

## [001]九州大学グローバルCOEプログラム新炭素資源 学ニューズレター

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**NOVEL CARBON RESOURCE SCIENCES**  
**NEWSLETTER**

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# M E S S A G E

**President of Kyushu University**

**Setsuo Arikawa**



Kyushu University, as the world's center of knowledge that is open to Asia and as one of key universities in Japan, is developing world-class education and research, prospering together with the city in which it is located, and playing its role as a university which citizens are proud of and rely on. To develop these characteristics further and grow yet more active as an internationally competitive university with its own individuality, Kyushu University has been implementing and promoting the Action Plan, in which we have two principal tasks, namely "Pioneering new fields of science based on our academic achievements" and "Developing Asia-orientation led by historical and geographical necessity".

The Global COE "Novel Carbon Resource Sciences; Coal-Based Eco-Innovations" is a world-leading educational and research setting. Eight departments in Kyushu University and Fukuoka Women's University collaborated to apply for this G-COE program, and it was successfully adopted by JSPS (Japan Society for the Promotion of Science). This G-COE's mission in our globalizing society is to establish the 21st century paradigm of environmentally burden-free usage of carbon resources. In order to accomplish this mission, "Novel Carbon Resource Sciences" strives to create research achievements which will lead the way in the world in future and to educate young researchers, especially PhD candidates, by bringing together researchers from all over the world through international, regional, and academia-industrial collaborations.

Kyushu University is committed to offering university-wide support for the activities of this G-COE.

**Chancellor of  
Fukuoka Women's University**

**Makoto Takagi**



Fukuoka Women's University has been in close relation with Kyushu University from the days of its foundation. Our antecedent school Fukuoka Prefectural College for Women was started in 1923 which was twelve years after the establishment of Kyushu Imperial University of the time. The two institutions since then have kept a tight contact both in education and research.

Our university is facilitated with a graduate school of Human Environmental Science, which involves sections concerning contemporary environmental measurement/environmental resource utilization education and study. Taking advantage of this institutional resource we are now committed to cooperate with Kyushu University for its Global COE Program. Incidentally our university is now planning a reform in education and research with such keywords as "human environment", "eco-system" and "Asia". We are quite pleased with timeliness or coincidence between our own reform planning and our present commitment to the Kyushu University G-COE Program since the program stands on similar basic concepts.

Both the universities have enjoyed a long history of cooperation. However, the present joint program where we are formally involved in collaboration through such a prestigious scientific aid from the government is certainly the first joint education/research approach in our over 85 year's history. Fukuoka Women's University is determined to devote itself to achieve the aim of the program.

**Professor, Program Leader**  
**Institute for Materials Chemistry and Engineering, Kyushu University**



## Hideo Nagashima

### For the first issue of NCRS Newsletter from the COE Leader

Nine months have passed since the Global COE program, Novel Carbon Resource Sciences (NCRS), was established by joint work of Kyushu University and Fukuoka Women's University. The first fiscal year was over at the end of March 2009, and we have just started the second year of the program with polishing up each educational matter based on high-quality advanced research. We have experienced a drastic change of world economy since the bankruptcy of Lehman Brothers Holding Inc.; the price of oil and coal which was the highest in last summer quickly dropped to one-third in the beginning of 2009, and now gradually goes up. As predicted, economic growth of developing countries apparently causes gradual mounting of the price of oil and coal, the risk for exhaustion of carbon resources of high quality, and environmental problems including increasing amount of green house gas emissions such as CO<sub>2</sub> and methane. *A Green New Deal: Joined-up policies to solve the triple crunch of the credit crisis, climate change and high oil prices* has opened the way to increasing use of renewable energy; however, that is not satisfactory in securing the stable energy supply to meet the demand of the people in the world for a large amount of energy. Although atomic power generation will be of great importance, power plants based on fossil energies, in particular coal, must owe the responsibility to supply a large portion of energy in next several decades.

Our COE program NCRS aims at establishing a new field of science for efficient use of carbon resources for energy and chemicals in view of global environmental sustainability, and education of young researchers in such a field. Efficient use of coal is one of the symbolic goals of NCRS. A project sponsored by NEDO regarding development of zero-emission power plants with efficient coal gasification technology started last year as a joint work with Central Research Institute of Electric Power Industry, and several members of our COE contribute to its success. Our COE members have also been creating new advances in science and technology of energy conservation, in particular from the viewpoint of materials, devices, and systems; catalysts, lithium ion battery, fuel cells, photonic and electronic devices, etc. At the same time, other members are concentrating on the prediction of the global climates from viewpoints of economics and environmental sciences, the efficient development of new resources, and the production of new materials for removing the pollutants. These researches used to be performed in different fields of sciences, and the results had been published in individual societies. We have started the fusion of these scientific fields by joint works and symposiums, which constitutes a good starting point for collabora-

tive research and education. We put much importance on continuous discussion with industries concerning contribution of our new results and findings to human society.

We believe that Asia is one of the most important fields in which the achievements of our COE program can be put into practice. In last fiscal year, we started cooperation with institutions in China, Korea, Indonesia, and Australia. Exchanges in various aspects of research and education started at the international symposiums in October at Fukuoka and March at Bandung. The symposium in last November was a good opportunity to invite students of Shanghai Jiaotong Daxue for discussion with students of Kyushu University. The circle of international cooperation will be expanded this year to India, Singapore, and other countries.

As regional collaboration, several trials for joint work have been done with professors of Fukuoka Women's University (FWU). A big news for us is that a student who studied in a master course in FWU has joined our COE program as a student of doctoral course in Kyushu University. A basis for regional collaboration with communities of northern Kyushu area has been established as Kyushu Society for Low-Carbon Systems.

In last fiscal year, we carried out many trials for establishing the best curriculum for graduate students in NCRS, which includes research proposals, planning of international symposiums, double major systems, on the job trainings. Many of them such as research proposals and on the job training are polished up and continued this year in similar systems, whereas some of them such as double major systems are needed to be reorganized by the starting of the NCRS Forum this year. We are proud of accepting many foreign students in our COE program. Special training programs of English conversation and/or English writing are powerful methods for better educations for both Japanese and foreign students, whereby amplification of educational outcome will be possible by better understanding between them. We will polish up the system as much as we can.

Last nine months were the days of trial and error for our COE members. We rushed to make a system for managing the program. The program contributes to assisting the students financially, which enables them to concentrate on advanced research and trainings. Members are making efforts to start collaborative research and education. We believe these to prove fruitful this year, and the results will be introduced one by one on this news letter. Hope the readers will enjoy.

# Summary of G-COE Program

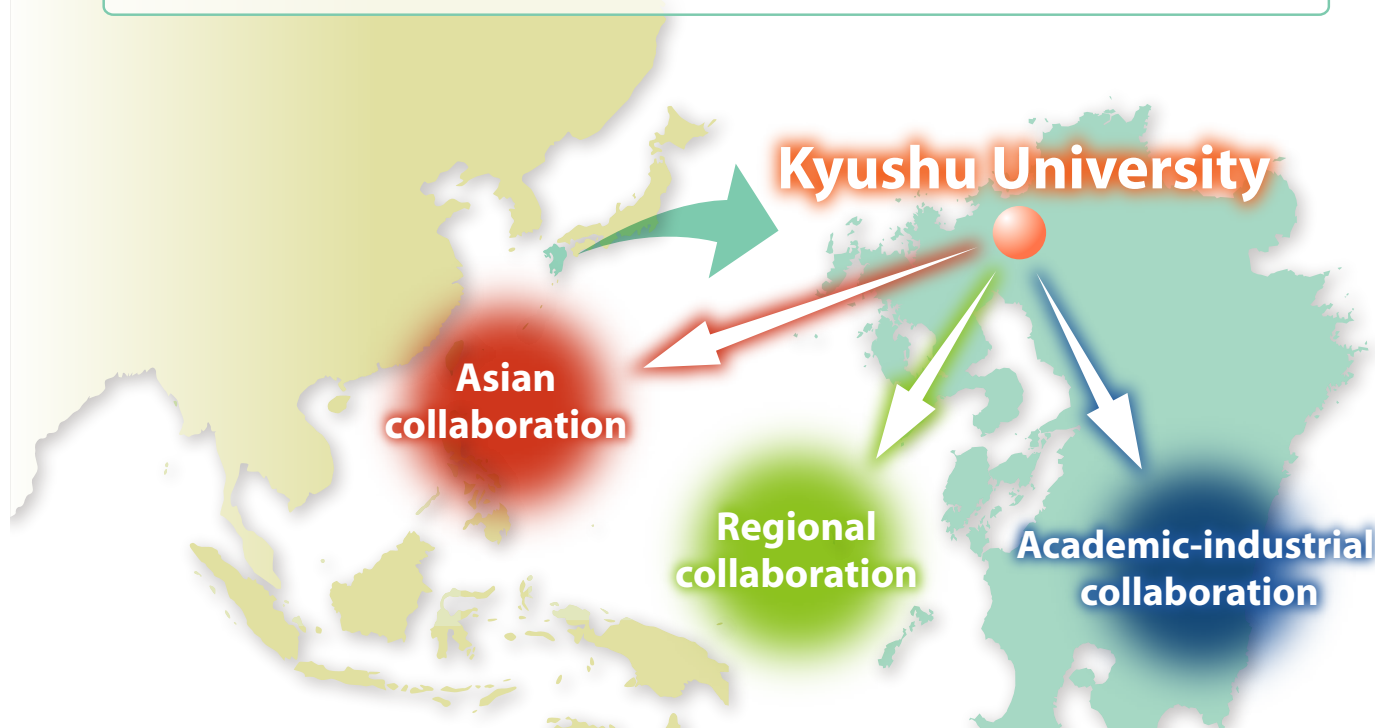
## "NOVEL CARBON RESOURCE SCIENCES"

### ■ Cooperation with local communities and Asian countries

The center takes full advantage of Kyushu University's location in Northern Kyushu, in close vicinity to China and Korea, areas heavily dependent on coal. This COE is to serve as a hub for the development of utilization technologies for fossil resources, such as coal, in Asia. We will be actively engaging in bidirectional

exchanges of researchers and students between Japan and the rest of Asia, so that we can conduct research and train experts to be able to provide solutions to problems that encompass the whole Asian region.

**Kyushu University** = rich history of leading coal research, future plans for an "Energy campus"  
**Northern Kyushu** = gateway to **Asia**, many fossil-resource related experimental facilities



### NOVEL CARBON RESOURCE SCIENCES

#### 20<sup>th</sup> century

More indiscriminate consumption of fossil resources

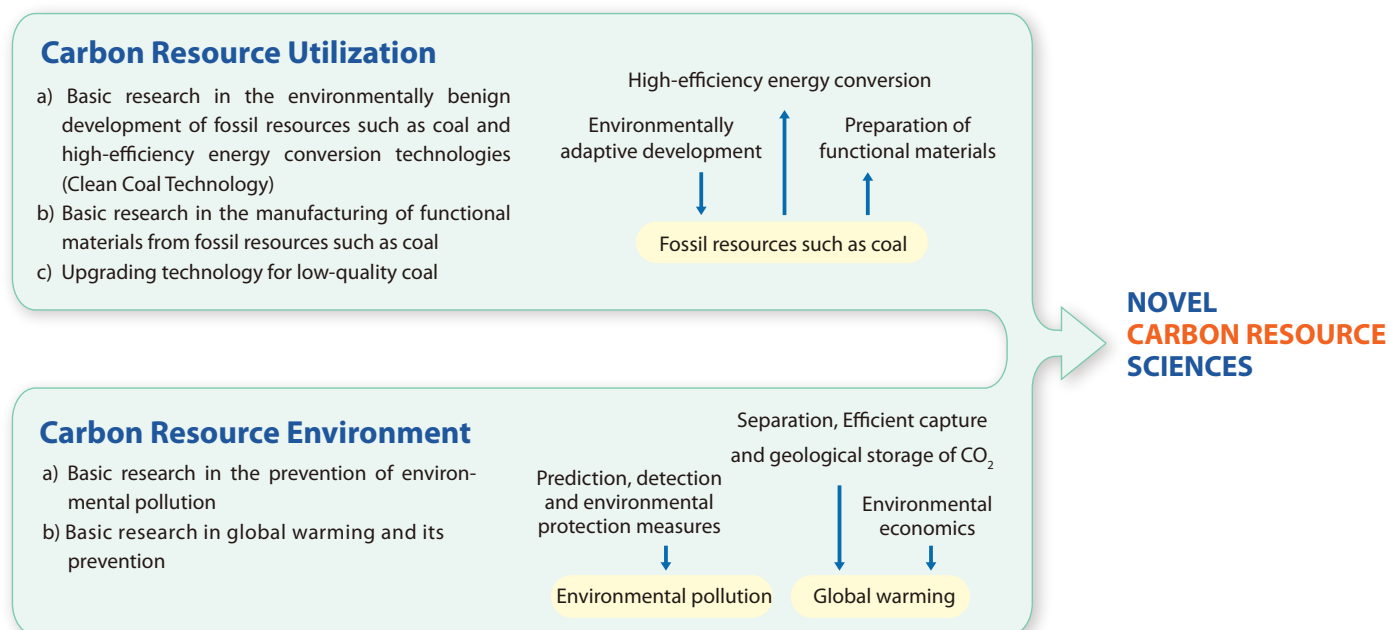


#### 21<sup>st</sup> century

More sustainable utilization of fossil resources

## Development and integration of two research fields

This COE is comprised of the two research clusters, Carbon Resource Utilization and Carbon Resource Environment, which will conduct the following advanced research projects.



