



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 Chemistry.

Japan Association for Chemical Innovation (JACI) and Green Sustainable Chemistry (GSC) Network JACI and GSCN

Kenji Fujiyoshi, President, Japan Association for Chemical Innovation

The chemical industry, which is based on chemistry and associated technologies, is the foundation of the spectrum of industries that provide materials needed by society. Thus the chemical industry is a mother industry whose mission is to produce new products and technologies as it contributes to society. It is absolutely necessary to be active through awareness of GSC in order to develop the chemical industry and solve a variety of the world's issues, including problems regarding resources and energy, which are directly linked to social and economic activities; problems in the water and food supplies on which the human race depends; and environmental problems such as global warming.

The Japan Association for Chemical Innovation (JACI) came into being as an incorporated association in April 2011, and made a new start as a public-interest incorporated association in April 2012. We aim at contributing to development of industries in Japan, reinforcement of international competitiveness, sustainable development of society and healthy economic growth. To achieve these objectives, the Green Sustainable Chemistry Network (GSCN) serves as a core organization. We will vigorously promote the dissemination and enlightenment activities of GSC with thorough collaboration among industries, educational institutions and the administration.

We therefore request your continued assistance and cooperation from every academic, business and governmental field so that the GSCN can fulfill its role as a core organization responsible for the realization of eco-friendly chemistry and the sustainable development of society.

The 11th GSC Award, Award from the Ministry of Economy, Trade and Industry**Innovative ethylene glycol synthesis process using a novel homogeneous catalyst**

Thoshiyuki Furuya, Kazuki Kawabe, Masahiko Yamagishi, Takayoshi Ono, Takenori Atsuda,
Takahito Nishiyama (Mitsubishi Chemical Corp.)

A new catalytic process for the manufacture of monoethylene glycol (MEG), developed by Mitsubishi Chemical Corp., achieved 99% or higher selectivity (previously 89%) as compared with existing processes that have been used around the world for more than 80 years. This technology realizes lean reaction (the above selectivity) and lean resource use while achieving 20% of process wastewater reduction according to our gradually changing awareness in this age of dwindling petrochemical resources.

The industrial manufacture of MEG started in 1925, and currently the worldwide production total ranges up to 2.064 million tons. It is also estimated that the future growth rate will continue to increase by 6-7% annually on a global basis. The present technology has two problems, as summarized below:

- 1) A large excess amount of water ($\times 20$ molar volume) is used;
- 2) The selectivity of the goal product, MEG, is limited to 89%.

Therefore, our company has developed a new catalytic method for the EG process, thus eliminating the problems inherent with the present method.

The first research and development started in 1979, but it was discontinued a short time later. The project was resumed after about 15 years, resulting in the success it enjoys today.

A key point in the attainment of the dramatic, highly selective MEG reaction is that the new reaction from EO to MEG using the new catalyst has a reaction speed more than several hundred times higher than that of the EO hydration reaction without a catalyst. Additionally, the reaction does not require an excessive amount of water (as in the current method) because the catalytic activity is fully exerted with water content, which is nearly the stoichiometric amount. Furthermore, the reaction needs only about half the reaction temperature and pressure of the existing method, enabling us to reduce the energy consumption because the catalyst is highly active.

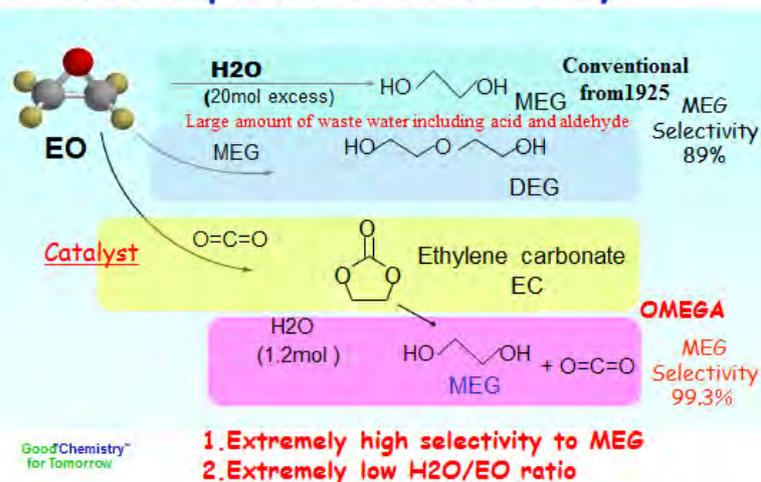
Given the eventual deployment of licensing of the developed catalytic method for the EG process, this process will need to be integrated with an ethylene oxide process. Therefore, as a partner we chose Shell, which possesses the technology. The license business was jointly promoted as the Shell OMEGA process, and is already operating commercial manufacturing at the following three plants:

