

JACI NEWS LETTER

Japan Association for Chemical Innovation

No.55 2015.5

HEADLINE

- 01 Making GSC-7 to a new GSC creation site
- 02 The STGA winners were dispatched to the 5th GSC Asia-Oceania Conference
- 04 Biomass conversion by solid catalysts
- 05 Mesoporous silica coated by transition metal oxides
- 06 A Special forum "Innovation Realization"
- 06 Announcing the fourth JACI/GSC symposium GSC-7 (July 5 – 8, 2015)

Making GSC-7 to a new GSC creation site



Department of Applied Chemistry,
School of Advanced Science and
Engineering, Waseda University
Professor

Masahiko Matsukata

The 7th International Conference on Green and Sustainable Chemistry (GSC-7) and the 4th JACI/GSC Symposium will be held at Hitotsubashi Hall and Gakushi Kaikan of Hitotsubashi University in Takebashi, Tokyo from this coming July 5th (Sunday) to 8th (Wednesday), 2015.

The International Conference on Green and Sustainable Chemistry (GSC) is held every 2 years in Europe, North America, and the Asia and Oceania region in turn since the first conference (GSC-1) was held at International Conference Center, Waseda University, in Tokyo in 2003. It has played a function as a place for exchanging the latest information related to GSC. In response to the Rio Declaration at the Earth Summit in 1992, Paul Anastas and John Warner proposed the 12 Principles of Green Chemistry in 1998 in order for chemistry to develop in harmony with the environment, based on the thought that it is an important issue to decrease negative influence of chemistry on the global environment. A new direction in chemistry called Green and Sustainable Chemistry, combining the above Green Chemistry and Sustainable Chemistry, a way of thinking to endeavor continuous growth with economic rationality, was adopted as the "The Statement 2003" at GSC-1 in 2003. Although I have heard that heated words were exchanged over the draft until the day of the announcement when the Tokyo Declaration was adopted, this way of thinking became established later.

GSC-7 in July will be held in Japan after an interval of 12 years as the GSC International Conference. Long-term global issues, such as problems related to resources and energy, global warming, water and food supply, and population, etc., have become more serious and complicated today, and the expectation for innovation based on chemistry is increasing as a driving force to resolve these problems and to lead to the continuous development of a more healthy and enriched society. GSC-7 plans lectures by people in top positions in industries, governments and Academia, presentations of the latest research results on GSC and exhibitions related to GSC activities, etc. and it is expected to be a place for discussing the future direction of GSC. I hope that many people participate in this place to create a new GSC and have active discussions.

July 2015 GSC-7
It's Coming!



The STGA winners were dispatched to the 5th GSC Asia-Oceania Conference



AOC-5 main venue

Five graduate students who received the 8th GSC STGA (Student Travel Grant Award) were dispatched to the 5th GSC Asia-Oceania Conference, which was held in Delhi, India from January 15 to 17, 2015.

GSC STGA is selected every year for the purpose of giving a chance to attend an international meeting and to expand knowledge and networks of personal relationships further for Japanese graduate students performing excellent research in the GSC field.

In this meeting, Paul Anastas and John Warner, who proposed the famous "12 Principles of Green Chemistry" in 1998, and David Constable, the director of the American Chemical Society Green Chemistry Institute, gave the keynote address on the Web and indicated approaches for problems that modern society is facing. John Warner and David Constable will come to GSC-7 (the 7th International Conference on Green and Sustainable Chemistry in Tokyo) that is held by JACI in July in Tokyo and each of them will give a lecture.



Wataru Aoki
Department of Chemistry &
Biotechnology, School of Engineering,
The University of Tokyo

By attending AOC-5 GSC, I was able to obtain several viewpoints and opportunities which I would not have been able to get in "normal life." Since researches of a wide variety of fields were presented at poster presentations, including studies more science oriented than chemistry such as the bad influence arsenic has on the human body, and the nutritional value of dried cucumber skin etc., it was especially impressive for me. The completely different viewpoints for GSC of many people were stimulating for me. In addition, this conference was the first international meeting for me and I reaffirmed the difficulty and importance of communicating in English through asking questions after oral presentations and having discussions at the poster session. Developing what I obtained and felt at this conference, I would like to continue to think about "what is 'genuine' GSC?" that was in the talk at the closing ceremony.