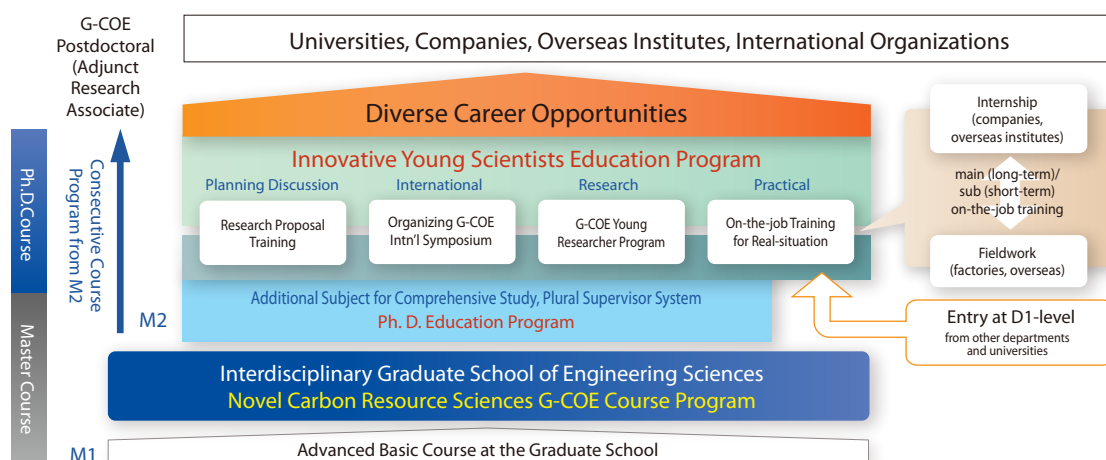
We strive to effectively integrate the academic fields that each cluster pursues, through inter-cluster exchanges, collaborations with the local communities, international collaborations, and academia-industry collaborations. These initiatives will

systematize the overall approach of the G-COE in Novel Carbon Resource Sciences leading to the development of innovative science and technologies for the effective use of coal.

## Human resource development with internationalism

This COE will implement the Research Proposal Training Program, the G-COE Young Researcher Program, in which graduate students and Ph.D. researchers will take leadership in conducting research, and a mandatory participation in the G-COE International Symposium, which will be held with

invited researchers from abroad. On-the-job training programs are two-fold: internship programs at private corporations or at research institutes abroad, and fieldwork programs abroad. Each program will have both short-term and long-term versions.



### Novel Carbon Resource Sciences G-COE Course Program

①consecutive course program from M2, ②novel carbon resource sciences-related subjects and practical English training are mandatory, ③double major system within the Ph. D. program, ④Ph. D. students will take leadership in a research proposal training program and a young researcher program, ⑤organizing and hosting an international symposium by students, ⑥long/short-term internship and fieldwork at institutes or companies abroad to foster independent advanced researchers with more diverse career opportunities

# G-COE Program Researcher Map



**九州大学**  
KYUSHU UNIVERSITY



**福岡女子大学**  
Fukuoka Women's University

Utilization of Fossil Resource

Basic Chemistry

Energy Materials, Environmental Materials  
Environmental Measurement  
& Maintenance

Economic Analysis  
& Evaluation

Development of Resource,  
Environmental Development



## Energy Utilization of Coal and Other Fossil Fuels: Development of Environmentally Efficient Technology

Coal upgrading and gasification, Energy conversion

### ● NEDO "Innovative zero emission coal gasification electric power project"

▶ P7

**Tsuyoshi Hirajima**

Advanced processing of  
carbon resources; Biomass  
utilization

▶ P16

**Seong-Ho Yoon**

Carbon nanofibers;  
Reaction engineering of  
carbon materials

**Jun Fukai**

Thermal analysis of coal  
conversion; Energy saving  
utilization of carbon fibers

**Jun-ichiro Hayashi**

Sustainable carbon cycle  
chemistry; Coproduction

**Isao Mochida**

Coal gasification;  
Carbon materials,  
Carbon nanofibers

**Yasutake Teraoka**

Functional inorganic materi-  
als; Environmental catalytic  
chemistry

**Katsuki Kusakabe**

Inorganic separation  
membrane; Separation of  
environmental pollutant

**Central Research  
Institute of Electric  
Power Industry, Other  
Universities**

Ehime Univ., etc.

### ● Ministry of Economy, Trade and Industry "Advanced Education for Effective Utilization of Fossil Resources"

### ● Kyushu society for low-carbon system

**Kyushu University**

G-COE, NEDO,  
JST, JST-MOST

**Kyushu Electric Power  
Co., Inc.**

Lignite utilization technol-  
ogy, nuclear power

**Kyushu Bureau of  
Economy, Trade and  
Industry**

**Local Businesses,  
Other Universities**

Kyushu Institute of  
Technology, Saga University,  
Kumamoto University, etc.

## Advanced Technological Development for Low Energy Consuming Society

| Basic chemistry  | Environmental material development   | Advanced electronic material development  | Energy material development  |
|--|--|---|--|
| <p><b>Katsuhiko Tomooka</b></p> <p>Organic synthetic chemistry; Efficient oxidation reaction</p> | <p><b>Hideo Nagashima</b></p> <p>Environmentally benign chemistry; Efficient metal complex catalysts</p> | <p><b>Shiyoshi Yokoyama</b></p> <p>Device applications of carbon resources; Polymer photonic materials</p>            | <p><b>Michitaka Ohtaki</b></p> <p>Thermoelectric device; Heat energy recovery</p>  |
|  | <p><b>Seong-Ho Yoon</b></p> <p>Carbon nanofibers; Reaction engineering of carbon materials</p>           | <p><b>Hiroki Ago</b></p> <p>Carbon electronics; Synthesis and applications of carbon nanotubes and graphene films</p> | <p><b>Shigeto Okada</b></p> <p>Energy active materials and storage technology for next generation rechargeable lithium battery</p> |

## Technology for Fossil Resource Development of Coal and Other Fuels

| Technology for resource development below the earth  | Technology for resource development in the ocean   | CO <sub>2</sub> Capture and storage (CCS)   |
|--|--|---|
| <p><b>Tsuyoshi Hirajima</b></p> <p>Advanced processing of carbon resources; Biomass utilization</p>  | <p><b>Masahiko Nakamura</b></p> <p>Marine-viewing vehicle; Positional controls of marine constructions</p> | <p><b>Kyuro Sasaki</b></p> <p>CO<sub>2</sub> Storage; CO<sub>2</sub>-ECBM; CO<sub>2</sub>-EOR</p> |
| <p><b>Kikuo Matsui</b></p> <p>Environmental restoration associated with resource development; Coal mining development and environmental issues</p> |  |   |

## Technology for Fossil Resource Utilization of Coal and Other Fuels

| Basic chemistry   | Economic analysis  | Separation, removal of pollution  | Environmental measurement  |
|---|--|---|--|
| <p><b>Akira Harata</b></p> <p>Ultrasensitive environmental analysis; Laser spectroscopic analysis</p> | <p><b>Toshiyuki Fujita</b></p> <p>Environmental economics; Analyses of global environmental issues</p> | <p><b>Yasutake Teraoka</b></p> <p>Functional inorganic materials; Environmental catalytic chemistry</p>           | <p><b>Itsushi Uno</b></p> <p>Numerical simulation of transborder air pollution; Aerial environmental modelling in Asia</p> |
| <p><b>Norio Miura</b></p> <p>Sensors for environmental concerns; Electrochemical devices</p>          |  | <p><b>Masaki Minemoto</b></p> <p>Analysis of flow and transport phenomena; Upgrade of various types of plants</p> | <p><b>Toshihiko Takemura</b></p> <p>Global scale simulation of aerosol</p>   |
| <p><b>Functional devices and materials for environmental concerns</b></p>                             |  |   | <p><b>Kazuhide Ito</b></p> <p>Chemical pollution of life environments; Indoor and environmental chemistry</p>              |

# Energy Utilization of Carbon Resources

## Micro Review

### De-ashing and Upgrading Low-grade Coal to Reduce the Environmental Load

Kyushu University Tsuyoshi Hirajima

Increasing world demand for energy has led to the exploitation of low-rank coal (LRC) as well as high-ash and high-sulfur coals. As a result, new technologies and economically viable methods aimed at reducing the environmental load have been developed to process such coals. For now, advanced coal cleaning technologies such as enhanced gravity technology and biobeneficiation, which can potentially be used to separate fine pyrite and specific minerals from coal, are considered as the most promising processes to exploit high-ash and high-sulfur coals. LRC still remains a local source of energy because of its high moisture content, low heat value, and high propensity toward spontaneous combustion. However, its prospective use can be enhanced considerably through hydrothermal treatment, a promising technology for upgrading LRC. This paper briefly describes these technologies.

#### 1. Introduction

In 2007, the annual consumption of coal as a primary source of energy was about 28.6% worldwide and around 24.2% in Japan, corresponding to shares in the power generation sector of about 40.3% worldwide and 25.2% in Japan <sup>1)–3)</sup>. However, according to forecasts of future primary energy demand, dependence on coal is expected to increase as its reserve-production ratio is long. Significant increase in the use of coal is anticipated, especially in the Asia-Pacific region, which is predicted to account for about 70% of the total coal consumption in 2030. In comparison with oil and natural gas, coal has a higher carbon dioxide exhaust coefficient; therefore, carbon dioxide emissions in the Asia-Pacific region are expected to further increase with the increased use of coal.

In 2007, as part of the “Cool Earth 50” initiative, Japan proposed for the world “to reduce, by 2050, the emissions of greenhouse gases in the world by half, compared to the current level.” To achieve this goal, it is important to develop innovative technologies that integrate separation, recovery, and storage of CO<sub>2</sub>. Kyushu University and the Central Research Institute of Electric Power Industry have carried out research on high-efficiency Integrated Gasification Combin (IGCC) tech-

nology. The development of such technology would enable the use of various coals while reducing the environmental impact; this is an important issue for a country like Japan—where more than 99% of the total demand for coal is satisfied by imported coal—since it will ensure a stable and long-term supply of coal energy resources <sup>4)</sup>. Therefore, it is becoming important to develop reformation technology <sup>5)</sup> to process coal with a low degree of coalification such as lignite (brown coal), whose utilization is limited to its area of production because of high self-ignition characteristics and poor transport and combustion efficiency due to high moisture and low calorific value. It is also important to develop advanced, effective technologies for (1) cleaning high-ash and high-sulfur coals; (2) utilizing coal ash after combustion; and (3) treating wastewater and acid mine drainage at mine sites.

With this background, the author’s laboratory has investigated the issues of advanced coal cleaning, upgrading of low-rank coal and biomass using hydrothermal treatment, effective use of combustion ash, groundwater remediation using a permeable reactive barrier (PRB) <sup>6)–8)</sup> and bio-mineral processing <sup>9)–12)</sup>. Biogenic manganese oxides, which are produced by manganese-oxidizing fungus under the limited carbon sources, were characterized and applied

to sorption of heavy metals in environments <sup>12)</sup>. For this work, the best paper award was provided by MMIJ in 2009. The details will be described elsewhere. This paper is a summarized introduction to studies carried out on de-ashing and upgrading low-quality coal.

## 2. Inorganic matter in coal

Mineral matter in coal can be classified into three categories:

- Primary minerals (inherent ashes) already present in plants from which coal originated;
- Secondary generated minerals (intermediate ashes), which include geological sediments, volcanic ashes, other inorganic matter deposits, old minerals metamorphosed by groundwater permeated through the coal bed, or new minerals added in the carbonization process; and
- Minerals in the hanging wall, foot wall, or intercalation mixed with raw coal (external ashes) during the mining process.

Most of the minerals contained in coal are reduced to ash after the coal is burned. Note that it is difficult to remove external, intermediate, and inherent ashes by physical coal cleaning in the same order.

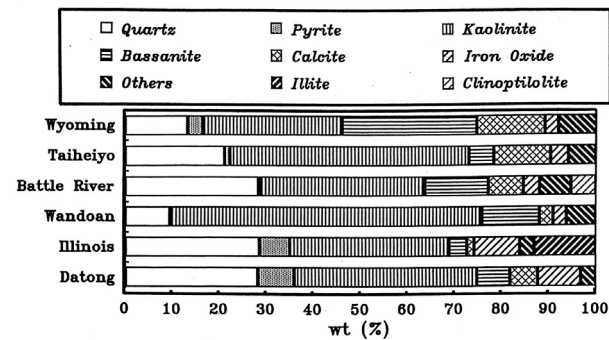


Figure 1 Mineral composition of coal

Figure 1 shows the composition of minerals in various types of coals cleaned at the mine mouth or coals from which external ashes were removed. The data for "others" in this graph were derived assuming that Mg, Na, K, P, and Ti are present as oxides. In most types of coal, quartz and kaolinite account for two-thirds of the total mineral weight, suggesting that both minerals constitute the main minerals in coal <sup>13)</sup>.