Honam, Korea: 390,000 t/y in May 2008; Petro-Rabigh, Saudi Arabia: 600,000 t/y in June 2009; and Shell Eastern, Singapore: 750,000 t/y in November 2009.

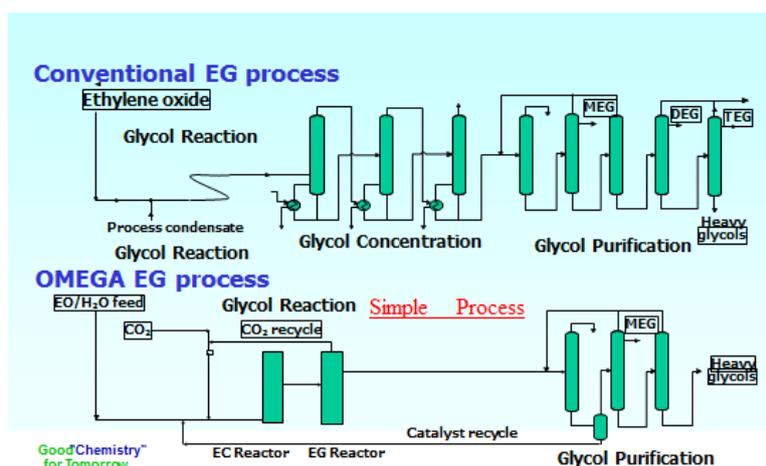
Previously, EG was produced through thermal reaction by adding $\times 20$ molar volume of H_2O . However, EG is produced using a catalyst in this technique. Consequently, the selectivity was increased from 89% to 99% or higher using $\times 1.2$ molar volume of H_2O (theoretically, $\times 1.0$ molar volume), reaching 99.5% at a commercial plant. The success of this innovative technology would go down in the chemical industrial history of the world as a technology of Japanese origin that created a revolution in the EG manufacturing process that had been used throughout the world for more than 80 years.

This is an eco-friendly technology associated with lean reaction (high selectivity), lean resource use, 20-30% of process wastewater reduction, and CO_2 emissions reduction according to our gradually-changing awareness in this age of dwindling petrochemical resources. It is hoped that this technology will be employed all over the world as a technology that contributes to the establishment of a sustainable society based on sustainable resources, although at present the source of the material is different.

OMEGA process chemistry



OMEGA PROCESS FLOW



The 11th GSC Award, Award from the Ministry of Education, Culture, Sports, Science and Technology

Environmentally benign synthesis method of organic modified metal oxide nanoparticles in supercritical water

Prof. Tadafumi Adschiri, WPI-AIMR, Tohoku University

We have developed technologies to continuously synthesize organic modified metal oxide nanoparticles at high concentration in water, which is the best reaction solvent for the environment, by using supercritical water but no organic solvents or catalysts. In supercritical water, organic molecules and metal-based aqueous solution can react in homogeneous condition while water molecules act as the acid/base catalyst; and therefore the organic modified metal nanoparticles can be synthesized. These hybrid nanoparticles can be dispersed well in solvents and polymers, and consequently such nanoparticles are applicable to fabricate organic/inorganic hybrid materials that have both of the functions of organic and inorganic matters at the same time. For example, organic nanoparticles, including boron nitride and alumina, disperse into resins at high concentrations and maintain low viscosity, resulting in improvement of both higher heat-transfer and fabricability. Accordingly, high thermally conductive flexible polymers, which are sought in the fields of automobile-related as well as electrical and electronics-related members, are successfully created. A continuous synthesis process for organic modified nanoparticles with a large scale of 10 t/year production has been already achieved.

