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

Expectations of GSCN and JACI

Atsushi Fukuda
Director, Fine Chemicals Office,
Chemicals Division, Manufacturing Industries Bureau,
Ministry of Economy, Trade and Industry (METI)

[GSC (Green Sustainable Chemistry)] is a Japanese-specific concept, which received consensus at the GC workshop held in 1999 with the participation of industry and academia regarding "the sustainable chemistry program" proposed by the chemical risk management committee in 1998. GSC has been supported mainly by the GSCN, which is composed of about 30 chemical societies and organizations. This important government policy entitled "green innovation" has long been anticipated by the chemical industry.

From the governmental body, the GSC concept won the 2nd (2002) GSC award with contribution from three Ministerial awards; Minister of Education, Culture, Sports, Science and Technology; Minister of the Environment and Minister of Economy, Trade and Industry. We have been making strong efforts toward GSC technology including adding GSC fields to the "technological strategy map" in 2008 and initiating the GSC's eponymous GSC fundamental technology development project. Furthermore, GSC was mentioned in a report in the "Chemical Vision Society" published in April, 2010, and also in the formulation report of the Fourth-stage Basic Program for Science and Technology at the Cabinet Council for Science and Technology published in December, 2010.

In this context, the Japan Association for Chemical Innovation was established this April and GSCN was regarded as one of their main activities.

The Japan Association for Chemical Innovation was established by developmentally integrating part of the Japan Chemical Innovation Institute (JCII), which has been responsible for the role of GSCN secretary in The Association for the Progress of New Chemistry. We would like to list the following three items regarding further growth of our chemistry based on our GSC technologies in future global competition.

First, we expect that “cooperation”, beyond domestic-friendly competition. will be more important in the future. Therefore, we would like to ask for the development of connections which contribute to deepening CTO company communications. Next is to discover new subjects for technological development or a standardization strategy for the future. These should be performed on the basis of the relationship between company- or industry-University cooperation. Third, it is very important to enhance activities such as human resource development or expansion of GSC concepts through GSCN activities. These items should be supported by industry. We would like to show our respect for the great efforts of those involved, and we wish continued effort can contribute to further development of our chemistry and chemical technologies in Japan.

Finally, we would like to thank the readers of this newsletter for their great cooperation.

<< 2010 GSC Award of Minister of Economy, Trade and Industry >>

Environmentally-friendly process for production of adamantane using a new solid acid catalyst

Masao Saito, Noriaki Hosotani, Jun Mase, Toshiaki Kusaba, Akio Kojima
Idemitsu Kosan Co.,Ltd.

ABSTRACT

Adamantane is a useful compound used as a photoresist material for semiconductor manufacturing or a chemical precursor for pharmaceutical products.

Although aluminum chloride has been as a most popular catalyst for adamantane manufacturing, it also produces much waste containing chlorinated solvents and brings environmental pollutions. We developed a new adamantane manufacturing process of higher efficiency and less waste applying a new solid acid catalyst to solve this pollution problem.

We completed the world's first adamantane manufacturing process using a solid acid catalyst of 300 ton annual production capacity in 2008.

Adamantane is a basket-shaped alicyclic saturated hydrocarbon in which 10 carbon atoms form the same structure as a diamond (Figure-1). The structure of adamantane bestows upon it unique characteristics including high thermal stability and high transparency, and therefore it has been used in various functional materials such as photoresist material for the manufacture of new semiconductors, pharmaceutical products, display materials and optical materials. We have been supplying our adamantane derivative products, Adamantate ™, and expanding

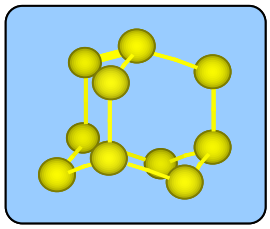

Fig.1 Adamantane

more applications.