In general, coal contains a very small amount of environmental pollutants such as As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Hg, Ni, Se, and V. These trace elements can be classified as (a) those combined with coal organic matter; (b) those contained in minerals as component elements; and (c) those coexisting with mineral component elements of coal as a result of substitution.

The percentages of these three categories of trace elements differ in different types of coal, but evidence shows that in most cases, trace elements coexist with minerals in coal. It is considered that the content of these heavy metals can be decreased by removing minerals from coal through the coal cleaning process <sup>14)</sup>.

## 3. Coal cleaning technology

Table 1 describes the properties important for coal cleaning and the corresponding separation technologies involved. Two of the predominant separation technologies now in use for coal cleaning are based on differences in grain gravity and surface wettability (hydrophobic and hydrophilic differences).

Recently, in Japan, considerable interest has been evinced regarding the reduction of coal ash, SO<sub>x</sub>, NO<sub>x</sub>, heavy metal elements (Hg, Cd, Pb, Cr, As, Se, etc.), and other environmental

Table 1 Properties and separation technology used for cleaning coal

| Selective Property      | Separation Technology          |
|-------------------------|--------------------------------|
| Color, Appearance       | Hand picking, Color sorting    |
| Specific gravity        | Gravity separation             |
|                         | (1) Dense medium separation    |
|                         | (2) Jigging                    |
|                         | (3) Flowing-film concentration |
|                         | (4) Pneumatic separation       |
| Surface wettability     | (1) Flotation                  |
|                         | (2) Oil agglomeration          |
| Magnetism               | Magnetic separation            |
| Electrical conductivity | Electrostatic separation       |
| Others                  |                                |

pollutants, as well as the removal of certain minerals from coal before combustion; this has led to a recognition of the importance of coal cleaning before utilization.

### 3-1. Recovery of fine combustible matter from coal washery waste through gravity separation in a centrifugal field

Although separation by specific gravity is one of the oldest and most widely used resource-processing technologies, its importance declined during the last century with the rapid development and spread of separation methods such as flotation, magnetic separation, and others<sup>15)</sup>. However, in recent years, because of the simplicity of the separation principle and processing device, gravity separation technology is being reviewed and improved not only for the field of mineral processing (beneficiation) and coal preparation but also for recycling resources and in the environmental field, where it is being used again. Therefore, various new and improved models have been developed<sup>16)–19)</sup>. In particular, machines and equipment to sort fine particles according to their specific gravity—such as the Falcon Concentrator<sup>20)</sup>, Knelson Concentrator<sup>21)</sup>, and Multi-Gravity Separator (MGS)<sup>22)</sup>—have recently been developed. Among these models, the author has used the MGS—a device developed by Richard Mozley Ltd. (Britain) for the separation of fine particles (1–300  $\mu\text{m}$ ) usually beneficiated using flotation—to carry out applied research on the recovery of fine combustible matter from coal washery waste.

The pilot-scale MGS is shown in Figure 2. The MGS can be described as a general-purpose shaking table rounded up and encased in a drum. By replacing the table with a drum, a force several times the normal gravitation force can be applied to particles. Accordingly, the MGS can separate finer particles than the general-purpose table. Feed slurry is fed into the middle of the drum inner surface, which is lined with polyurethane. As the drum is slightly inclined to the horizontal ( $3^\circ$ – $5^\circ$ ), feed slurry runs naturally toward the back end of the drum. Pulled by the centrifugal force ( $<25\text{ G}$ ), heavy

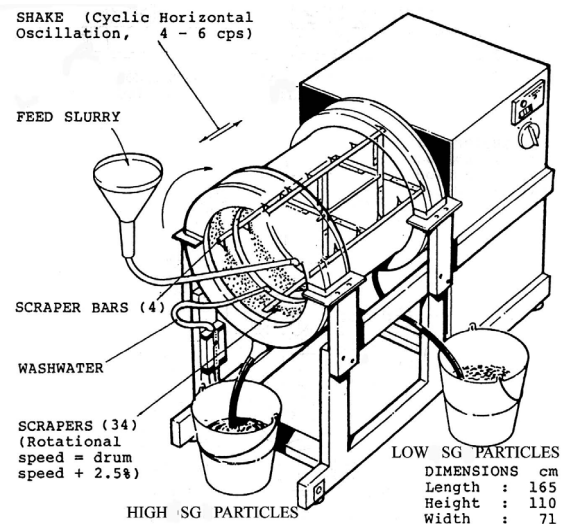


Figure 2 MGS pilot scale

particles and high specific-gravity particles are pinned to the drum surface and form a concentrated base layer. Above this layer is a relatively dilute intermediate layer in which low specific-gravity particles are suspended. Finally, there is an upper layer composed of a relatively clear aqueous phase. Shaking movements (frequency 4.0–5.7 cps; amplitude 12.7–19.0 mm) accelerate the separation, driving high specific-gravity particles deeper into the drum surface. These high specific-gravity particles are carried by scrapers, which rotate faster than the drum (rotational speed = drum rotation speed + 2.5%), and are recovered at the high-density product outlet. Low specific-gravity particles that were mixed with the high specific gravity particles are again separated at this stage. Water added near the opening washes away the loosened low specific-gravity particles, reducing the quantity of low specific-gravity particles misplaced with the high specific-gravity particles. Low specific-gravity particles are carried in suspension by a flowing film and released at the opposite end of the drum.

The author conducted a study on the possibility of recovering combustible matter from coal washery waste by combining the cyclone and MGS fine particle separation processes<sup>23)</sup>. Coal in coal washery waste has a low degree of coalification (low-rank coal) and requires a large amount of reagents (collector) to

modify its surface wettability; as a result, it is difficult to carry out coal cleaning by flotation. Figure 3 shows an example of the flow chart of the process used to recover combustible matter from coal washery waste; it also indicates the distribution, caloric value, and ash content of each product. Through this process, a clean coal product was recovered from conventionally discarded fine particles residues of coal washery; the product had a yield of 37% and calorific value of 5940 kcal/kg. The ash content was 18%; the recovery rate, 57%.

Processing methods that use the difference between the surface wettability, such as flotation and oil agglomeration (OA), may not attain the ideal separation level proposed theoretically by sink-float analysis of coal. The primary cause of the poor sorting performance is that particles containing both coal and mineral (middling particles), and pyrite particles, easily become hydrophobic; consequently, it is difficult to remove them by methods using the surface wettability. A recent study reported that middlings containing less than 5 wt% coal can be recovered through flotation. On the other hand, the MGS is extremely effective in removing ash and particles, including high-density materials such as pyrite, which cannot easily be removed by flotation and OA. Pyrite, in many cases, also contains trace amounts of heavy metals. From the viewpoint of removing environmental pollutants, it is thought that MGS-like specific gravity coal-dressing machines will become increasingly important in the future for removal of particulates. One of the major advantages of MGS technology is that it can attain a high level of separation efficiency without grinding the middling to liberate particles, and without using flotation reagents or using a dense medium.

As part of the MGS application, the author obtained satisfactory results for studies carried out on the collection of hollow spherical particles of ash (cenospheres) from coal combustion<sup>24), 25)</sup>; recovery of phosphorus resources from sewage sludge<sup>26), 27)</sup>; recycling of the bulk of concrete debris<sup>28), 29)</sup>; and other related studies on the recycling of resources.

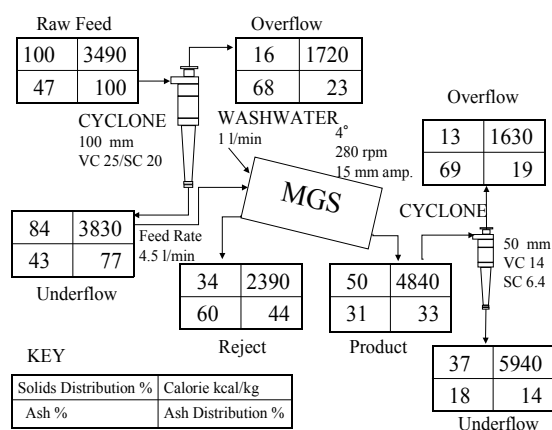


Figure 3  
Process and test results for the recovery of fine combustible matter from coal washery waste water

### 3-2 Modification of mineral surfaces using microorganisms and their application to flotation

Due to the future increase in power demand in Asia, it will be difficult to import high-quality coal, which is mainly used in Japan at present. Therefore, it will be necessary to utilize high-ash and high-sulfur coals, as well as coal with a low degree of coalification. In addition, it is thought that as an essential pretreatment process for coal gasification, the removal of certain minerals such as quartz, pyrite, etc., will become important.

Flotation is a separation technique that uses the difference in air bubble adhesion to mineral matter and coal in water. Flotation separation technology based on the adsorption of microorganisms onto mineral surfaces to control the surface wettability of minerals (also referred to as bio-flotation) is expected to be a low-cost sorting method; however, the role and mechanisms of microbial adhesion are largely unknown. Using two microbial strains hitherto unused in the field of mineral processing, the author evaluated the surface properties and studied the interaction between the cells and minerals to understand the mineral separation and mutual attachment mechanisms<sup>30)–32)</sup>. The author used an *Escherichia coli* strain<sup>32)–34)</sup> (hereinafter referred to as *SIP-E. coli*), which is

modified for the gene carrying the silica-induced protein (SIP) produced by thermophilic bacteria. The other strain used was *Ferroplasma acidiphilum*<sup>35), 36)</sup>, which has recently been isolated from areas containing pyrite deposits; it can grow autotrophically, using the energy evolved from the oxidation of ferrous ions to ferric ions in pyrite as an energy source to fix atmospheric carbon. In the results of the hydrophobic evaluation of these microorganisms, it was found that *SIP-E. coli* was hydrophobic and *F. acidiphilum* had hydrophilic properties. Due to this research, the possibility of using *SIP-E. coli* as a collector and *F. acidiphilum* as a depressant in flotation could be examined.

The results obtained for the flotation of quartz, hematite, and corundum after the addition of *SIP-E. coli* are shown in Figure 4; those obtained for the flotation of pyrite after the addition of *F. acidiphilum*, in Figure 5. The flotation and adhesion behavior of microorganisms with regard to various minerals was explained using the extended DLVO (Derjaguin, Landau, Verwey, and Overbeek) theory and surface wettability difference between the above-described microorganisms. According to the extended DLVO theory<sup>37)</sup>, the total energy resulting from the interaction between minerals and microbes ( $G^{\text{Tot}}$ ) is given by the sum of the electrostatic interaction energy ( $G^{\text{EL}}$ ), acid-base interaction energy ( $G^{\text{AB}}$ ), and Lifshitz-van der Waals energy ( $G^{\text{LW}}$ ). The  $G^{\text{EL}}$  and  $G^{\text{AB}}$  values are obtained from measurements of the zeta potential and contact angle, respectively, and  $G^{\text{LW}}$  is calculated based on the Hamaker constant, which can be obtained from the Lifshitz-van der Waals free adhesion energy. From these results and those of the flotation experiments, a high floatability is observed in the pH range (calculated by the extended DLVO theory) where *SIP-E. coli* can attach to the surface of quartz, while a low floatability is observed in the pH region where *F. acidiphilum* can be attached to the surface of pyrite. Therefore, the adhesion behavior of *SIP-E. coli* and *F. acidiphilum* to each mineral can help predict the ability of minerals to undergo flotation. In addition, as the pyrite surface becomes hydrophilic after the

attachment of *F. acidiphilum*, it is apparent that this microorganism can be used as a pyrite depressant in the desulfurization of coal via flotation. Currently, the application of this microorganism to other sulfide minerals is under consideration.