Nanoparticles are regarded as a "key" material for nanotechnology. Numerous nanoparticle synthesis methods have been proposed, and some material systems have been commercialized. However, more versatile methods of large-scale synthesis are desired, and in most cases organic surface modification is sought in consideration of the application of nanoparticles. Meanwhile, the existing nanoparticle synthesis methods do not always fully satisfy the objectives of versatility, large-scale synthesis and organic modification, and a large amount of organic solvent is used for synthesis. Additionally, enormous energy is required for the concentration, separation and collection of nanoparticles.

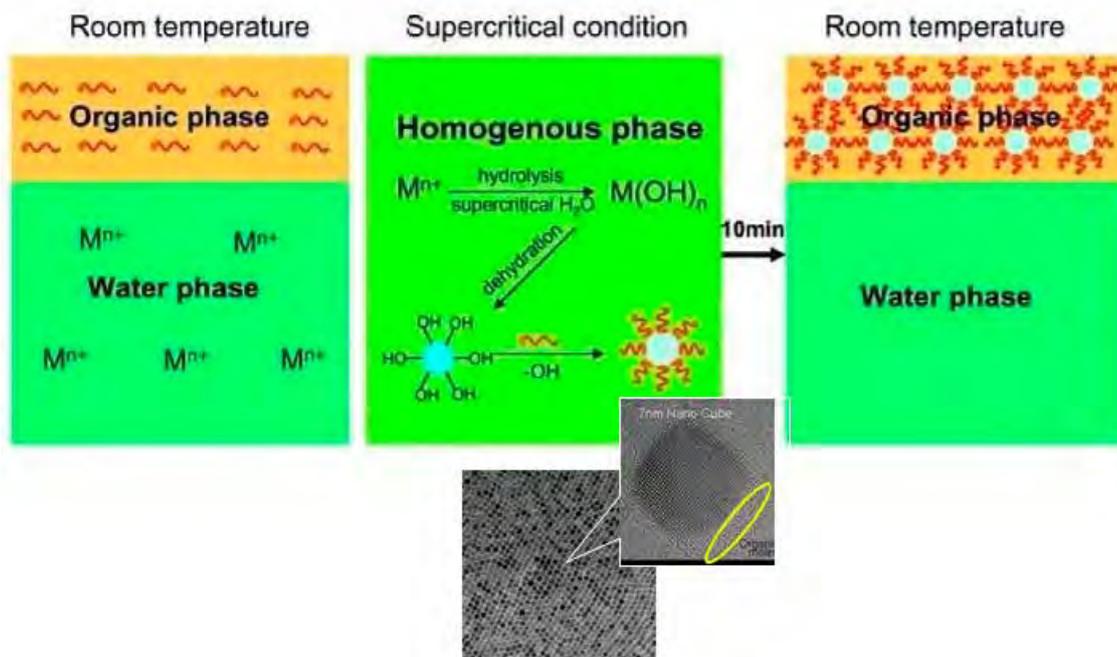
Adschiri et al. proposed a technique using supercritical water as reaction solvent based on hydrothermal synthesis methods, which are the most widely applicable to material systems. In the supercritical hydrothermal synthesis

field, the reaction rate of the hydrothermal synthesis reaction is faster by double digits or more, and the solubility of the metal oxides thus produced decreases by double digits. As a result, an extremely high degree of supersaturation can be achieved, while nanoparticle synthesis can be achieved even in a high concentration condition. To realize such synthesis and conditions, we have proposed and developed a flow type of reaction system for supercritical hydrothermal synthesis. Furthermore, organic modifications are essential for the development of nanoparticle applications. Because inorganic aqueous solution and organic molecules are miscible at any ratio in the supercritical field, the organic modification of nanoparticles can be performed even in a high concentration. Moreover, not only expensive modification agents but also general-purpose items such as oils are available for modification reaction under such conditions.

A scale-up study of the synthesis process for these organic modified nanoparticles is progressing, and a 10 t/year scale process has been completed.