Until now, adamantane has been industrially synthesized through the isomerisation of tetrahydrodicyclopentadiene (THDP), which is obtained by the hydrogenation of dicyclopentadiene, with an aluminium chloride catalyst (Aluminum Chloride method). However, the conventional manufacturing process is associated with various problems, including the following: 1. THDP requires approximately twice the weight of aluminium chloride in order to complete the reaction and the aluminium chloride catalyst cannot be recycled. Much waste is therefore generated (aluminum waste, acid waste); 2. Heavy hydrocarbons (tar waste) are produced as a by-product and cannot be recycled; 3. Chlorinated solvents are required, which are not environmentally friendly; 4. It is a low efficiency batch process.

To solve these problems, we have developed a new adamantane manufacturing process. In the conventional Aluminum Chloride method, both catalyst and precursor are liquids, making separation of the product from the catalyst after the reaction cumbersome. In our new process, however, we applied a fixed-bed flow reaction system in which the solid acid catalyst is fixed in the reaction vessel. For the solid acid catalyst, we developed a new catalyst which is more suitable for adamantane synthesis. In contrast, the traditional commercially available solid acid catalyst does not have sufficient capability for the industrial manufacture of adamantine due to the following: 1. decomposition of THDP causes the decrease in yield of adamantane; 2. rapid catalyst deactivation is caused by heavy by-products. Through our efforts, we were able to develop an industrially applicable catalyst by adding water and aromatic compounds to the rare earth elements and Pt supported catalyst.

We succeeded in establishing a high efficiency adamantane manufacturing process by applying a fixed-bed flow reaction system and using a new solid acid catalyst. This system does not require chlorinated solvents and does not produce waste. Additionally, by-products produced from the reaction can be recycled as petrochemical raw materials. Thus, this new system has advantages over the conventional synthesis method in terms of resource utilization as well as cost (Figure-2).

We built our manufacturing plant inside the Idemitsu Kosan Tokuyama factory in 2008 and succeeded in carrying out the world's first practical implementation of the adamantane manufacturing process using this new solid acid catalyst system. This plant has an annual

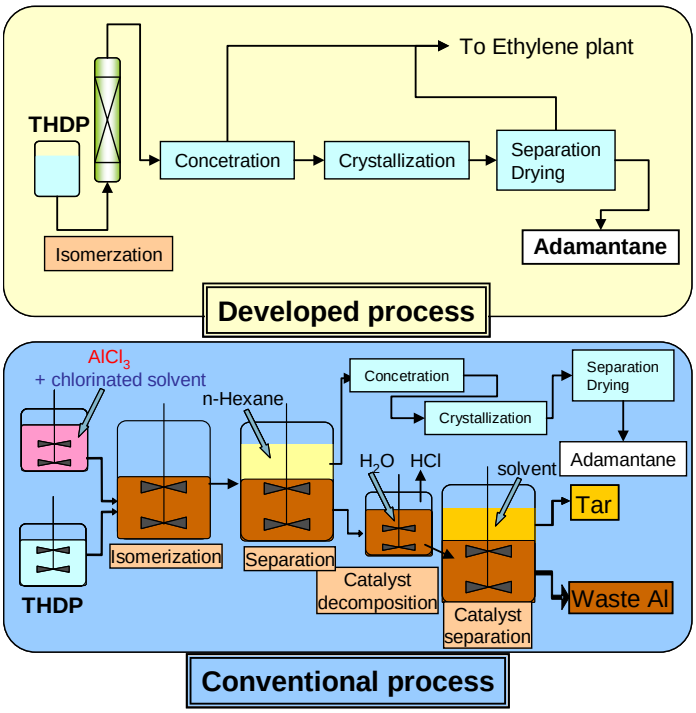

Fig-2 Comparison of the Adamantane processes

adamantane production capacity of 300 tons.

This technology is a very unique system for isomerisation of alicyclic saturated hydrocarbons using a solid acid catalyst. The problems observed from conventional synthesis have been eliminated and the by-products can also be recycled. We therefore consider this new system to be an example of industrialization with the added achievement of an environmentally friendly green process. We are hopeful that this new technology can contribute significantly to GSC development.