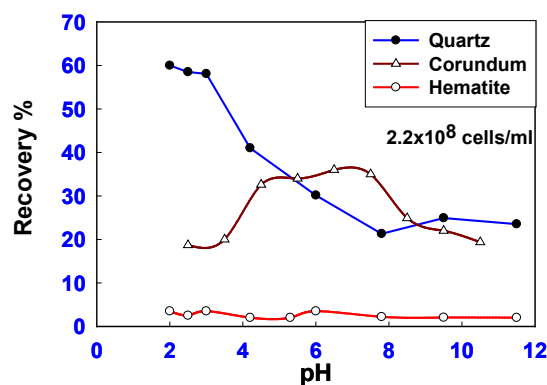


Figure 4 Flotation results for each mineral (*SIP-E. coli* additives)

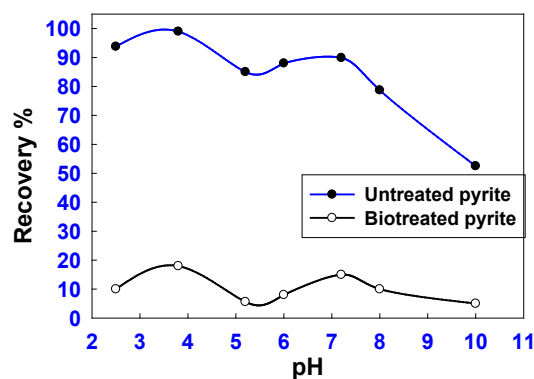


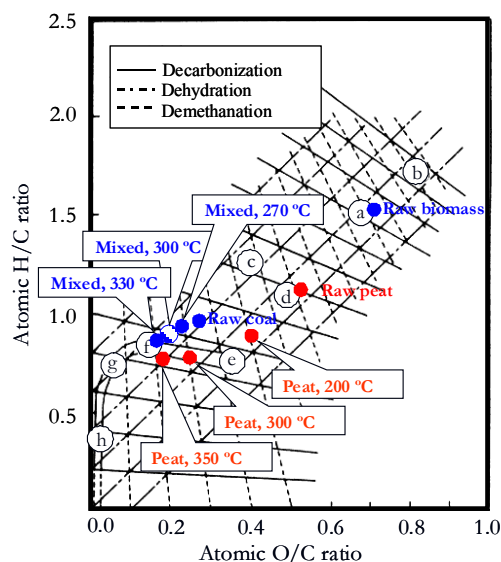
Figure 5 Flotation results for pyrite (*F. acidiphilum* additives)

## 4. Technology for improving the properties of a biomass and low-rank coal mixture

### 4.1 Characteristics of low-rank coal

Coal is formed when peat are altered physically and chemically. This process is called "coalification." During coalification, peat undergoes several changes as a result of bacterial decay, compaction, heat, and time. Therefore, the degree of coalification depends on the pressure, duration of time, and geothermal environment. As coalification progresses, the coal progressively changes into peat, lignite (brown

coal), sub-bituminous coal, bituminous coal, and anthracite (smokeless coal). Of these, sub-bituminous coal and lignite have low degrees of coalification. They are therefore called low-rank coals.



**a: Wood, b: Cellulose, c: Lignin, d: Peat, e: Lignite, f: Sub-bituminous, g: Bituminous, h: Anthracite**

Figure 6 Coal band plots

Figure 6 shows a plot of the different coalification levels, or coal bands; the atomic O/C and H/C ratios are plotted along the horizontal and vertical axes, respectively. As shown in the figure, the above series of coals is located in one band called the coal band. In other words, the evolution from wood to peat to lignite occurs after progressive dehydration, decarbonization, and demethanation through a reaction that eventually transforms the coal into anthracite<sup>38)</sup>. Low-rank coal such as lignite has a higher water content and lower calorific value, but it ignites spontaneously. As a result, it is only used near mine mouths. However, it is ecologically desirable because of its low sulfur and ash content<sup>39)</sup>. Therefore, improving the quality of low-rank coal requires removing the moisture and, at the same time, changing the properties that control the ignition process.

## 4.2 Upgrading technology for biomass and low-rank coal mixture

According to the Biomass Nippon Comprehensive Strategy (Cabinet decision as of December 27<sup>th</sup>, 2002), the concept of biomass represents the amount (mass) of biological resources (bio); thus, biomass is defined as a family of renewable resources of organic nature and biological origin, excluding fossil resources. Burning biomass results in the emission of carbon dioxide, one of the greenhouse gases that cause global warming. This carbon dioxide is fixed from the atmosphere by photosynthesis and has carbon-neutral characteristics that maintain the balance of atmospheric CO<sub>2</sub>. Therefore, replacing fossil fuel with a portion of biomass can reduce carbon dioxide emissions.

Methods to improve the quality of low-rank coal and biomass are roughly divided into evaporation and non-evaporation methods. The non-evaporation method is more advantageous since less energy is needed for the upgrading process<sup>39)</sup>. With the evaporation method, the operating temperature and pressure are low, but the energy consumption due to the change in the state of water is high. The Upgraded Brown Coal (UBC) process developed by Kobe Steel Ltd is an evaporation method that has been improved at a low cost; from the start of the 2006 fiscal year, it has been applied in a large-scale demonstration plant with a 600-t/d output. Commercialization of this process is expected to start after 2010<sup>5)</sup>. The UBC process originates from slurry dewatering technology, which is the pretreatment technology for lignite (brown coal) liquefaction. While coal is being dewatered and stabilized in the oil, it can develop the water repellency characteristic and suppress the self-ignition characteristic. However, property modifications by removing oxygen from lignite cannot be performed because of low temperature treatment. In the hydrothermal treatment method (non-evaporation), the hydrophilic functional group on the surface of coal decomposes during the surface property modification process to make the surface hydrophobic. At the same time, the tar-like substance generated by the upgrading process is absorbed in the coal voids and

blocks them to facilitate dehydration. Moreover, since it is difficult to re-adsorb water after surface property modification, the process is more suitable for upgrading high-moisture lignite and biomass. JGC Corporation has conducted research on Coal Water Mixture (CWM) and modification of low-rank coal” at a temperature of 300 °C and pressure of 120 bar; using the results of this research, it has developed a technology to improve the quality of low-rank coal by hydrothermal treatment. The usefulness of this technology has been examined through laboratory tests and demonstration tests at a pilot plant <sup>40), 41)</sup>.

To reduce CO<sub>2</sub> emissions from solid fuel and utilize low-grade coal and woody biomass to produce fuel, the author has conducted research on upgrading single low-rank coal as well as a mixture of coal with woody waste biomass <sup>42)–47)</sup>.

Alaska Beluga coal, as an example of a low-rank coal (C: 61.2 wt%; O: 32.8 wt%), and cedar wood, as a representative biomass (C: 48.5 wt%, O: 45.6 wt%), were both used in upgrading tests. After separately grinding both materials, each sample was mixed with water to produce a slurry with a concentration of 10-wt%. First, tests were carried out in a 1-L autoclave at 300 °C and 12 MPa. Figure 6 shows the relationship between the H/C and O/C atomic ratios of the upgraded products. The value of the upgraded product is plotted on the so-called coal band; it appears that as the dehydration and decarbonization reactions occur in a short time, coalification continues and high-calorie products with modified property are obtained. Thus, the figure shows that by controlling the upgrading condition, it is possible to obtain a mixture of coal and biomass (bio-coal) having improved quality that meets utilization purposes. Fourier transform infrared (FT-IR) spectrum measurements reveal a loss of the cedar wood cellulose characteristic peak at 1064 cm<sup>-1</sup> before the upgrading process. Instead, the peak derived from an aromatic product became strong. Similar behavior was identified for the mixture product. In addition, <sup>13</sup>C NMR measurements revealed that the equilibrium moisture content decreases as the aromatic-

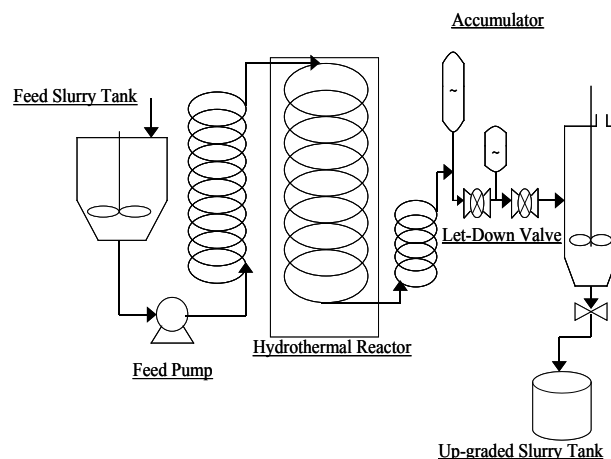


Figure 7  
Schematic diagram of a bench-scale continuous apparatus

ity increases.

A bench-scale apparatus with a 1-kg/h capacity for continuous processing was used to carry out tests on upgrading a low-rank coal and biomass mixture <sup>45)</sup>. Figure 7 shows a schematic diagram of the device. First, Beluga coal, cedar wood, and water were introduced into a slurry tank, mixed, and stirred to form a slurry with an adjusted concentration of 10 wt%. Then, the pressure of the hydrothermal reactor was set to 12 MPa; after adjusting the temperature to 300 °C, the slurry was supplied into the hydrothermal reactor through the feed pump. The flow rate of the slurry supply was adjusted so that there was a 30-min slurry retention time in the reactor at a temperature of 300 °C. After a residence time of 30 min, the hydrothermal treated slurry was then cooled, sequentially decompressed using two accumulators and decompression valves, and collected in the upgraded slurry tank.

Figure 8 shows the elemental analysis results on a dry-ash-free basis for different ratios of cedar in the mixture, while Figure 9 illustrates the gross calorific value of the product. Regardless of the mixture ratio, the oxygen content in the mixture was reduced by about 20%. The carbon content was more than 70%, and the gross calorific value—above 7200 kcal/kg—and dehydration of the product were significantly improved. Continuous operation was carried out

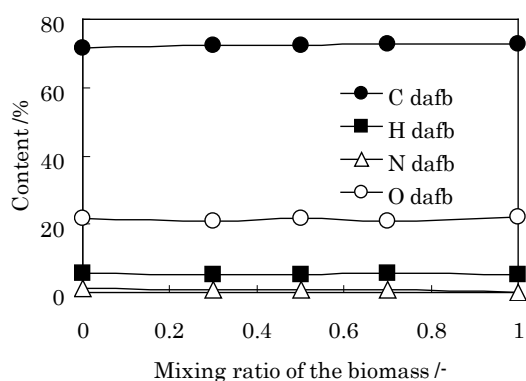


Figure 8  
Effect of the cedar mixing ratio on the results of element analysis of the solid product (dry-ash-free basis)

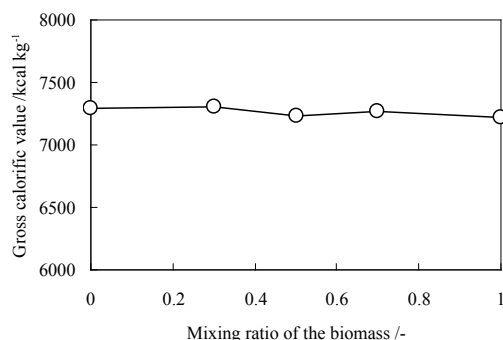


Figure 9  
Effect of the cedar mixing ratio on the gross calorific value of the solid product (dry ash free basis)

without any problems, suggesting that continuous operation can be effective for property modification when upgrading a mixture of low-rank coal and woody biomass.

## 5. Conclusion

In Japan, where more than 99% of the total demand for coal is satisfied by imported coal, ensuring a long-term stable supply of coal energy resources is of great importance; in addition, the development of prospective technologies that allow the use of a wider variety of coals while reducing the related environmental impact is needed. In order to increase the use of coal, the first consideration should be to reduce environmental pollutants such as coal ashes, carbon

dioxide, sulfur oxides, nitrogen oxides, and heavy metal elements. Anticipating the growing need for clean coal, progress is being made in the development of multi-gravity separators and other advanced fine-particle gravity separators, in the refinement of the froth flotation and oil agglomeration processes, and in research on more economical technologies. Moreover, assiduous development efforts are being directed toward technologies that dewater and upgrade low-rank coal, low-cost technologies that desulfurize and de-ash high-sulfur and high-ash coals, dry coal separation technologies that can be used in arid or cold regions, and other coal cleaning technologies that can contribute to preserving the global environment. Thus, a wide range of studies are being carried out in different fields, and substantial progress in these fields is eagerly anticipated.

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## Elucidation of Reaction Mechanism of O<sub>2</sub>/CO<sub>2</sub> Coal Gasification and Application to Various Coals in Asia

Kyushu University Seong-Ho Yoon

### 1. Summary

Electric power generation provided by gasification of coal which is abundantly available all over the world, is expected as an important energy source until a stable energy-supply system with renewable energies is established. However, further improvement in efficiency is needed to accomplish the goal of “cutting global greenhouse gas emissions by half from the current level by 2050” advocated by “Cool Earth 50” and to secure huge amounts of additional energy required for carbon dioxide capture and storage (CCS).

Under the project of NEDO “Innovative Zero-emission Coal Gasification Power Generation Project”, we devised the process which utilizes CO<sub>2</sub> recovered from the coal gasification system as a part of oxidant and greatly improves the efficiency of the system (Figure 1). The tasks concerning this next-generation cycling-recovering IGCC system include clarification

and demonstration of the effect of CO<sub>2</sub> for improvement of coal gasification efficiency, optimization of dry gas purification technology, feasibility study (FS) of utility-scale plants, as well as CO<sub>2</sub> recovery and utilization from the long-term perspective. Its adaptability to various kinds of coal in Pacific Rim regions will also be tested. Central Research Institute of Electric Power Industry and Kyushu University will jointly tackle these tasks and aim for completion of basic and applied technology development. The technology acquired through the research will be world-leading one in both fields of environment and energy. This project will enable students to learn and study practically, and thus contribute to the development of human resources which will lead the research and development in the future. The project is also expected to make international contributions for Asian and other Pacific Rim regions through technical transfer and cooperation.