We have also found that surface of thus synthesized nanoparticles are densely modified with organic molecules, and these particles can be dispersed in organic solvents at high concentrations. Additionally, it has been confirmed that the viscosity was extremely low regardless of a highly concentrated colloidal system. Therefore, the development of nano-inks and nano-fluids, which are necessary for the development of manufacturing technologies for printable devices including printed electronics, are expected. When organic modified ultra-high thermally conductive nanoparticles, such as BN and Al₂O₃, were dispersed in polymer resins, the highly concentrated packing of 80 vol.% and higher was achieved while keeping high workability (low viscosity) due to the high affinity to resins. As a result, nonconventional hybrid materials possessing both workability and high thermal conductivity were able to be produced. Additionally, the creation of hybrid macromolecule materials is expected in a wide range of fields, including electrical and electronic engineering, automotives, energy and the environment, medical technology, building materials, etc. A scale-up study of the synthesis process for these organic modified nanoparticles is ongoing, and a 10 t/year scale process is now operating.

The environmentally benign technology for synthesizing organic modified nanoparticles can be a new foundation for industrial technology. A consortium aiming at technology transfer, incubation and human-resource development related to this technology has been established, and more than 70 companies are participating in the consortium. This also indicates the considerable impact this technology will have.



The principle of supercritical method



Application areas: Ultra-high thermally conductive hybrid macromolecules



Supercritical hydrothermal synthesizer developed in this study (10 t/year)

The 11th GSC Award, Award from the Ministry of the Environment

Development of Compact Fuel Processing System for Residential PEFC System ‘ENE-FARM’

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While an aggressive target of global greenhouse gas reduction was set as a national policy, in the residential sector, a “residential PEFC (Polymer Electrolyte Fuel Cell) cogeneration system” (unified brand: ENE-FARM) was developed and commercialized in order to achieve energy saving and suppression of CO₂ emission. We have successfully developed a fuel processing system, which uses city gas or LPG as a raw fuel. It does not need any catalyst replacement for 10 years. It achieves compact size and high performance, and reduces environmental load to about one half compared to a conventional system in LCA. It has been successfully adopted for commercial systems. In the future, further popularization of environmentally friendly “ENE-FARM” is expected.

1. Introduction

In order to achieve energy saving and reduction of CO₂ emission in the residential sector, popularization of

PEFC cogeneration systems for household use is expected. The electrode catalyst of PEFC, which is the power generation unit, is poisoned by CO in hydrogen fuel. It is said that the acceptable concentration is around 10 ppm. In the conventional technology, PSA (Pressure Swing Adsorption) can reduce CO concentration in hydrogen gas to the level and achieves long-term operation. However, when the PSA was applied to residential use, there were a number of problems, such as size, efficiency, treatment of wastes, noise control, and other environmental restrictions,

2. Development of compact fuel processing process

By using its accumulated catalysis technologies, Osaka Gas developed a compact fuel processing process (Fig.1) for supplying hydrogen to PEFC. The raw fuel is city gas or LPG. The biggest challenge was reduction of CO concentration in the hydrogen fuel. It was solved by developing a new CO preferential oxidation removal catalyst. By using the newly developed catalyst, we succeeded to remove the CO in the hydrogen fuel gas to 1 ppm, even when a slight amount of air was added ($O_2/CO=1.5$) (Fig.2). Furthermore, for the steam-reforming catalyst, we succeeded to reduce the amount of activated noble metal to about 1/3 although the catalytic activity was kept high. In addition, by developing a start/stop special method with no use of nitrogen, it became possible to use our high performance CO sift catalyst, which had 50,000 hours of actual performance. Moreover, the amount of our high performance desulfurization agent was also reduced by increasing the activity. It has been confirmed that all of those catalysts and agent need no replacement for 10 years by our own enforced degradation method, and so on.

3. Development of compact fuel processing system

In the meantime, Osaka Gas developed a compact fuel processing system that contributed to the maximum of above catalysts and agent. This system has a unique plate construction without parallel in the world. It can be produced at a low cost by press working form flat plates to containers and automatic welding. It comprises all reactors (desulfurizer, reformer, CO shift converter, CO remover), heat exchangers, and boilers (Fig.3).

4. Contribution to GSC

This fuel processing system is remarkably compact and achieves high efficiency as compared to conventional hydrogen generation system using PSA. Moreover, it can be used for 10 years without replacement of catalysts and agent. It achieves high energy saving. It can greatly suppress consumption of virgin materials and emissions of wastes. It is assumed to greatly contribute to GSC. Furthermore, it made great contribution to commercialization of ENE-FARM.