Hironobu Sakaguchi
Division of Applied Chemistry, Graduate
School of Engineering, Osaka University

This conference in India all boils down to one word, energetic. Getting off an airplane and leaving the airport, I was immediately surprised by the strong air of excitement of the Indian people. Although I have heard that India has grown enormously in recent years, it was "seeing is believing." The conference center was also filled with an air of excitement. It was a different type but the same level or even stronger enthusiasm compared to around the airport and the streets of New Delhi. I clearly felt it at the social gathering for students that was held on the 3rd day of the meeting. The students were still undergraduates and they had almost no research experience. However, when I saw their sincere attitude toward chemistry with my own eyes, I was shocked and ashamed at the same time because I felt I was not seriously thinking about chemistry when I was at their age. I had a great experience both in and outside the meeting, which was worth everything. Making the excitement that I felt in India my motivating force, I will go back to my usual research life on a new note.



The landscape of Delhi city

Reflecting the constant strong interest of the Indian people, many lectures and presentations were about environmental problems with water, atmosphere, and biomass with many attendees who came from Asian countries such as Indonesia, Thailand, and China, etc. STGA students emphasized that they were much inspired.

However, the most surprising thing for the students must have been the seriousness and enthusiasm of Asian students at a social gathering for students. It seemed that the Asian students' enthusiasm, taking in every word of Japanese students while throwing questions and arguing with them, became hopes and tasks such as "how can we make a contribution as Japanese in the future," in the STGA students and the hopes and tasks surely became grounded in STGA attendees.



A social gathering for students

Attending an international conference as a graduate student was a precious experience. I could obtain new viewpoints to deepen my research by thinking about how to explain my research results to the researchers in different fields and getting comments. Especially, since it was an international conference, I could interact with researchers attending from all over the world and feel their environment and culture through their research. Therefore, I could learn about various countries as if I had a tour around the world. Although it was a short trip, thanks to JACI support, I was able to meet various researchers and learn that research in the GSC field progresses in many different forms depending on the country. I would like to proceed with research which can be performed because I am in Japan.



Hyunhee Shim
Division of Applied Chemistry, Graduate School of Engineering, Osaka University

I attended the 5th GSC Asia-Oceania International Conference which was held in New Delhi. By listening to research presentations in a wide variety of fields in GSC, I could expand my knowledge regarding GSC's actual situation which was very informative. In addition, I could strengthen cultural exchanges with people in different fields at poster sessions and the social gathering with local students and gain inspiration. I will make even more of an effort based on the precious experience I obtained in this meeting. Although it was a short time, I hope I have a future relationship based on a friendly rivalry together with other GSC STGA winners who went to this meeting. At last, I deeply appreciate GSCN for giving me this opportunity.



Kento Taniguchi
Department of Applied Chemistry, School of Engineering, The University of Tokyo

Researchers from many fields attended the AOC GSC-5 and I felt a high level of attention to GSC from each field. At the same time, I could have a great opportunity to know about activities of GSC based on various points of view. Although all presentations were quite interesting, a talk at the special session on the first day of the meeting was very impressive for me: GSC holds good only after three factors, "Cost," "Performance," and "Sustainability" together. It was a great result to act in concert with the four other STGA winners and to have a fruitful experience rich in content. I would like to perform research using this experience in the future so that I can contribute back to the society through my research.



Takashi Toyao
Materials Science and Engineering, Graduate School of Engineering, Osaka Prefecture University

Biomass conversion by solid catalysts

Atsushi Fukuoka, Professor, Catalysis Research Center, Hokkaido University

In order to realize a sustainable society, it is necessary to reduce greenhouse gases. As a method to achieve this goal, studies to use biomass as a resource are actively being performed all over the world. Regarding biomass applications, although biomass can be a renewable carbon source, considering its small quantity of resources, it is better to aim at synthesizing chemical products which are difficult to make from petroleum. Furthermore, in case of using a solid catalyst, the process needs to have an advantage over other competitive methods such as using enzymes and sulfuric acid etc.

First, we look at the amount of biomass resource in order to consider biomass applications. Based on materials of the Ministry of Agriculture, Forestry, and Fisheries, the proportion of biomass is 1 and 10 percent of primary energy in 2008 in Japan and all over the world, respectively. It is expected to be 3 and 12 percent in 2035 for each, only increasing slightly (materials of the 4th Biomass Utilization Promotion Council of the Ministry of Agriculture, Forestry and Fisheries, 2012.2.2). Based on this trial calculation, even when we use all available biomass in Japan, we can only reduce greenhouse gases by 3 percent. In other words, it indicates that the amount of biomass resource is small in Japan and its effect to reduce CO₂ is limited. There is a possibility that such a prediction falls short when a great technological innovation occurs. However, we would like to humbly accept it now. Considering this, I think we had better use biomass in order to effectively utilize petroleum as much as possible in Japan. When we do so, I think we should try to pass the above trial calculation related to greenhouse gas reduction as much as possible by reducing CO₂ emission through individual biomass application technologies and accumulating the amount of reduction. I think that these technologies will be used not only in Japan but also in other countries with a large amount of biomass resources and it will contribute to reduce greenhouse gases.

