the immobilization of a large number of metals--including scandium, osmium, palladium, platinum and gold--to their unique polymers, and have developed a variety of oxidation, reduction, and carbon-carbon bond forming reactions. Furthermore, the polymer-incarcerated method was shown to stabilize alloyed metal nanoclusters and these catalysts demonstrated high reactivity and unique selectivity. In addition, the authors have focused on the use of polysilanes as a support material and developed a novel polysilane-immobilized palladium catalyst. This heterogeneous catalyst was shown to be highly active for hydrogenation reactions and was utilized in a continuous flow system.

The authors have also conceptualized new ideas and catalytic systems for asymmetric catalysis. This group was the first to report the catalytic asymmetric Mannich-type reactions, and various unique catalytic systems for asymmetric reactions were reported using chiral niobium, titanium, silver, indium, scandium, zinc, copper and bismuth catalysts. In addition, the authors have also examined catalytic asymmetric reactions using alkaline-earth metals (which are abundant) and developed asymmetric carbon-carbon bond forming reactions through the use of chiral metal amides. The practical application of alkaline-earth metals was demonstrated by the development of a immobilized chiral calcium complex and its application for asymmetric carbon-carbon bond forming reactions to a continuous flow system. Furthermore, highly-controlled catalytic asymmetric reactions in aqueous solvents, which were previously difficult to accomplish, have been achieved in various types of enantioselective reactions, as noted above.

Some of the catalysts developed by this group are widely utilized, and a select few have already been employed in practical applications. The fundamental research developed by the authors is being examined for their practical application through industrial-academic partnerships with several corporations.

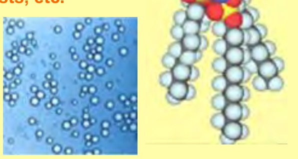
The authors hope to contribute to the further advancement of GSC for Society by significantly extending the development of innovative, practical GSC-oriented catalysts through basic research.

Development of a truly effective catalyst that achieves highly selective reactions

Development of organic reactions using water as a solvent

Lanthanide triflate, Lewis acid-surfactant-combined catalyst (LASC), chiral metal catalysts, low-valent metal catalysts, etc.

Aldol reaction
Esterification reaction
Michael reaction
Etherification reaction
Mannich-type reaction, etc.

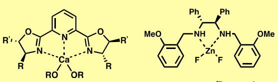


Development of innovative polymer-immobilized metal catalysts

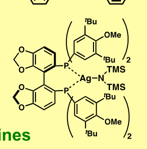
MC catalyst
PI catalyst

Hydrogenation reaction
Allylic reaction,
Oxidation reaction,
Dihydroxylation reaction
1,4-Addition reaction, etc.
Flow chemistry

Catalytic asymmetric reactions



Asymmetric catalyst based on a new concept



Activation of imines
Aqueous reaction
Alkaline-earth metals, etc.

The 12th GSC Award, Award from the Ministry of the Environment

Development of Green Recycling Technology for Rare Earth Metals

Toru H. Okabe, University of Tokyo; Masahide Okamoto, Hitachi, Ltd.; Sakae Shirayama, Kyoto University;
Osamu Takeda and Yoshiaki Umetsu, Tohoku University

Rare earth metals are essential to the manufacture of neodymium magnets, which in turn contribute to solutions to environmental and energy-related issues. However, because the production of rare earth materials is under oligopolistic control in China there has been a strong need for the development of rare earth recycling technology from the standpoint of resource security. Given this background, the authors have successfully developed a new recycling process for the rare earth materials contained in neodymium magnets, that is, a molten metal extraction process and a molten salt extraction process. These are green (environmentally sound) processes that do not produce any harmful liquid waste; thus they can be implemented in Japan and other industrialized countries, where stringent environmental regulations are in place. These techniques are more efficient than the current wet process and are capable of extracting and separating rare earth materials without producing any liquid waste. Currently, Hitachi, Ltd. is conducting benchmark tests based upon a recycling technique that uses the molten metal extraction process.