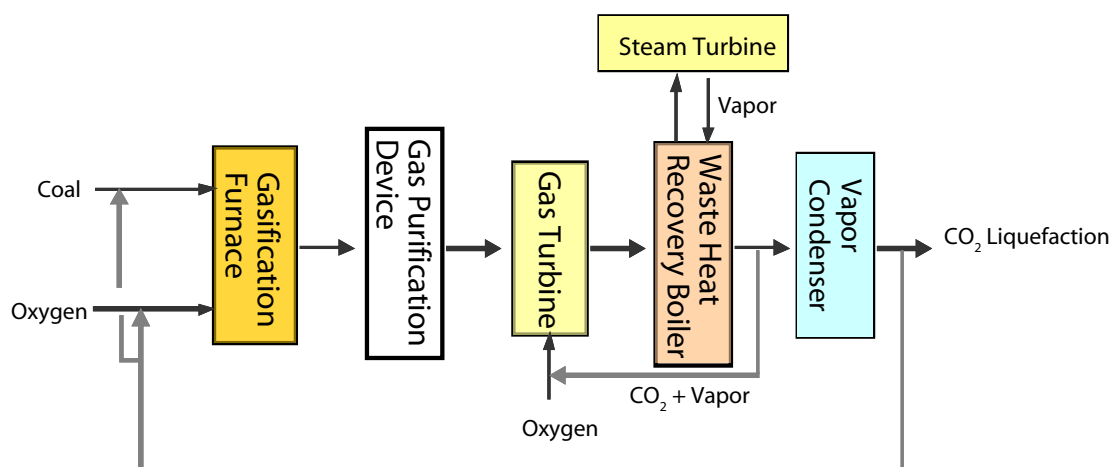


Figure 1 Thermal power system of CO<sub>2</sub> cycle recovering coal gasification

## 2. Research sharing

Kyushu University takes part in the research theme of “elucidation of reaction mechanism of  $O_2/CO_2$  coal gasification and application to various coals in Asia” to intensively investigate the following six items.

- a. Structures of coals and chars and reactivity of gasification
- b. Analyses and behaviors of minerals in coals and their effects on gasification
- c. Analyses of properties, structures, and behaviors of ashes formed during gasification
- d. Manipulation of CO-enriched gases
- e. Pre-treatment of coals
- f. Flow analyses in gasification furnaces

## 3. Research results in 2008

Kyushu University takes part in the research theme of “elucidation of reaction mechanism of  $O_2/CO_2$  coal gasification and application to various coals in Asia” to intensively investigate the following six items.

- a. Structures of coals and chars and reactivity of gasification

The structures of coals and chars were determined by SEM and TEM observations and measurements of  $^{13}C$ -solid NMR spectra and the amount of absorbed nitrogen. Next, pyrolysis of coals and chars and reactivity of gasification were analyzed by TGA changing the conditions of gas compositions and heating rates. Furthermore, simple flow apparatus and numerical analysis system were constructed to elucidate mechanism of  $O_2/CO_2$  gasification of coals, especially to clarify the roles of  $CO_2$  and to establish simulation.

- b. Analyses and behaviors of minerals in coals and their effects on gasification

Trace inorganic components in coals were analyzed qualitatively and quantitatively by XRD, XRF, and ICP measurements. Additionally, gasification behaviors of  $O_2/CO_2$  gas were traced by TG-DTA analyses and FT-IR spectra.

- c. Analyses of properties, structures, and behaviors of ashes formed during gasification

Components and structures of coal ashes prepared under various conditions (gas components and temperatures) were analyzed by XRF, XRD,  $^{27}Al$ -solid NMR, SEM, and TEM-EDX measurements. In addition, additives to control viscosity of slag were selected and predicted. Furthermore basic experimental apparatus was constructed to elucidate behaviors of ashes under the conditions of high temperatures and normal pressure.

- d. Manipulation of CO-enriched gases

Laminar and turbulent burning rates of  $H_2-O_2-CO_2-H_2O$  premixed propagation flame and effects of  $CO_2$  concentration on the rates were studied by using constant-volume combustion apparatus. Next, the effects which components of gases and composition of reaction tubes influenced on carbon deposition were examined. Furthermore, the effects of residual oxygen in  $CO_2$  were investigated by measurements of the amount of  $CO_2$  absorbed in coals and TG-DTA analyses.

- e. Pre-treatment of coals

Property modifications of high-moisture, high-ash, and high-sulfur coals in hydrothermal treatments together with varying and removing minerals and sulfur contents were examined by using a batch-wise and pressurized hydrothermal apparatus.

- f. Flow analyses in gasification furnaces

The validity of the model of turbulent heat transfer was examined to analyze heat transfer phenomena and the effect on radiant heat transfer of  $CO_2$  gas was studied by comparing basic experiments of heat transfer with the results obtained from empirical formula and numerical analyses. Moreover, the behaviors of ashes in gasification furnaces and on piping walls were analyzed by using self-made calculation program.

# Chemical Utilization of Carbon Resources

## Micro Review

## Structural recognition and selective synthesis of carbon nanofibers and their applications in energy and environmental fields

Kyushu University Seong-Ho Yoon

Carbon nanofibers (CNFs) have various fibrous structures and surface properties together with higher crystallinity and surface area than conventional carbon blacks, and thus are anticipated to realize high performance and new functionalities in various application fields. Herein, we first introduce our new concept of CNF structure elucidated through AFM and STM observations, and then some results of CNFs designed and optimized based on our structural model of CNFs as energy and environment conservation devices.

### 1. Introduction

Carbon materials have been used broadly as absorbents and reinforcements, etc. since ancient days. The recent nano-carbon research, which began with the discovery of fullerene, has been leading to the development of a variety of new nano-carbon materials, and it is strongly expected that such high surface area carbon materials having higher regularity and homogeneity than conventional ones will exert new functions. Especially, carbon nanofibers (CNFs) offer unique and various fibrous structures and surface properties together with higher crystallinity and larger surface area than conventional carbon blacks. Accordingly, it is expected that excellent absorptive property, catalytic and catalytic support functions will be exerted by conducting surface modifications and porosity controls appropriately. Catalysts with such characteristics of CNFs show higher functionalities than conventional carbon materials in various applications, such as green chemical catalysis for hydrogenating and dehydrogenating aromatic molecules; desulfurization and denitrogenation of exhaust gas; deep hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodenitrogenation (HDM) of petroleum; and high-performance catalysts for fuel cells, etc. In order to put CNFs into practical use, it is indispensable to accurately understand their configurations and structures, which are closely related to physical properties and functions. Based on such understandings, it becomes possible to

conduct selective synthesis, structural control and optimization according to the purpose of use.

In this paper, we first introduce our new recognition of structures of CNFs, and outlines the researches into the catalytic support functions of energy-saving and environment-preservation materials based on the selective synthesis and structural analysis of various CNFs, and the optimum control of CNF structures and properties.

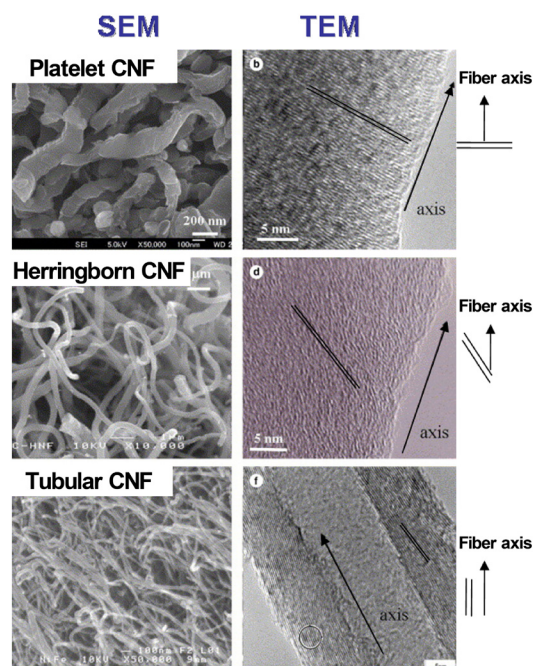


Fig. 1  
Electron microscopy images of the three kinds of standard CNFs

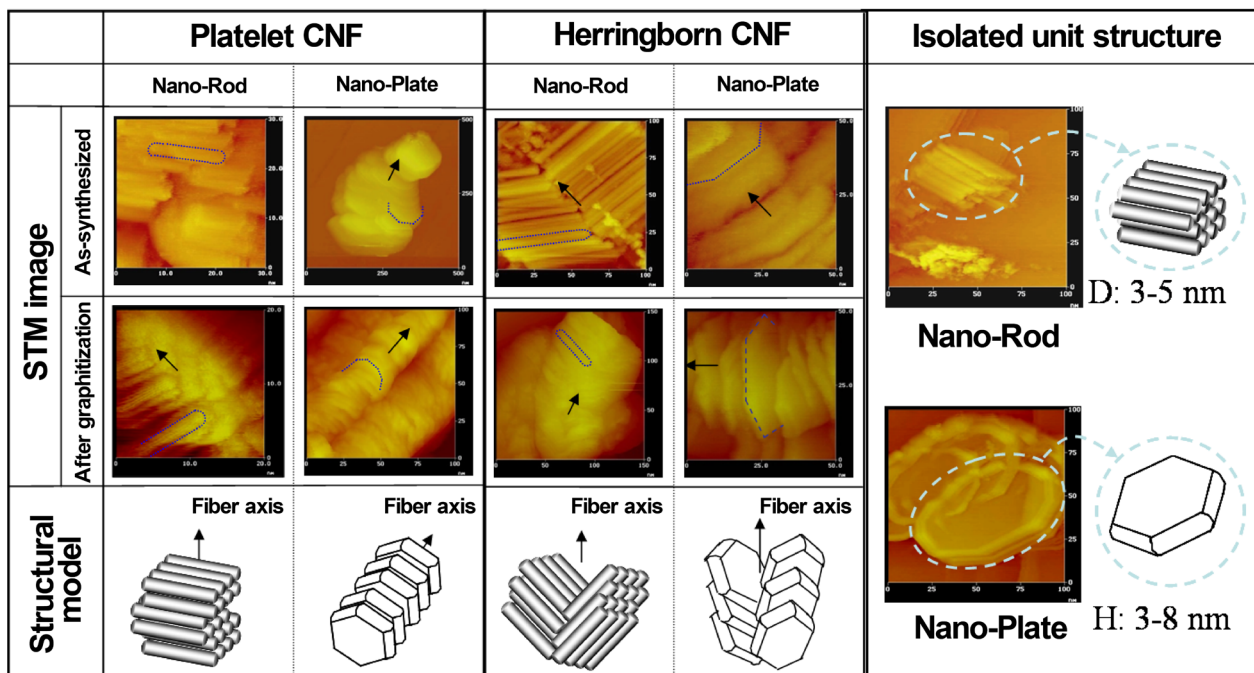


Fig. 2

Structural analysis of CNFs by STM observations, and structural models of Nano-Rod and Nano-Plate

## 2. Recognition of CNF Structures

Fig. 1 shows the electron microscopic images of three kinds of standard CNFs. The structures, fiber sizes, and surfaces of these standard CNFs can be well-controlled by detailed condition adjustments at each synthesis stage. We also succeeded in synthesizing a large amount of CNFs by using originally-designed vertical-type CNF mass production system.

Through the three-dimensional structural analysis of these three kinds of CNFs using STM and AFM, we found for the first time that each of the three kinds of CNFs is constituted by two kinds of fundamental structural units: Nano-Rod and Nano-Plate, as shown in Fig. 2. Furthermore, by modifying the quantity ratio between the two basic structural units and alignment to the fiber axis, we proposed a variety of new structure models, including the Nano-Rod-integrated type, the Nano-Plate-integrated type, and their mixed type (See Fig. 2).

## 3. Application of CNFs into Energy-Saving and Environment-Preservation Materials

Although a method of collecting  $\text{SO}_2$  in atmosphere or exhaust gas as sulfuric acid using

activated carbon has been already put into practical use, we newly succeeded in improving desulfurization performance significantly by using heat-treated pitch-based activated carbon fibers (ACFs). To realize higher performance, the material surface should be able to remove sulfuric acid, the reaction product, to restore and maintain the reaction site swiftly. Then, we hydrophobized the ACF surface by growing highly-hydrophobic CNFs directly from the ACF surface and producing CNF-ACF composite, and achieved higher desulfurization activity than conventional ACFs. Here, in order to prevent the decrease in the ACF surface area due to CNFs grown on the ACFs, metallocene,

Effects of deposition amount of metallocene (CNF growth catalyst); measurement temperature: 70 °C

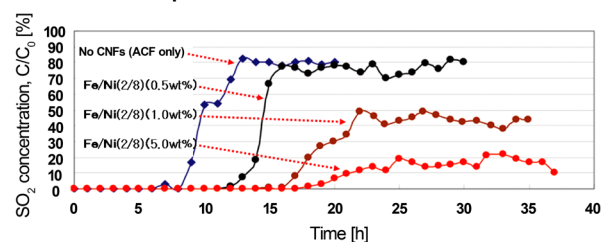


Fig. 3

Desulfurization activity of CNF-ACF composites

Table 1

Results of single cell tests of mesoporous and intermediate fiber diameter CNFs as the catalyst support for DMFC negative electrodes

| CNF type; platinum amount [mg/cm <sup>2</sup> ]                           | Maximum power density [mW/cm <sup>2</sup> ] |       |       |
|---|---|-------|-------|
|   | 30 °C                                       | 60 °C | 90 °C |
| Mesoporous CNF-40 wt% Pt-Ru supported catalyst / 1.33 mg                  | 62  | 122   | 197   |
| Intermediate fiber diameter CNF-40 wt% Pt-Ru supported catalyst / 1.33 mg | 76  | 140   | 246   |
| Commercial catalyst / 2 mg (Johnson Matthey-60 wt%; HISEC10100)           | 55  | 121   | 162   |
| Commercial catalyst E-TEK (60 wt%) / 2 mg                                 | 40  | 116   | 140   |

which does not enter the ACF pore easily, was used as the catalyst for CNF growth, and the composite was produced. The obtained CNF-ACF composite turned out to be highly active with the improved desulfurization time and the SO<sub>2</sub> leakage amount at the steady state, as shown in Fig. 3.