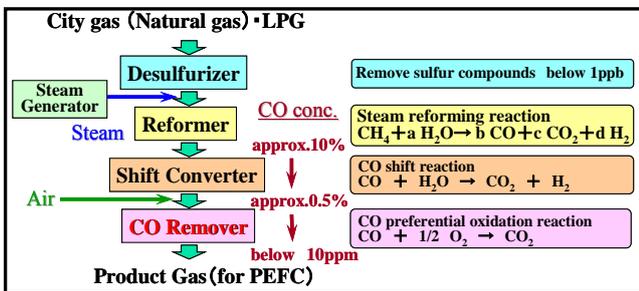


Fig.1 Fuel processing process for PEFC

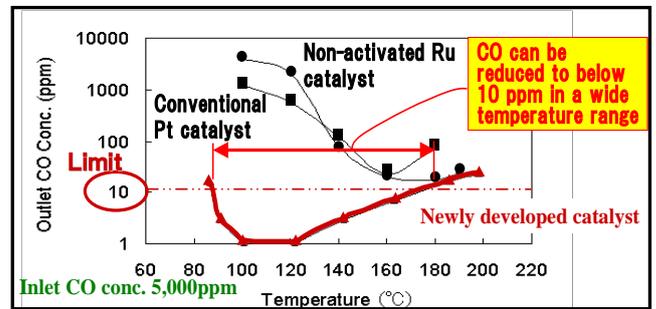


Fig.2 Performance of developed CO removal catalyst

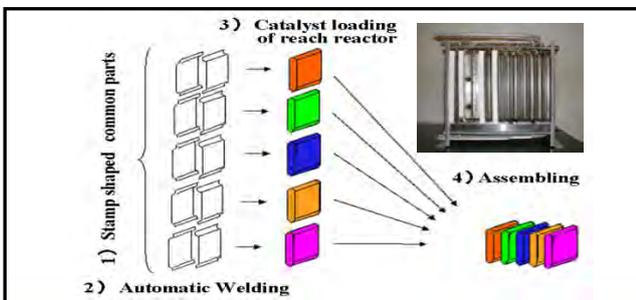


Fig.3 Assembly and appearance of Fuel Processor

The 11th GSC Award**Development of a new process for a solvent-free man-made leather**

Osamu Takemura, Jiro Tanaka, Manabu Nakano, and Yasuhisa Komatsubara (Kuraray Co. Ltd.)

CLARINO has been a world's leading brand of man-made leathers in a variety of fields since our beginning of operation in 1965. We have been dealing with issues including electrical power and water conservation, and there have been also urgent tasks such as reduction of organic solvent use and carbon dioxide emissions. However, such efforts have limitations if it is based on our initial manufacturing process at the time of founding. To make a breakthrough in these circumstances, we started working on innovation processes from 2004, started up a pilot plant in 2006, and began full-scale production from November 2009 after about three years of technological and product development processes, under our new concept of providing environment-friendly man-made leather with rational and stable quality based on our innovative manufacturing technologies.

The new technology is a process that changes traditional solvent-using facilities completely. More specifically, this technology is a rational eco-friendly process that enables us to simplify the process flow (about one fifth at most) as well as to reduce carbon dioxide emissions by about 35%, organic solvent usage by more than 99%, and drainage volume by about 70% (conventional ratio, respectively). These were achieved by combinations of the state-of-the-art technologies including: (1) eco-friendly microfiber technology, (2) nonwoven technology, (3) bulky nonwoven technology, and (4) water-emulsion processing technology.

(1) Eco-friendly sea-island fibers (Fig. 1)

Water-soluble resins are used as a sea component, thereby completely eliminating organic solvent usage from the extraction steps. Melting and decomposition temperatures of these water-soluble resins are close to each other, and a temperature range suitable for spinning is extremely narrow. Therefore, this project was started from the planning and development of the spinning facilities as well as a unique spinning method, which are being operated under strict control.

(2) Highly dense and uniform nonwoven sheets technology (Scheme 1)

The process flow from spinning to making nonwoven sheets was substantially simplified, and stabilization of quality and shortening of a lead time were realized by combining the special spinning technology and high-speed entangling technology.