(contact address:masao.saito@si.idemitsu.co.jp)

<< 2010 GSC Award of Minister of Education, Culture, Sports, Science and Technology >>

R&D of Organic Radical Battery with Environmental Friendliness

Kentaro NAKAHARA, NEC Corporation

ABSTRACT

Recently, research on high-performance secondary batteries, which support electric vehicle or clean-energy techniques, has been progressed to achieve a low-carbon society.. We developed an environmentally friendly secondary battery, the “Organic Radical Battery”, by utilizing redox reactions of organic radical polymers which have robust unpaired electrons. Since this battery does not require heavy metal compounds such as lead, manganese or cobalt, which are necessary for conventional secondary batteries, it has opened up a new research field, plastic rechargeable batteries. This battery is therefore expected to contribute significantly to green sustainable chemistry (GSC).

In modern mobile societies, “secondary batteries” are a necessary energy source for various electronic devices such as mobile phones and laptop computers. Recently, such batteries have been applied to the use of electric vehicles or clean-energy techniques with the goal of achieving a low-carbon society. In conventional secondary batteries, heavy metal compounds such as lead, manganese, nickel or cobalt, are required as material for the cathode. However, several concerns in the use of these materials have arisen concerning environment pollution,, toxicity, resource exhaustion, and cost increases. To overcome these problems, we synthesized an organic radical polymer containing robust unpaired electrons, and developed a secondary battery, the “organic radical battery”, by applying the polymer as the cathode active material. This battery is not only environmentally friendly, but also capable to high-rate use. To commercialize this battery as a new thin and flexible secondary battery, research is therefore being progressed.

One of the organic polymers we have synthesized is polymethacrylate (PTMA), which contains 2,2,6,6-

tetramethylpiperidine-1-oxyl (TEMPO) in its side chain (Figure 1). When the composite electrode of this polymer and carbon powder is used as the cathode in lithium batteries, it changes the structure of nitroxyl radicals into oxoammonium salt at the voltage over 3.6 V and can store positive charge. By utilizing this reaction as the charging reaction, and the reverse reaction as the discharge reaction, we developed the secondary battery, named an “organic radical battery”.

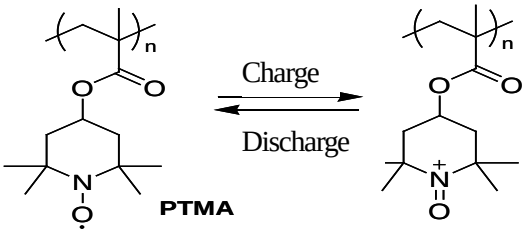

Figure 1. An example of charging/discharging reaction of the organic radical polymer

The synthesized PTMA (Molecular weight 241) can store 1 electron per monomer unit, therefore, 1 g of the polymer can store 110 mAh of electric charge in total.

We also succeeded in synthesizing material which can store 135 mAh of electric charge per gram. We confirmed that organic radical batteries made of these materials do not show significant degradation even after 1000 charging and discharging reactions. A high current can also be created by discharging the entire capacity of the battery in approximately one minute. The high practicability of this battery has been proven.

Research on new practical applications of these organic radical batteries such as an emergency power source for computers, smartcards, or as a flexible battery to fit in a wearable terminal, are being developed. In particular, the thin organic radical battery (less than 1 mm in thickness) the size of a 500 yen coin possesses over 2 W output and has also proven to be stable after more than 10,000 pulse discharge cycles. It is therefore expected to be used as a power source for small devices which require high power output.

Research on organic radical batteries is sparking a new research field of plastic rechargeable batteries, new polymer syntheses, and-new hole-transport materials. This organic radical battery is expected to significantly contribute to further development of green sustainable chemistry.