Fuel cells are expected to be used as the environmentally-friendly next generation energy technology. Carbon materials are important ones that determine the battery performance as a support of electrode catalyst. Carbon materials also function as a collector, but the quantitative correlation between the fine structure or surface property of carbon materials and electrochemical catalytic activity remains to be clarified. Thus, we clarified the characteristic correlation with fuel-cell catalyst activity, using three kinds of CNFs whose surface structures can be controlled as the metal catalyst support, and attempted to high-activate the direct methanol fuel cell (DMFC) as catalyst support, with the structural optimization of CNFs, the introduction of meso-pore, and the high dispersion using a nano-dispersion device. As shown in Table 1, when Pt or Pt-Ru was singly-dispersed on the mesoporous CNFs and the herringbone CNFs of intermediate fiber diameter, the catalyst showed over 1.3 times catalytic activity even when the Pt amount was half of that of conventional commercial catalyst.

Lastly, we introduce our results about the development of negative-electrode materials for lithium-ion batteries by conjugating CNFs with Si or SiO particles. As current commercial

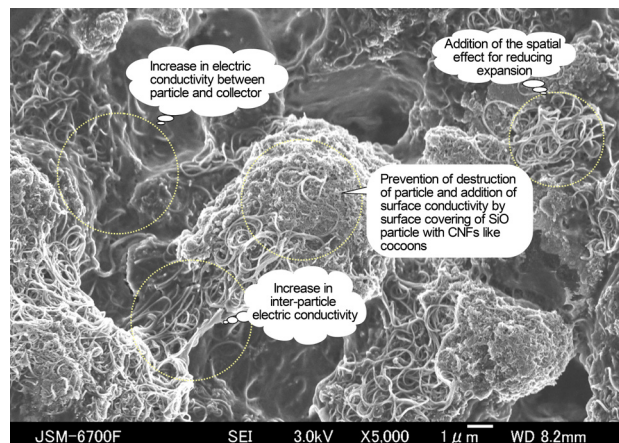


Fig. 4

SEM image of cross section of negative electrode of lithium-ion battery using CNF-SiO composite

negative-electrode materials for lithium secondary batteries, graphitic carbon materials are mainly used. However, there is a demand for the early practical application of higher-capacity materials than graphitic ones. Si-series negative-electrode materials have theoretical capacity much higher than graphite, but there is a shortcoming that the introduction of lithium ions induces volumetric expansion and particle surface destruction, resulting unstable cycle characteristics. We grew CNFs on the Si-series negative-electrode materials and conjugated them for inhibiting volumetric expansion and adding electric conductivity. The prepared CNF-Si and CNF-SiO composites demonstrated lower volumetric expansion, more than two times higher capacity, and comparable cycle characteristics as compared with commercial graphite negative electrode.

Fig. 4 shows the scanning electron microscopic images of the cross section of the negative electrode of the ultrahigh capacity lithium-ion battery based on the CNF-SiO composite. From characteristic examinations using the CNF-SiO composite as the negative-electrode material of lithium secondary batteries, we found that CNFs adhere to the SiO surface firmly and it becomes possible to inhibit the expansion of electrode due to the addition of conductive property and the securing of dilation

space. Furthermore, the high-rate discharge characteristic was also observed, suggesting its possible applications as electrode materials for electric automobiles, etc. that require large current discharge. If initial efficiency is improved (80%) and a safety test progresses in future, the applicability of this new material can be expected.

## **4. Conclusion**

Some of our pioneering studies about the new structural recognition of CNFs, new characteristics of functionalized CNFs based on the recognition, and their applications, which are becoming trends in the research into nano-carbon materials, are introduced. To expand the application fields of CNFs, clarification of basic reactions and development of supporting technology are indispensable to achieve selective improvement, surface modification, and optimization of metal supporting for optimum functionalizations. It is more useful to develop practical materials that

can achieve a good balance between the CNF costs and performance. By conducting the selective production, structural analysis, characteristic study, applicability test and optimization of CNFs, it is expected to contribute to the fields of electric energy conversion, storage, discharge, energy-saving materials, heat transfer, pollutant reduction, green synthesis, and purification for mitigating and preventing global warming and air pollution.

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## Introduction of the Group Research

# Organoiron Catalysts: Advanced Science and Technology for Production of Organic and Polymer Materials with Sustainability

Hideo Nagashima, Mitsunobu Kawamura, Daisuke Noda, Yusuke Sunada  
Institute for Materials Chemistry and Engineering, Graduate School of Engineering Sciences,  
Kyushu University

### Hideo Nagashima (Doctor of Engineering)

A Professor of Institute for Materials Chemistry and Engineering, Kyushu University  
After the completion of Ph.D. in Department of Chemical Engineering, Graduate School of Engineering, Tokyo Institute of Technology in 1982, he worked as a Reader, a Lector and an Associate Professor in Toyohashi University of Technology. Then, in 1997 he moved to Institute of Advanced Material Study Kyushu University, which was reorganized as Institute for Materials Chemistry and Engineering in 2003. He is engaged in education in Department of Energy Science and Engineering at Faculty of Engineering and Department of Molecular and Material Sciences at Interdisciplinary Graduate School Engineering Sciences.



### Mitsunobu Kawamura

Apr.2002-Mar.2004

Master degree in pharmacology in Graduate School of Pharmaceutical Sciences, Hokkaido University

Apr.2004-Mar.2007

Ph.D. in pharmacology in Graduate School of Pharmaceutical Sciences, Hokkaido University: Awarded Ph.D. in Pharmacology

#### Research experience

Apr.2005 DC2 in Research Fellowship for Young Scientists, JSPS

Apr.2007 Research Fellow in Faculty of Pharmaceutical Sciences, Hokkaido University

Sep.2007 Postdoctoral Researcher in Institute for Materials Chemistry and Engineering

Aug.2008 Postdoctoral Researcher in G-COE, Kyushu University



### Daisuke Noda

Apr.2005-Mar.2007

Master Degree in Department of Molecular and Material Sciences Graduate School Engineering Sciences, Kyushu University

Apr.2007-Present

Ph.D. in Department of Molecular and Material Sciences Graduate School Engineering Sciences, Kyushu University

Sep.2008 -Present

Course Student of G-COE (NCRS), Kyushu University



### Yusuke Sunada

Mar.2001

Completed Master Degree in Science in Department of Chemistry, Graduate School of Science, Nagoya University

Apr.2001-Mar.2004

Ph.D. in science in Department of Chemistry, Graduate School of Science, Nagoya University: Awarded Ph.D. in Science

#### Employment Experience

Apr.2003 DC2 in Research Fellowship for Young Scientists, JSPS

Apr.2004 PD in Research Fellowship for Young Scientists, JSPS

Dec.2004 A Reader in Institute for Materials Chemistry and Engineering

Apr. 2007 An Assistant Professor in Institute for Materials Chemistry and Engineering, Kyushu University



## 1. Introduction

As shown in my lecture, “Catalysts to save the earth”, a catalyst is defined as a substance that changes the speed of a chemical reaction without undergoing a permanent chemi-

cal change itself in the process [T.L. Brown et al. “Chemistry” 11th ed. Pearson Education International (2009)]. Activation energy of the chemical reaction is thus lowered by addition of a small amount of the catalyst as shown in Fig. 1.

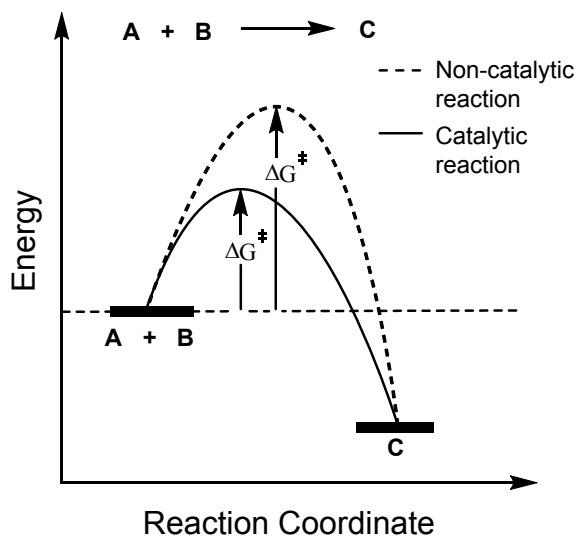


Fig. 1  
Potential energy diagram of catalytic reaction.

When the role of the catalyst is seen in detail, people recognize that the catalyst is bound to the reactant to form several reaction intermediates; transition states of the reaction between the intermediates are different from those of non-catalyzed reactions. It is important that the catalyst is regenerated after the product is eliminated from the final reaction intermediate. In other words, the catalyst is reusable many times; in extreme ideal cases, the catalyst works forever in the reaction vessel unless otherwise deactivation occurs. These excellent features of the catalyst play important roles in many facets of human life and advanced research in both academic and industrial point of views has been actively carried out. In our COE program, Dr. Teraoka and his colleagues are studying environmental catalysts such as those effectively decompose NO<sub>x</sub> and other pollutants, whereas Dr. Yoon and Mochida are actively developing new catalyst systems for gasification of coals, desulfurization of oils, and fuel cells. Nagashima group is concentrating to develop new molecular catalysts which contribute to producing organic and polymer materials for medicines, electronic devices, and engineering plastics; they are actually useful in laboratory and industrial scales. In the molecular catalysts, compounds containing both organic and metallic components, typically organotransition metal

complexes are used as the catalysts. The organometallic catalyst has excellent features for not only lowering the activation energy to accelerate the reaction but also establishing highly selective reactions by controlling the structure and electric property of the reaction intermediates. By virtue of these, chemists can achieve highly efficient production of desired products without forming the undesired by-products.

The COE program New Carbon Resource Sciences (NCRS) aims at establishing the new paradigm for efficient use of carbon resources (for conversion to energy as well as chemical uses) with complete protection of global environments. Catalysts and catalyses are one of the important key issues which members are actively investigating as described above. Our studies on the molecular catalysts are one of the research projects which fulfill the requirement to produce chemicals necessary for human life with high efficiency and selectivity. Development of effective molecular catalysts leads to industrial application for the production of electronic devices and engineering plastics, for example, those for automobiles. Organic and polymer materials thus produced from carbon resources by taking advantage of the molecular catalysts have high quality which realizes light weight devices, which make possible “the downsizing of the product” taking part in reducing total energy cost. Fundamental of research on the molecular catalysts is called as organometallic chemistry, in which various organometallic compounds often having carbon-metal bonds have been actively investigated. Activity of this field is well known as three related Nobel Prizes, conductive polymers by Dr. Shirakawa et al., catalytic asymmetric synthesis by Dr. Noyori et al., and catalysis for olefin methathesis by Grubbs and coworkers.