(3) High dense, bulky nonwoven sheets technology

A unique shrinking method, which takes advantage of shrinkage and extraction properties of the sea-island fibers, is adopted to develop nonwoven sheets with excellent stability of its shape and physical properties. These nonwoven sheets that have a highly entangled fully dense structure consist of ultrafine fibers achieved both superior physical properties (peel strength and tear strength) with less resin amount as well as a natural hand texture like genuine leathers (low resilience and high fulfillment). These characteristics contribute to expansion of the product lines.

(4) Water-based emulsion technology

Elimination of the organic solvent usage was achieved by use of a water-based emulsion (Em) as a binder instead of traditional solvent-based polyurethane. The water-based Em readily moves to the surface in synchrony with water movement during drying; therefore, we are concurrently developing not only products that make active use of such phenomena but also products in which the migration is inhibited conversely.

A new, eco-friendly man-made leather called TIRRENINA, which has been produced on the basis of our technology, allows production without organic solvents while overcoming the disadvantages of traditional man-made leather with a combination of a newly developed ultrafine fiber and water-based resin technologies,

giving it advantages including a favorable texture, physical properties and functionality. For example, in suede products we have successfully combined appearance, fine touch and depth of color (high color-fastness). In full-grain products, we have achieved a structure similar to genuine leathers, flexibility (low resilience) and a full hand texture (high fulfillment) and fine wrinkling on the surface during bending through the combination of a highly dense, uniform ultrafine fiber nonwoven sheets and a special binder. Furthermore, high breathability/moisture permeability, surface strength and flexibility have been achieved for the first time. Additionally, advanced applications such as precise polishing and filtering are expected through the combined high surface smoothness and packing structure of ultrafine fibers and finely expandable hydrophilic resins.

We regard the man-made leather TIRRENINA, which our technology has made possible, as a next-generation eco-friendly man-made leather. Thus the switchover from traditional products is in progress. We expect that eco-strategies in this industry (including the leather industry) will grow in earnest through the worldwide development of eco-friendly man-made leathers by our company, which is a leader in man-made leathers, making man-made leathers the *de facto* standard.

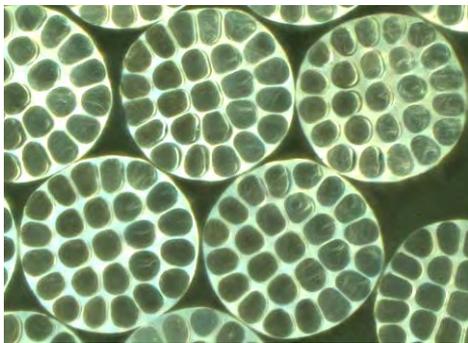
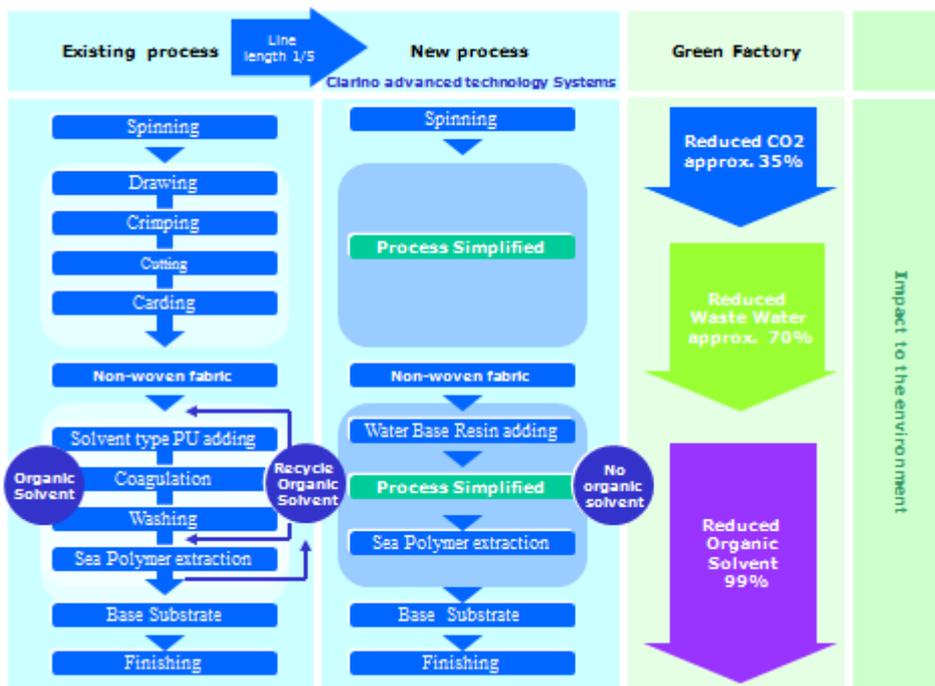