Next, let us think about biomass conversion by solid catalysts. Figure 1 shows the number of papers with both biomass and catalyst as keywords. The number of papers has been dramatically increasing during the last 15 years and 1,409 papers were published all over the world in 2014. As catalysts, the so-called homogeneous catalyst, such as enzymes and sulfuric acid etc., have been used for a long time. However, solid catalysts that are easily separated and reused are being used more often recently. In such a circumstance where competitive methods

exist, I think the following two points are important, 1) to synthesize a chemical product that has an advantage by using biomass over petroleum as raw material, 2) to make a process that has an advantage by using the catalyst over other methods.

An example of 1) is polycarbonate form isosorbide as monomer and already being introduced in this column (Komaya, JACI News Letter No. 53, 6 [2014]). This resin has good transparency and optical characteristic, and it is used in our daily life products such as cell phone cases, etc. Due to the large potential of the reduction of the amount of petroleum use and CO₂ emission in its manufacturing process, there is enough significance to use biomass. It seems that starch is currently being used as raw material. If inedible biomass, cellulose, can be used as raw material, it will lead to a further CO₂ reduction. As an example of 2), I would like to introduce sorbitol dehydration reaction by a solid catalyst. This reaction is a method to synthesize isosorbide in 1) and sulfuric acid is currently being used as a catalyst in the reaction. However, sulfuric acid cannot be reused and it needs to be neutralized and disposed of after use. As an alternative to sulfuric acid, the use of solid acid was examined. However, isosorbide yield was 40 to 60% with sulfated zirconia and zeolite and the yield decreased 10 to 15% compared to the sulfuric acid method. Recently, we found that isosorbide yield can be improved to the same level as sulfuric acid by zeolite optimization. Since this catalyst is reusable, it can be more beneficial than the process with sulfuric acid.

Research of biomass conversion may temporarily slow down due to the decline in oil prices. However, if you keep in mind the above two points, I think that the use of biomass will accelerate as a renewable carbon source and catalytic chemistry on a solid surface involved with biomass can be developed.

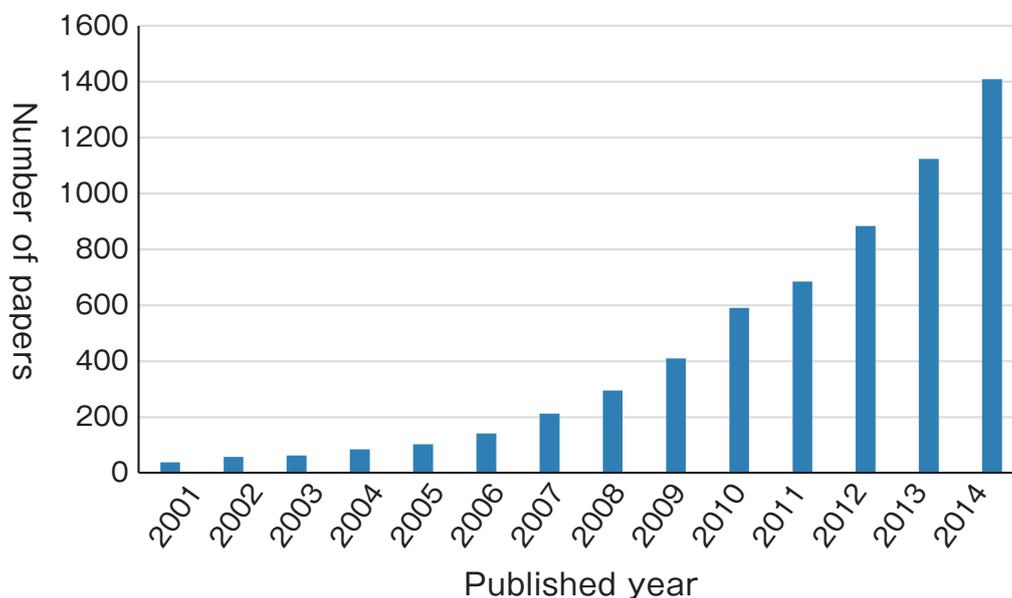


Figure 1 The number of papers with both Biomass and Catalyst as keywords (The author counted papers based on Web of Science.)