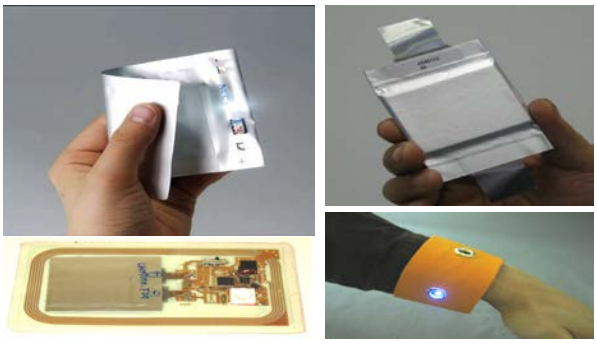

Figure 2. Images of different types of organic radical batteries

<< 2010 GSC Award of Minister of the Environment >>

Development of Powdered Photocatalysts for Hydrogen Production from Water using Sun Light

Tokyo University of Science, Professor Akihiko Kudo
E-mail: a-kudo@rs.kagu.tus.ac.jp

It is the big theme how to produce hydrogen of a clean energy from a viewpoint of energy and environmental issues. It is indispensable to develop a clean method for hydrogen production being independent of fossil fuels. The ideal hydrogen production method is water splitting using renewable energy. Photocatalytic water splitting has been paid attention as a candidate for it.

Photon energy is converted to chemical energy accompanied by a largely positive change in the Gibbs free energy through water splitting. This reaction is similar to photosynthesis by green plants from the viewpoint of the uphill reaction with the positive change in the Gibbs free energy. Therefore, photocatalytic water splitting into H2 and O2 in a stoichiometric ratio is regarded as artificial photosynthesis. The characteristic point of water splitting using a powdered photocatalyst is the simplicity. Therefore, powdered photocatalyst systems will be advantageous for large-scale application of solar water splitting because of the simplicity. So, photocatalytic water splitting is an attractive reaction and will contribute to an ultimate green sustainable chemistry and solving energy and environmental issues resulting in bringing an energy revolution.

The Honda-Fujishima effect of water splitting using a TiO2 electrode was reported in the early stage of 1970's. Numerous researchers had extensively studied water splitting using semiconductor photoelectrodes and photocatalysts since the finding. However, efficient materials for water splitting into H2 and O2 under visible light irradiation had not been found. Accordingly, the photon energy conversion by water splitting using photocatalysts had been considered to be pessimistic. However, new photocatalyst materials for water splitting have recently been discovered one after another. Although the photon energy conversion using powdered photocatalysts is not at the stage of practical use, the research in photocatalytic water splitting is being advanced. The photocatalytic water splitting is still a challenging reaction even if the research history is long.

In such background, we have developed a highly active NiO (0.2 wt %)/NaTaO3:La (2%) photocatalyst for water splitting. Under irradiation of the light from a 200-W Xe-Hg lamp, H2 and O2 evolve in the form of bubbles without any sacrificial reagents as shown in Fig. 1.

Fig. 1 Highly efficient water splitting over NiO/$NaTaO_3$:La photocatalyst

Although this photocatalyst responds to only UV light, it should be stressed that this photocatalyst has demonstrated the highly efficient water splitting

even using a powdered system. On the other hand, a lot of visible light-driven photocatyalysts were developed by the original strategy for design of photocatalysts. The system in which SrTiO3:Rh is combined with BiVO4 in the presence of an Fe3+/Fe2+ redox couple was developed for overall water splitting under visible light irradiation according to a Z-scheme. This Z-scheme system was active even with a solar simulator. In other words, solar hydrogen production from water has been accomplished using a powdered photocatalyst system with visible light response. We have also examined the photophysical and photocatalytic properties of solid solutions of sulfides based on ZnS according to the band engineering. Solid solutions consisting of combinations of CuInS2, AgInS2, and ZnS show the high photocatalytic activities for H2 evolution from aqueous sulfide and sulfite solutions under visible light irradiation. Ru/Cu0.25Ag0.25In0.5ZnS2 especially showed excellent activity for the H2 evolution solution with a solar simulator (AM-1.5). These photocatalysts will be able to be used for the recovery of hydrogen from water and abundant sulfur compounds in nature, and petroleum and mining industries.

Thus, some breakthroughs have been achieved for photocatalysts for water splitting. These results contribute to new aspects of science for photocatalysis.

<< 2010 Green and Sustainable Chemistry Award >>

Development of New Environmentally Benign Process of Perfume Compound

Ryoji Sugise, Takashi Doi, Masashi Shirai, Yoshihiro Yoshida, Eiji Sajiki
UBE industries Ltd.