Fig. 1



Scheme 1. Manufacturing process for TIRRENINA and its effect on eco-friendly manufacturing

Manufacturing Process of Carbonic Acid Esters by Direct Activation of Carbon Dioxide

Nobuhisa Miyake, Budianto Nishiyama, Masaaki Shinohata and Hajime Nagahara (Asahi Kasei Chemicals Corporation)

Tomonari Watanabe (Asahi Kasei E-materials Corporation)

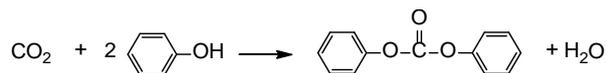
Carbonic acid ester is an important compound in the chemical industry. For example, diphenyl carbonate (DPC) is used as a raw material in polycarbonate, etc. The awardees have developed a new process for the production of DPC that can be used as a safe source of carbonyl groups instead of highly toxic phosgene or carbon monoxide, and have achieved their process through the direct activation of carbon dioxide. The new process produces solely DPC and water by using phenol and carbon dioxide as raw materials. Thus it is a process that accords with the GSC concept, in that it produces carbonic acid ester safely with high selectivity and energy-efficiency.

A carbonyl group (-CO-) is a "functioning organic group" of substances applied to many fields related to daily life and used for polycarbonate (PC), urethane, electrolysis solution for lithium-ion batteries, etc. Sources of the carbonyl group include 1) phosgene, 2) carbon monoxide and 3) carbon dioxide (CO₂) (a comparison among these compounds is shown in Fig. 1). Mainly, phosgene has been used on the basis of its high reactivity. However, as shown in Fig. 1, there remains the problem that phosgene and carbon monoxide are extremely toxic.

The new process developed by the awardees is a technology based on a new, non-phosgene method for polycarbonate manufacturing process using by-product CO₂ as a raw material. This process is an innovative process by which to produce DRC and DPC using CO₂ as a carbonyl source without additional raw material by directly activating CO₂.

Features of the new process:

- 1) No additional raw material is required because CO₂ is directly activated. Furthermore, this is a clean process in which only "water" is released from the system.
- 2) The process uses safe raw materials and requires no additional raw materials; thus there is no restriction in terms of site location for industrial manufacturing.
- 3) As shown in the overall reaction below, CO₂ is stoichiometrically used to produce DPC:



- 4) DPC is extremely useful as a carbonyl source, as it can be used in various chemical manufacturing processes.
- 5) Energy consumption of the new process is small.

(Note: For example, when energy consumption of the process up to PC is converted into CO₂ emissions and compared with the CO₂ emissions of the traditional phosgene method for PC production, it can reduce the emissions to a large extent.)

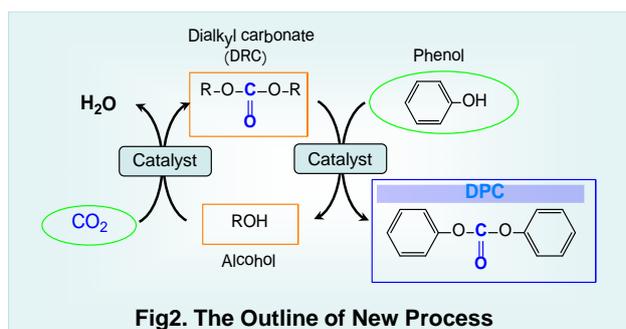
As shown in Fig. 1, CO₂ is a safe and inexpensive raw material, but it has very low reactivity. Various synthesis methods have been developed to overcome this low reactivity, but to date no such method has achieved a level sufficient for industrial manufacturing. As a result of our development of catalyst technology and the building of a reaction system, we have overcome the issue of low reactivity in CO₂. Furthermore, we have completed the technology by developing a manufacturing process at an industrially available level and facilitating engineering considerations, thus establishing the technology and implementing long-term pilot operations to add improvement in terms of the manufacturing technology. The outline of the new process is shown in Fig. 2. First, DRC is obtained using an organic metal compound as an activating agent for CO₂. Then, the DRC is reacted with phenol to obtain a target substance, DPC, through transesterification and disproportionation reactions. All the intermediate products of this new process are recycled in the system;

therefore, the raw materials are phenol and CO₂ but the products are only DPC and water. Consequently, DPC can be manufactured without problems in regard to the procurement of raw materials, the safety of intermediate products and the limitation of site locations.