Mesoporous silica coated by transition metal oxides

Junko Nomura KONDO, Associate Professor
Tokyo Institute of Technology, Chemical Resources Laboratory
Japan Science and Technology Agency, an independent administrative institution, Precursory Research for Embryonic Science and Technology (PRESTO)

Although there have been various reports in the past regarding transition metal oxide materials with regular nanostructure and their synthetic methods, their application is prevented by thermal instability of the prepared material and high price of the precursor materials. Therefore, by utilizing inexpensive mesoporous silica, which can stably maintain a regular nanostructure, as a substrate, and forming a film with a transition metal oxide on it, we built a nanospace surrounded by a transition metal oxide. As a result, we were able to derive the surface characteristic and atmosphere of space specific to each transition metal oxide. Here, the selective uptake of a dye molecule of an aqueous solution into nanopore space hydrophobized by a tantalum oxide film formation is introduced.

Regularly arranged nano/mesoporous inorganic substances were developed for the purpose of application in the uptake of large molecules, that cannot be the target of zeolite due to the sub-nanosized pores, into a fine pore and the shape-selective material conversion system. Mesoporous silica, whose inorganic phase was amorphous silica, where cylindrical fine pores were arranged in a two dimensional hexagonal structure, was reported in the 1990s. Since then, regarding amorphous silica, substances with various regular space arrangement structures were prepared and a wide range of inorganic materials were also synthesized such as metal oxide, composite oxide, carbon, and metal, etc. Among them, mesoporous materials consisting of a transition metal oxide are diverse, since each bulk and surface characteristic is different. Although there were high expectations for applications using their characteristics, they have not been used as an actual material due to their thermal instability and high price of their precursor materials. Therefore, we performed regulations on the "atmosphere of space" and "functionalization of material to be the surface" by preparing a transition metal oxide film on mesoporous silica. Here, hydrophobization of nanopores by tantalum oxide film formation is introduced as an example.

There are many surface hydroxyl groups on the surface of silica and metal oxides, which are obtained by the regular preparation method (calcination at about 500°C), due to the amorphous structure and the coordinative unsaturation of their surface. Since water can easily adsorb on the surface, the surface of oxide is hydrophilic. When it is further calcined at a high temperature, dehydration and condensation are caused between the surface hydroxyl groups and it is changed to a hydrophobic surface. In the case of a mesoporous material, the surface characteristic is directly reflected to the atmosphere of meso-space. Therefore, the surface and the atmosphere inside of the fine pores of the mesoporous silica and general metal oxides are hydrophilic. It is not well known that, among many oxides, the surface of amorphous tantalum oxide (calcined at about 500°C) does not have hydroxyl groups and the pore space of mesoporous tantalum oxide is very hydrophobic. Although dilute organic substances dissolved in water can be selectively captured in the hydrophobic spaces of mesoporous tantalum oxide, it is not practical because tantalum is costly. By forming a film of tantalum oxide on the surface of mesoporous silica, hydrophobization of the surface can be performed without using organic substances that have a lower thermal, irradiation and chemical resistance.

An image of mesoporous silica forming a film of tantalum oxide (Ta/Si=0.13), measured by emission scanning electron microscopy (FE-SEM) is shown in Figure 1. Regularly arranged fine pores can also be observed after forming the

fine film. In Figure 2, pictures of neutral red solution (100 ppm), and mesoporous silica treated with the neutral red solution before and after forming a film of tantalum oxide are compared. Mesoporous silica slightly decreased the color of the solution and about 30% of dye molecules were encapsulated into fine pores. On the other hand, mesoporous silica with a film of tantalum oxide adsorbed 99.7% of dye molecules. As a result, white powder was colored in red and is observed on the bottom, while the color of the solution almost disappeared. This suggests that the atmosphere of the pores of mesoporous silica was changed from hydrophilic to hydrophobic, and large dye molecules were selectively separated.

Furthermore, there is a possibility that this can be applied as a catalytic reaction site enabling "selective reactant inclusion" and "effective product release" by building a catalytic site within the pore space and selecting a different system, hydrophilic or hydrophobic, between the space of the mesoporous material and its solvent.