2-Methyl-3-(3,4-methylenedioxyphenyl) propanal (MMP) is an aroma chemical which has been widely used in perfumes, cosmetic items and shampoos. MMP has been traditionally produced from sassafras oil obtained from tree root. However, depleted supplies of natural resources as a result of destructive lumbering and deforestation have become serious problems. We therefore successfully developed a new process of MMP from available industrial materials.

MMP is an aroma chemical which possesses a fresh scent similar to melons or watermelons. MMP was originally produced from sassafras oil obtained from the sassafras tree, which grows gregariously from southern China to Vietnam and Cambodia (Figure 1). However, due to destructive lumbering, such trees are facing extinction, and deforestation for the sassafras oil supply has caused serious problems such as flooding, landslide, etc. Additionally, sassafras oil can be used as a precursor in the production of the synthetic narcotic drug MDMA. To protect the environment and prohibit illicit drug production, lumbering has been banned, imports and exports restricted, and the trees have been registered on the IUCN endangered species Red List. However, despite these efforts, deforestation has not declined. Furthermore, the traditional synthesis of MMP

brings a large environmental damage since 200 kg of timber is required in order to produce 1kg of MMP, and the yield of MMP from the sassafras oil is estimated to be around 30%.

To overcome these problems, we (UBE industries) developed a new process for complete chemical synthesis of MMP using the commercially available chemical, methylenedioxybenzene (MDB), as a starting material. During the development of this process, we found that MDB and methacrolein derivatives form a C-C bond with high selectivity in the presence of catalytic amount of a Lewis acid. To the best of our knowledge, no previous report on practical C-C bond forming reactions of aromatic compounds with methacrolein derivatives exists, and this is the first report detailing the establishment and industrialization of the complete chemical synthesis of MMP. This new catalytic reaction can also be applied to produce other aroma compounds or pharmaceutical intermediates. UBE process consists of 4 catalytic reactions and does not require any organic solvent (Figure 1). Furthermore, excess reactive substrate, if present, can be recycled in the next batch. Therefore this synthetic process can minimize waste generation and realized green sustainable chemistry.

We initiated commercial manufacturing of MMP in 2004. Our concept of stable supply, high quality and an environmentally friendly process has been recognized by users, allowing a smooth transition to replace the traditional synthesis method. By 2008, our method achieved approximately 100% international market share and our product became the global standard. Responding to increased market share and demand, the capacity of the manufacturing plant has gradually increased from 500 t in 2006 and is expected to reach 800 t in 2011 (Figure 2).

By applying this new MMP synthesis method, we can stop destructive lumbering of endangered trees, which is estimated at more than 500,000 per year, and we can contribute to the protection of forests and the maintenance of biodiversity. Importantly, CO_2 emission from this new synthesis method is less than 1/40 of that generated by the original method, which will result in a reduction of more than 200,000 t of CO_2 emission per year.

As described above, our “made in Japan” chemical technology has allowed the establishment of a stable MMP supply using an environmental friendly method that contributes significantly to achieving a sustainable society.

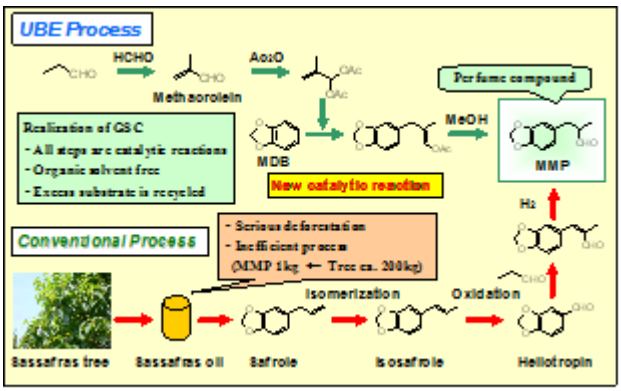

Figure 1. New process of manufacturing MMP and conventional process

Figure 2. MMP manufacturing plant (production capability: 800t)