DPC is a useful compound that is applicable to various chemical products. Because this technology is also economically advantageous, it can be expected to spread throughout the world. All the problems of traditional technologies, including hazardous nature of raw materials, low reactivity, additional raw materials, co-products and waste products, are eliminated with the new process. Also, the process produces carbonic acid ester safely with high selectivity and energy-efficiency. Therefore, the new process is a manufacturing process in accordance with the GSC concept.

		CO	CO ₂
TLV	0.1ppm (TWA)(ACGIH2002)	25ppm (TWA)(ACGIH2001)	5000ppm (TWA)(ACGIH2001)
Reactivity	Extremely high	High	Extremely low
Others	Corrosive		Inexpensive

Fig1. Comparison of Carbonyl Source



The 1st GSC Encouragement Award

Development of a Nitrogen Fixation System Using Transition Metal Complexes

Nishibayashi Yoshiaki, School of Engineering, University of Tokyo

The Haber-Bosch process, which is referred to as making "bread out of air," was developed at or around the beginning of the twentieth century. Since then, the same basic method has been used in ammonia synthesis. However, that process, which supported the world's population explosion, is an energy-consuming process that uses fossil fuels as raw materials and generates enormous amounts of carbon dioxide. Therefore, we have succeeded in the development of a reaction system to efficiently produce ammonia from nitrogen gas under very mild reaction conditions, doing so through the use of transition metal complexes in which a nitrogen molecule coordinates to the central metal. The fascinating results suggest the potential development of next-generation nitrogen fixation systems.

The Haber-Bosch process is an industrial nitrogen fixation method used to obtain ammonia from nitrogen and hydrogen, mainly with the use of iron oxide as catalyst under extreme conditions of high temperature and pressure. This method was developed at or around the beginning of the twentieth century, and it has been used ever since. However, that conventional method is an energy-consuming process; therefore, development of more efficient nitrogen fixation methods is one of the most important research challenges for chemists to achieve. It was very difficult, but we squarely addressed the issue and successfully obtained fundamental findings for the development of next-generation nitrogen fixation methods.

We have developed a reaction system by which to efficiently produce ammonia from nitrogen gas under very mild reaction conditions through the use of transition metal complexes in which a nitrogen molecule coordinates to the central metal. Thus we were able to synthesize ammonia from nitrogen and hydrogen under very mild reaction conditions based on the new concept that nitrogen and hydrogen molecules--which are two different, small molecules with very different characteristics--would directly react to each other through activation on transition metal complexes. This became the first example of ammonia synthesis from nitrogen and hydrogen under very mild reaction conditions. Subsequently, we found that a clathrate

compound, which can be synthesized from fullerene (C_{60}) and a kind of sugar called γ -cyclodextrin, has a nitrogen fixation ability that converts nitrogen molecules to ammonia. The coordination of nitrogen molecules on transition metals and activation steps was essential for all previously known nitrogen fixations. In contrast to these systems, this is the first example of conversion from nitrogen molecules to ammonia using only fullerene derivatives, which consist of only carbon, hydrogen and oxygen, under mild conditions. These are stoichiometric ammonia synthesis reactions, but nevertheless they are academically interesting and very important findings.

We in fact succeeded in developing not only stoichiometric reaction but also ammonia synthesis reaction mediated by catalysts. Particularly, we created a nitrogen-linked dinuclear molybdenum-nitrogen complex with pincer-type ligands and a molybdenum-nitrogen complex with ferrocenyl diphosphine ligands; ammonia synthesis reaction mediated by catalysts and silylamine synthesis reaction mediated by catalysts, as equivalent to ammonia, under very mild reaction conditions at ordinary temperatures and pressures from nitrogen gas. Both of them are highly efficient reaction systems that have not previously been achieved.

As mentioned above, these results are important findings regarding the development of next-generation nitrogen fixation methods originating from Japan.