Rare earth metals are essential to the fabrication of neodymium magnets, which represent an ace card for the solution of environmental and energy issues. Consequently, the demand for rare earths has risen steeply each year. However, the production of rare earth materials is under oligopolistic control in China. As a negative effect of this situation, at some point in the past the exportation of rare earth materials from China had stopped, creating a serious supply shortage and sending the Japanese industry into a panic. The development of recycling technology for rare earth materials, including dysprosium which is others essential to the fabrication of hybrid vehicle motors, is of critical importance from the standpoints of a stable supply of resources and the alleviation of the environmental load that arises through the processes of mining and metal extraction.

The current recycling process is a wet process that uses strong acids, requiring lengthy steps for the separation of rare earth materials and producing large quantities of liquid waste, which includes heavy metals and organic solvents. Thus it has a significantly adverse environmental impact. Therefore, in Japan, where stringent environmental regulations are in place, the disposal of the liquid waste entails high costs, making the prosecution of recycling a daunting task. The current situation is that the majority of scrap magnets is exported for recycling to China and other countries where environmental regulations are less stringent. However, because recycling can be a safeguard against supply disruptions, it is important to accomplish recycling through the efficient recovery of scrap in Japan and the use of environmentally benign technology (green technology), but without the need to transport the scrap overseas.

The authors have pursued the development of rare earth recycling technology for more than 15 years. We have succeeded in the development of a neodymium magnet recycling process, more specifically green (environmentally sound) processes that do not produce any harmful waste liquid and can therefore be implemented in Japan. Among these is a molten metal extraction process that involves direct extraction (in the form of pure metals) of rare earth materials from magnetic alloy scrap, using molten magnesium and other liquid metals as extraction agents. This technology is based on the novel idea of efficiently separating and recovering rare (and valuable) metals through the proper combination of scrap (waste) materials, including magnets and magnesium. To date, we have successfully extracted neodymium at an extraction rate of 99% or better from magnet alloys, obtaining neodymium with a minimum purity of 98% and magnesium with a purity of 99% or better. Hitachi, Ltd., with the technical cooperation of Toho Titanium Co., Ltd. and a research grant from NEDO's New Resources Circulation Promotion Project, has conducted benchmark tests using this technology and is studying the feasibility of using the technology in practical applications.

The molten salt extraction process is a method wherein the rare earth materials present in a magnet alloy are selectively chlorinated, using chlorides and other molten salts as extraction agents, for efficient separation. This method permits the separation of the rare earth materials from the extraction agent and, further, the separation of rare earth materials from one another. This process can achieve the significantly efficient separation of components as compared to the wet process, without producing liquid waste.

The recycling of rare earth materials significantly contributes to environmental protection in addition to improving resource security. Currently, China is facing serious problems of environmental contamination attributable to the mining and smelting of rare earth ores. This technology, as it advances, is expected to reduce the environmental load associated with future operations.

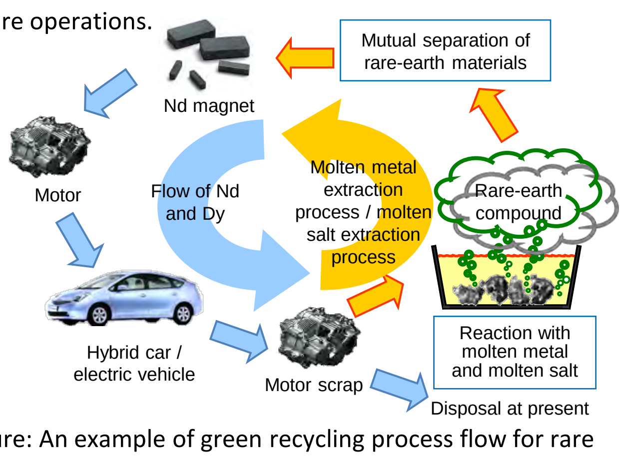


Figure: An example of green recycling process flow for rare earth metals.

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The 2nd GSC Encouragement Award

High efficient synthesis gas production process utilizing CO_2 as a raw material

Chiyoda Corporation
Fuyuki Yagi, Shuhei Wakamatsu, Tomoyuki Mikuriya, Osamu Hirohata, Takenori Kanda

Chiyoda CO_2 reforming catalyst can generate synthesis gases by CO_2 and H_2O reforming under lower H_2O/Carbon and CO_2 /Carbon ratios in feed gas compared to conventional steam reforming catalyst due to high resistance against carbon deposition under severe condition. Therefore, this catalyst produces synthesis gases with variable H_2/CO ratios more efficiently. Chiyoda CO_2 Reforming Process can utilize CO_2 from exhaust gas of other plants and CO_2 in gas fields.