It is extremely important that excellent features of catalysts and catalysis have contributed to human life for recent several decades; however, the severe requirements for environmentally sustainability urges to discover a new paradigm for 21st century. As described, a small amount of a catalyst can produce products with

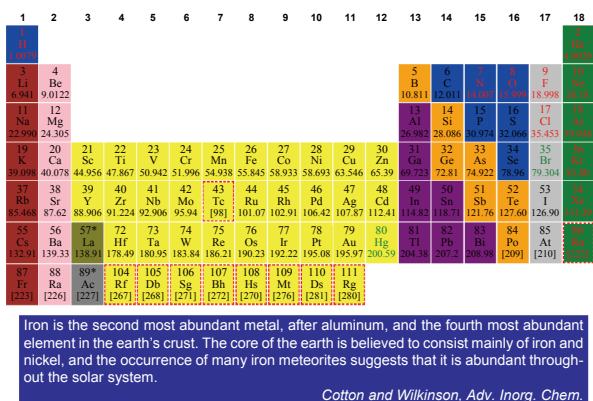


Fig. 2  
The position of the iron (Fe) in the periodic table.

| Ranking | Element | Clarke number | Ranking | Element | Clarke number | Ranking | Element | Clarke number |
|---------|---------|---------------|---------|---------|---------------|---------|---------|---------------|
| 1       | O       | 49.5          | 10      | Ti      | 0.46          | 19      | Ba      | 0.023         |
| 2       | Si      | 25.8          | 11      | Cl      | 0.19          | 20      | Zr      | 0.02          |
| 3       | Al      | 7.56          | 12      | Mn      | 0.09          | 21      | Cr      | 0.02          |
| 4       | Fe      | 4.7           | 13      | P       | 0.08          | 22      | Sr      | 0.02          |
| 5       | Ca      | 3.39          | 14      | C       | 0.08          | 23      | V       | 0.015         |
| 6       | Na      | 2.63          | 15      | S       | 0.06          | 24      | Ni      | 0.01          |
| 7       | K       | 2.4           | 16      | N       | 0.03          | 25      | Cu      | 0.01          |
| 8       | Mg      | 1.93          | 17      | F       | 0.03          |         |         |               |
| 9       | H       | 0.83          | 18      | Rb      | 0.03          |         |         |               |

Fig. 3  
Abundance of the elements in the earth crust.

| Name       | Chemical symbol | Abundance | Name       | Chemical symbol | Abundance |
|------------|-----------------|-----------|------------|-----------------|-----------|
| Oxygen     | O               | 61%       | Iron       | Fe              | 60ppm     |
| Carbon     | C               | 23%       | Zinc       | Zn              | 33ppm     |
| Hydrogen   | H               | 10%       | Copper     | Cu              | 1ppm      |
| Nitrogen   | N               | 2.60%     | Manganese  | Mn              | 0.2ppm    |
| Calcium    | Ca              | 1.40%     | Iodine     | I               | 0.2ppm    |
| Phosphorus | P               | 1.10%     | Molybdenum | Mo              | 0.1ppm    |
| Sulfur     | S               | 0.20%     | Selenium   | Se              | 0.2ppm    |
| Potassium  | K               | 0.20%     | Chromium   | Cr              | 0.03ppm   |
| Sodium     | Na              | 0.14%     | Cobalt     | Co              | 0.02ppm   |
| Chlorine   | Cl              | 0.12%     |            |                 |           |
| Magnesium  | Mg              | 270ppm    |            |                 |           |

Fig. 4

The essential elements of the human body  
(Abundance of each element in the human body).

low energy; this is good enough for 20th century. However, society of 21st century requests complete removal of the catalyst from the product with low cost. Furthermore, it is desirable that the recovered catalyst is reusable.

One of the reasons that our NCRS program pursues epoch-making catalysts and catalytic processes is attributed to the requirement for establishing this new paradigm. In other words, catalysts in the next generation should be highly efficient and providing high selectivity of the reaction. Moreover, the catalyst used should be separable from the product with ease and recoverable and reusable for next run of the reactions. In extreme cases, elements which do not affect the environment and organisms at all are preferable for the catalyst component when we consider the case that a trace amount of the metal remains in the product.

## 2. Importance of iron as the element

Iron is a middle in the periodic table, and the fourth abundant elements in the earth crust (Fig. 2, Fig. 3). Iron is believed to exist abundant in solar systems, and there would be no shortage as the resources in future. In the evolution of organisms, they were always careful for effective use of abundant element dissolving in water. Soluble iron ions are one of them, and iron is the most abundant transition metal element in a human body. This means that iron is not poisonous even if some amounts of iron are dosed from outside. All of the living systems require any compounds containing iron for life, and in other words, iron is safe to all of the organisms (Fig. 4).

Catalysis of iron has been investigated for a long time. Habor-Bosch process is a well known industrial process for the production of  $\text{NH}_3$  from  $\text{N}_2$  and  $\text{H}_2$  at high temperature. Iron is a main component of the catalyst at high pressure (200-500 atm) and high temperature (400-600 °C). It is well known that enzyme containing iron converts  $\text{N}_2$  to  $\text{NH}_3$  in the nitrogen cycle in the earth. However, molecular catalysts containing iron have not been fully developed in both industry and laboratory. Iron-catalyzed processes often required harsh conditions, not giving versatility of the reactions. In last several decades, other transition metals such as palladium, rhodium, nickel, and cobalt are frequently used in the production of chemicals, but catalysis of organoiron compounds has been obscure.

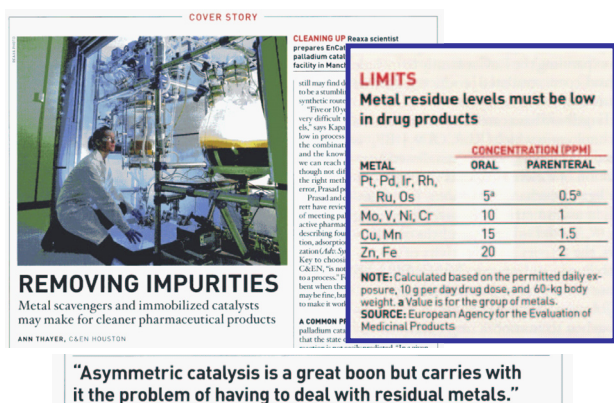


Fig. 5

Importance of molecular catalysts in organic synthesis and necessity of separating metals used as catalysts from the products.

However, the paradigm for 21st century actually needs the iron catalysts. The molecular catalysts generally have advantage on the efficiency and selectivity. In contrast, separation of the catalyst from the product is problematic, which is necessary time, cost, and energy. In Fig. 5 is shown an article of Chem. Eng. News from American Chemical Society, proposing severe limit for residual metals in the product formed by the molecular catalysis. This is a proposal for medicines; however, there is similar requirement for lower limit of the residual metals in the production of electronic devices and engineering plastics for keeping the desired property of the materials.

As shown in Fig. 5, zinc and iron are special elements due to their safety. If the molecular catalysis by iron can be widely applicable to many chemical processes, people can use medicines without care to their potential toxicity. If the iron is used as the catalyst and the used catalyst is easily removable from the product and reusable, such chemical processes would be ideal for saving the resources and for saving energy.

### 3. Difficulty in research on the organoiron complexes

Research on the organoiron complexes is necessary for the development and improvement

of iron catalyzed chemical processes. The experiments are in particular focused on isolation and characterization of the reaction intermediates. A problem which makes such research projects difficult is attributed to paramagnetism of common organoiron complexes as shown in Fig. 5. The most difficult problem is effective use of Nuclear Magnetic Resonance (NMR) as a tool for the research; the paramagnetism of iron sometimes give extremely broad or no resonances on NMR. It is also problematic that paramagnetism often causes unstability of the iron compounds to air and moisture. Because of these difficulties, there are only a few research groups in the world, which have fundamental knowledge and skills enough to carry out the research for organoiron compounds; Nagashima group is one of them as shown in an article of newspaper. Experiments to treat unstable iron compounds require patience and time for concentration; however, our research group makes a team of four people to obtain results which leads the world-wide community.

### 4. Summary of the results by Dr. Kawamura

One of the results which we have recently reported are iron catalyst for living radical polymerization. Living polymerization is a term for addition polymerization of which polymer end is always reactive with monomers, giving polymers having desired molecular weight with narrow molecular weight distribution. Block copolymers which are received considerable attention from materials scientists can be synthesized by living polymerization with ease. Among several living polymerization processes, those through radical intermediates are important due to the fact that many polymers useful for industry and academic are produced easily. In particular, transition metal catalyzed processes called ATRP (AtomTransferRadical-Polymerization) are one of the topics in polymer chemistry.

Nagashima group has been involved in collaborative work with DIC Ltd. in a framework of Kyushu University-Industry collabora-

tion, and developed a series of new iron catalysts having triamine ligands called TACN which are effective for industrial production of block copolymers. A report described by Dr. Kawamura in this volume is a part of our recent results, showing that certain TACN-Fe(II) complexes efficiently catalyze the living polymerization of several monomers. Previous TACN-Fe(II) catalysts reported from Nagashima group is advantageous for removing the catalysts from the polymer formed and the recovered catalysts are recyclable. In contrast, newly developed TACN-Fe(II) complexes by Kawamura shows higher catalytic activity to minimize the usage of iron for production of polymers. Removal of metallic impurities from the product is easier when the content of impurity is minimum. By using this, Kawamura's catalyst is facilely removable from the product, The high efficiency and facile removal of the metallic component from the polymer are suitable for the aim of NCRS.

### 5. Summary of the results by Mr. Noda

Another recent result from Nagashima group was done by Mr. Daisuke Noda, a D2 student in 2008. The Grignard coupling reaction, where an organomagnesium compound is coupled with an organic halide in the presence of certain transition metal catalyst, has now become important chemical processes for production of aromatic molecules for electronic devices and medicines. In previous studies, nickel and palladium complexes have been frequently used as the catalyst. The 21th paradigm again requests to find efficient iron catalysts for Grignard coupling reactions, too.

As shown in the article of Nikkei, an effective catalyst system composed of Fe(III) salts and tetramethylethylenediamine (TMEDA) was discovered by Dr. Masaharu Nakamura, a chemist of Kyoto University. He requested a collaboration with us, because our group can carry out a mechanistic study through isolation and reactions of organoiron intermediates. Mr. Noda carried out careful experiments over a year, and his results results in proposal of an new catalytic cycle, which was accepted last month in a communication to the Editor of Journal of American Chemical Society. This collaborative work was carried out in a framework of Grant-in-aid for Scientific Research on Priority Area (Synergy of Elements) as a representative outcome of the collaborative work in the priority area.

### 6. For the future

It may be an extreme insistency that all of the molecular catalysts and catalyst systems should be carried out by the catalyst systems consisting of environmentally benign elements, and iron is a typical element for this purpose. However this should be a proposal from the Grobal COE program NCRS to the world. The 'detailed and fine' chemistry of iron is difficult to be achieved due to the paramagnetism of many of the iron compounds as described, providing big challenge in the academic society. In contrast, efficient usage of iron catalysts in industrial chemical processes is more important in the next generation due to the low cost and environmentally benign property of iron. We believe that further active studies in our research group actively contribute to progress of NCRS.

## Research Report

### Development of Environmentally Friendly and Reusable Iron Catalysts for Atom Transfer Radical Polymerization

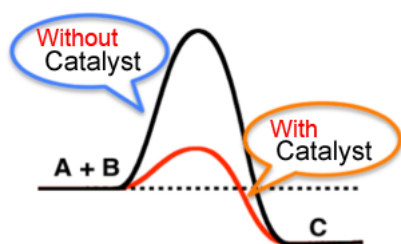
Kyushu University Mitsunobu Kawamura

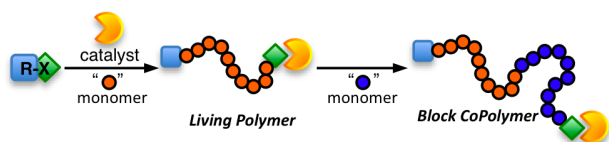
Catalysts play an important role to save the energy and resources. Easily available, low-priced and low-toxic catalysts are highly desirable for the age to come. We have recently reported ionic iron complex  $[(\text{Me}_3\text{tacn})_2\text{FeCl}_3]^+[(\text{Me}_3\text{tacn})\text{FeCl}_3]^-$  (**1**) as powerful and environmentally friendly catalyst for well-controlled atom transfer radical polymerization (ATRP) of styrene and methyl methacrylate (MMA). The catalyst **1** is readily soluble in methanol and its solubility and robustness allow us to recover the catalyst from the resulting polymers. Furthermore, the recovered catalyst was reusable for ATRP without the loss of efficiency.

The definition of catalysts is “a substance that increases or reduces chemical reaction rates without itself being changed”. Catalysts are widely used, and the examples of the use of catalysts include cleansing emission from vehicles, transforming the carbon resources such as coal and oil into chemical materials required for synthesizing plastics, etc. In general, the chemical reaction transforms starting materials to thermodynamically stable products by imposing energy on the starting materials. Since the catalyst reduces the activation energy, it achieves “energy-saving process during the chemical reaction”. Catalysts are also the substance to achieve “resource-saving process during the chemical reaction”, because they do not change their structure before and after the reactions, and a small amount of catalysts can be repeatedly used to create a large amount of products. Furthermore, since the catalysts themselves are the chemical substance, the scientists can control their structure. Controlling the catalysts’ structure is directly connected to controlling the chemical reactions such as selectivity. Therefore,

if the catalysts are well designed, “one can produce anything in any amount in resource-saving and energy-saving ways”. As is described, the catalysts are the key substance for energy-saving and effective use of resources.