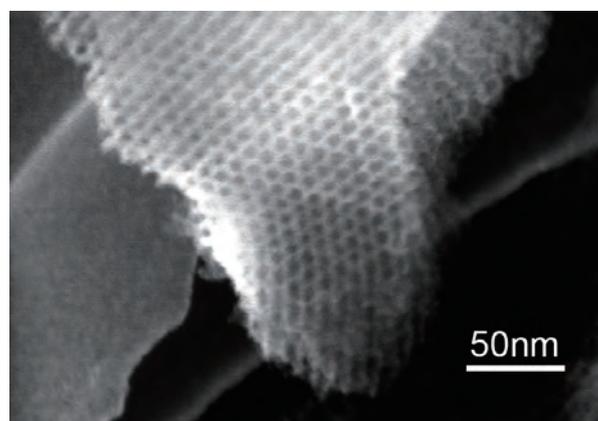


Fig.1 FE-SEM image of mesoporous silica forming a film of tantalum oxide

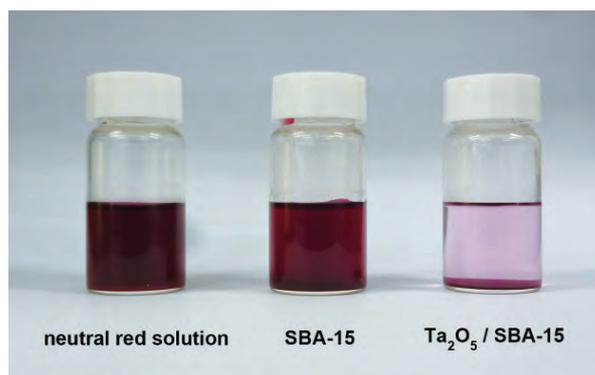


Fig.2 Neutral red adsorption of mesoporous silica (SBA-15) before and after forming a film of tantalum oxide

A Special forum "Innovation Realization" was held.

"The 4th Special Forum," the last event of the "Special Forum" for the JACI members for fiscal year 2014, was held on March 25th. Two appropriate lectures for the theme "Innovation Realization" were performed and the conference room was packed to overflowing.



Lecture 1 was titled "A new challenge for Hayabusa-2," presented by Dr. Makoto Yoshikawa, JAXA mission manager. He introduced many companies' technologies condensed into "Hayabusa-2," which was launched in December last year and is underway aiming at "Asteroid 1999 JU3." (The picture of Hayabusa-2 is cited from the JAXA website.)

Lecture 2 was presented by Dr. Hiroshi Kobayashi, professor of the Faculty of Engineering at Tokyo University of Science, with the title "Aiming for realization of independent life as long as we live." He introduced the development of a muscle suit that is a wearable power assist system, as well as starting a venture business, and performed a demonstration of the suit as a developer. (The picture shows Dr. Kobayashi putting the suit on a woman.)



We will continue to provide various topics in the special forum. Please look forward to the next forum.

July 2015 4th JACI/GSC Symposium 7th GSC International Conference in Tokyo

- ◇ When: July 5-8, 2015
- ◇ Where: Hitotsubashi Auditorium, Hitotsubashi University (Takehashi, Tokyo)
- ◇ Main theme: "For the further development of GSC"

Readers are invited to visit the dedicated website, <http://www.jaci4gsc7.org>, also from the Association home page.



JACI-News Letter No. 55 - Publication Data
JACI News Letter
Publishers: Japan Association for Chemical Innovation (JACI)
Sanbancho KS Building 2F, Sanbancho 2, Chiyoda-ku, Tokyo, 102-0075
03-6272-6880 <http://www.jaci.or.jp/>
Editors: JACI Department of General Affairs

The GSC Network of the JACI is composed of the following organizations:
Japan Chemical Innovation and Inspection Institute, The Society of Chemical Engineers, Japan, Japan Association for International Chemical Information, Kansai Chemical Industry Association, Advanced Scientific Technology & Management Research Institute of KYOTO, The Kinki Chemical Society Japan, The Society of Silicon Chemistry JAPAN, Japan Thermosetting Plastics Industry Association, The Society of Polymer Science, Japan, The Society of Polymer Science Association, Sagami Chemical Research Institute, National Institute of Advanced Industrial Science and Technology, Chemical materials Evaluation and REsearch BAse, Catalysis Society of Japan, Japan Petrochemical Industry Association, The Japan Petroleum Institute, Research Institute of Innovative Technology for the Earth, Tokyo Metropolitan Industrial Technology Research Institute, The Electrochemical Society of Japan, Japan Surfactant Industry Association, The Chemical Society of Japan, Japan Chemical Industry Association, The Ceramic Society of Japan, Japan Electronics Packaging and Circuits Association, Japan Paint Manufacturers Association, Japanese Society for Biomaterials, The Japan Society for Analytical Chemistry, Japan Analytical Instruments Manufacturers' Association, Noguchi Medical Research Institute, Japan Bioindustry Association, National Institute for Material Science, Plastic Waste Management Institute, The Society of Synthetic Organic Chemistry, Japan, RIKEN