The synthesis gas production technology with reforming of natural gas is widely used for chemical synthesis such as oxo alcohol, acetic acid and so on. Because this reforming reaction needs high temperature and significant energy consumption, optimizing overall system and reducing energy consumption is very important. Chiyoda has developed catalyst and process in order to reduce energy consumption of reforming process.

In general, not only steam but also CO_2 is used to obtain synthesis gas for chemical synthesis. However, conventional catalyst must be operated with high steam/carbon ratio (S/C) and high CO_2 /carbon ratio (CO_2 /C) to prevent catalyst deactivation by carbon deposition. Consequently, excess steam and CO_2 increase reformer heat duty. Energy consumption in CO_2 removal unit, located after reformer (as shown in Fig.1) is also higher because of excess CO_2.

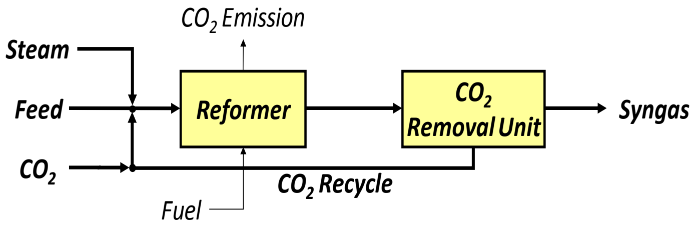

Fig.1 Reforming Process Flow

With these points in mind, Chiyoda has developed catalyst and process in order to reduce energy consumption of reforming process. Chiyoda's CO_2 reforming catalyst (Noble metal catalyst) has higher resistance for carbon formation. So this catalyst can be used in lower S/C conditions and lower CO_2 /C on carbon deposition region as shown in Fig.2. More efficient operation can be performed for the synthesis gas production by Chiyoda's CO_2 reforming process.

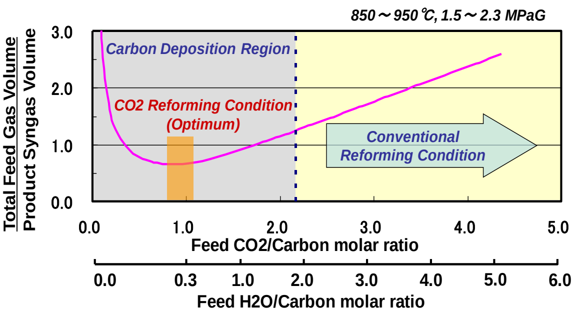

Fig.2 Operation condition and feed gas volume per product gas (H_2/CO=1.0)

For example, as shown in Fig.3, in the case of production of synthesis gas in which H_2/CO ratio is 1.0, Chiyoda CO_2 reforming process can reduce 20% of reformer duty and 85% of energy consumption in CO_2 removal unit. As a result, exhaust CO_2, inclusive of utility consumption can be reduced by around 40%.

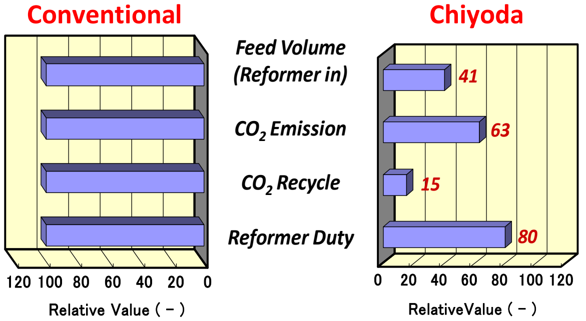

Fig.3 Comparison of each balance in reforming plant (H_2/CO=1)

Chiyoda CO_2 reforming process can utilize CO_2 from exhaust gas from other plants and CO_2 in gas fields. This technology can contribute to Green sustainable chemistry because of efficient production of synthesis gases with variable H_2/CO ratios for oxo alcohol, acetic acid and methanol process.

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