From medicines to plastics, our life is supported by many organic compounds. The organic compounds are synthesized through chemical reactions that mainly use hydrocarbons as starting materials. Currently, only part of these processes is the catalytic reactions. In order to utilize various organic compounds and allow for prosperous lives in the era where shortages of resources and energy are the global concern, it is essential to save energy, effectively use resources, and utilize catalytic reactions as much as possible. Based on this background, the development of the catalyst and catalytic reaction is highly pursued, and new catalysts are being developed. However, most of the catalysts developed so far are composed of transition metals, including precious metals. Unfortunately, most of the transition metals are very scarce and expensive. They also have negative impact on the human body and environment due to their toxicity. The catalysts that would be used to produce things that support our lives should be of low-cost and easily available, low-toxic, and environmentally friendly. We have been researching the possibility of using “iron” as a catalyst to meet these needs. In this review, we will introduce the recently successfully devel-





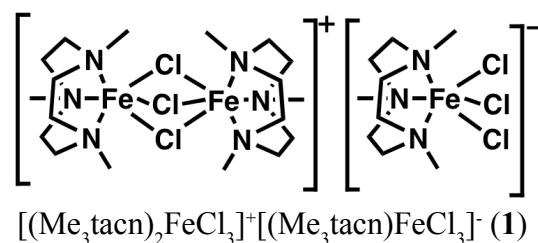
oped iron catalysts for producing polymers.

The polymers are essential materials, and there is an increasing demand for polymers having well-controlled fine structures. It is widely known that Controlled Radical Polymerization (CRP) is an effective method for producing well-controlled polymers. Particularly, transition metal catalyzed Atom Transfer Radical Polymerization (ATRP) is a representative example of CRP. The ATRP is widely used not only in the laboratory but also in the industry <sup>1)</sup>. During the ATRP reaction, the radicals, which are produced by the reaction with alkyl halides and transition metal catalysts, react with various monomers to proceed the polymerization. By adding another monomer after the reaction, it is also possible to produce block co-polymers.

In principle, during the course of ATRP process, the catalyst always exists near the reactive terminal groups and controls polymerization reaction. Therefore, in order to produce well-controlled polymers, equimolar amounts of the catalysts against alkyl halide will be needed. Thus, because the ATRP requires a comparatively large amount of catalysts, the catalysts in the resulting product (i.e. polymer) would become an issue. If the catalyst remains in the polymer, the polymer colors. Furthermore, if a toxic transition metal is included, the safety of the polymer will also become an issue. These issues are directly related to the value of the polymer as products. Unlike other organic compounds that can be purified by various methods such as distillation, it is difficult to remove catalysts from polymers. Therefore, the catalysts for the ATRP are required to have not only ability to control reactions but also those to separate from polymers and to secure the safety of the polymers. There have been continuous efforts to solve the problem of “how to remove the catalysts from the polymer”. So far, the facile removal of the catalyst from the polymer has

been investigated by using two-phase systems, such as solid-liquid or liquid-liquid systems. Matyjaszewski and coworkers also recently reported that the use of 0.001 mol% of a highly active copper catalyst for the alkyl halide had resulted in a well-controlled polymer <sup>2)</sup>. However, strict reaction conditions are required.

One way of purifying polymers is the precipitation. When polymers dissolving in an organic solvent are dropped into alcohol or water, the polymer would be precipitated. When catalysts are dissolved in the alcohol or water, they will be removed from the polymer. Thus, “controlling the solubility of catalysts” is a simple and clear solution of the separation of catalysts from the polymer. However, the organometallic compounds in general have high affinity for organic solvents, and it is not so easy to develop organometallic catalysts that can be easily dissolved in water. Recently, we have developed the ionic iron complex  $[(\text{Me}_3\text{tacn})_2\text{FeCl}_3]^+ [(\text{Me}_3\text{tacn})\text{FeCl}_3]^-$  (**1**) <sup>3)</sup> as an effective catalyst for ATRP of styrene <sup>4)</sup>.



This iron catalyst (**1**) has the ionic structure and is readily soluble in methanol; therefore, most of the catalyst can be removed from the product through simple precipitation process. The photograph below compares the appearance between the polymer synthesized by Ru catalyst and the polymer synthesized by the iron catalyst (**1**). We only purified the products by simple precipitation. The color of the polymers is the clear evident how the residual catalysts significantly affect coloration, and how the iron catalyst (**1**) can be efficiently separated from the polymer.

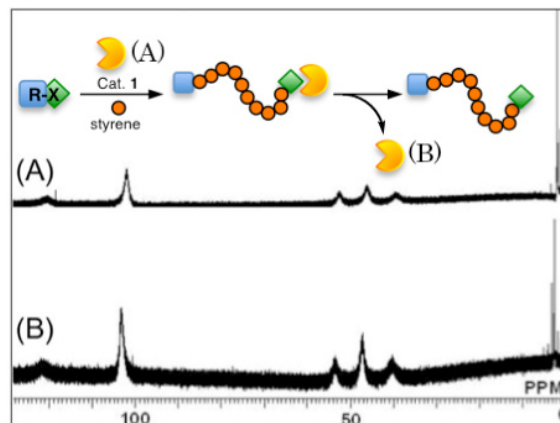
This iron catalyst meets the need of low cost and low-toxicity and furthermore, it is



almost completely removable from the polymer, i.e. this catalyst is an ideal environmentally-friendly catalyst. In addition, the recovered iron catalyst is reusable. This catalyst has a robust Triazacyclononane (TACN) backbone, and it keeps the same structure from the beginning of the reaction (A) to the stage after the separation of catalysts from polymer through precipitation by methanol (B). Therefore, although all the operation must be done under nitrogen atmosphere, if the separated iron catalyst after precipitation is concentrated and dried, it can be used for the second, third, or fourth polymerizations with consistent results.

As is described above, this iron catalyst (1) has very attractive characteristics that are required as the ATRP catalysts: reaction control, separation ability, low-toxicity, and reuse.

Currently, based on the iron catalyst (1), we are designing the TACN ligand to develop higher-performance catalysts such as improving the rate of polymerization and enhancing the universal use of monomer etc. The catalysts are



the key for energy-saving and effective use of resources, and their significance will increase in the future. Particularly, the “iron” catalyst is the ideal catalyst characterized by “low cost, easy availability, and low-toxicity”. We would like to continue our efforts in developing the new “iron” catalysts, beyond polymerization.

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## Effect of TMEDA on Iron-Catalyzed Coupling Reactions of Aryl Grignard Reagents with Alkyl Halides<sup>1</sup>

Kyushu University Daisuke Noda

A new reaction mechanism for the iron-catalyzed cross-coupling reaction of aryl Grignard reagents with alkyl halides using (TMEDA)FeAr<sub>2</sub> and (TMEDA)Fe(Ar)Br is proposed on the basis of the isolation and reaction of these organoiron intermediates.

The iron-catalyzed Grignard coupling reaction has received increasing interest from an environmental point of view. In this reaction, a special feature of the iron-catalyzed reaction, which is not easily accessible with commonly used nickel- and palladium-catalyzed reactions, is the successful coupling of alkyl halides with Grignard reagents, which is achieved either by catalysis of ferrates or by additive effects of amines and phosphorus compounds<sup>2</sup>.

Despite the great synthetic utility of these iron-catalyzed reactions, their mechanism has not been fully studied because of the paramagnetism and instability of the alkyliron intermediates. The mechanism of the “ate” catalyst has only recently been proposed by Fürstner and co-workers on the basis of the isolation of possible ferrate intermediates. In contrast, the effect of additives, in particular that of tetramethylethylenediamine (TMEDA), requires further investigation. Although Sen and co-workers and later Fürstner et al. reported the possible involvement of (TMEDA)Fe-(CH<sub>2</sub>Ph)<sub>2</sub> from detection of the coupling product in the reaction with allyl bromide, the fate of the iron species was not investigated fully<sup>3</sup>. In this report, we propose a mechanism for the iron-catalyzed cross-coupling reactions of ArMgX with alkyl halides using (TMEDA)FeAr<sub>2</sub> and (TMEDA)Fe-(Ar)Br on the basis of the isolation and reaction of these organoiron intermediates.

The coupling reaction is generally performed by treatment of RX with a mixture of ArMgX and TMEDA (1 equiv with respect to ArMgX) in the presence of FeCl<sub>3</sub> (5 mol%) in

THF. M. Nakamura, E. Nakamura and coworkers reported slow addition of ArMgX/TMEDA increases the yield and selectivity of the coupling product<sup>4</sup>. We selected the reaction between 2,4,6-Me<sub>3</sub>C<sub>6</sub>H<sub>2</sub>MgBr (mesityl-MgBr) and 1-bromooctane (**1**), which are coupled by catalysis of FeCl<sub>3</sub> (5 mol%) in the presence of TMEDA to give 1-octyl-2,4,6-trimethylbenzene (**2**) in 32% yield after 18 h at room temperature. A controlled experiment in 1:4 THF/C<sub>6</sub>D<sub>6</sub> in the absence of **1** provided evidence for the formation of (TMEDA)Fe(mesityl)<sub>2</sub> (**3**), the <sup>1</sup>H resonances of which were in accord with those of the same complex prepared according to the literature method. This strongly suggests that **3** is involved in the catalytic cycle as an intermediate (Figure 1-A).

The reaction of isolated **3** with 2 equiv of **1** revealed the formation of a new iron complex, suggested by NMR evidence to be (TMEDA)Fe(mesityl)Br (**4**), in ~90% yield. GC analysis of the organic products showed that **2** was formed in 76% yield based on **3** along with unreacted **1** (124% yield). We found that **4** could be synthesized by treatment of **3** with (TMEDA)FeBr<sub>2</sub> in 51% yield.

Two significant findings were obtained from further reactions of **4** with another equivalent of **1** or mesityl-MgBr. First, the reaction of **3** with 1-bromooctane was much slower than the reaction of **3** with **1** (Figure 1-B). Second, **4** reacted with mesityl-MgBr to regenerate **3**. These results suggested the catalytic cycle shown in Figure 1, in which **3** (formed from FeCl<sub>3</sub>, mesityl-MgBr, and TMEDA) reacts with **1** to give the coupling products **2** and **4** (Figure 1-C). The

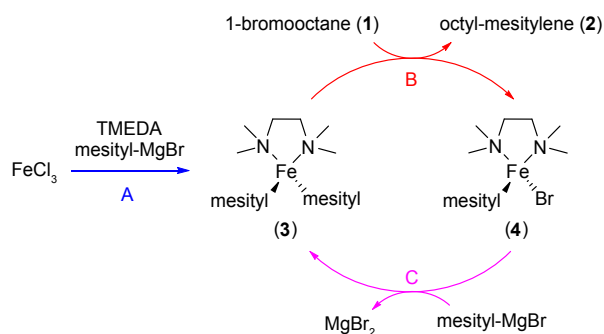
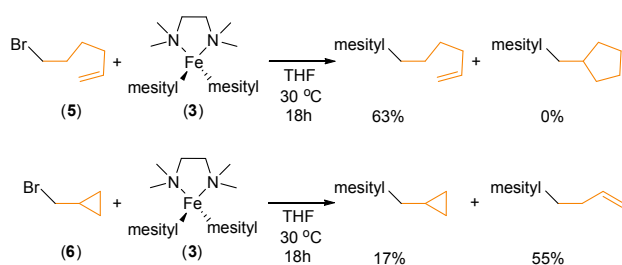


Figure 1



Scheme 1

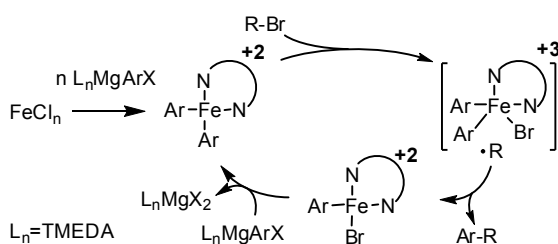


Figure 2

resulting **4** is allowed to react with mesityl-MgBr to regenerate **3**, which initiates the second run of the catalytic cycle in contact with **1**.

The use of a “radical clock” provided further insights into the mechanism. Treatment of **3** with 1-bromo-5-hexene (**5**) resulted in the exclusive formation of 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{C}_4\text{H}_8\text{CH}=\text{CH}_2$  with no radical cyclization. A similar reaction of **3** with bromomethylcyclopropane (**6**) gave a 17:55 mixture of 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{CH}_2(\text{cyclopropyl})$  and 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2\text{C}_2\text{H}_4\text{CH}=\text{CH}_2$  (Scheme 1). It is known that estimated rates of the radical cyclization of 5-hexenyl radical and radical ring opening of cyclopropylmethyl radical are  $1.0 \times 10^5$  and  $1.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ , respectively, at 25 °C. The above results apparently suggest that one-electron oxidation of Fe(II) to Fe(III) is involved in the reaction of **3**

with R-Br and that the lifetime of the radical intermediate is too short for the cyclization of 5-hexenyl radical to occur but long enough to promote partial ring opening of the cyclopropylmethyl radical. In other words, the radical species generated by reaction of R-X with Fe(II) quickly coupled with the mesityl group on the iron, as shown in Figure 2. As M. Nakamura, E. Nakamura and coworkers reported, the product of the catalytic coupling of PhMgBr with **5** was dependent on the reaction conditions used. When PhMgBr, **5**, TMEDA, and a catalytic amount of  $\text{FeCl}_3$  were mixed at -78 °C and the resulting mixture was warmed to room temperature, the product was exclusively  $\text{PhCH}_2(\text{cyclopentyl})$ . In contrast, no radical cyclization was observed when a mixture of PhMgBr and TMEDA was added (slow-addition method). These results suggest the existence of two processes, one involving a short-lived radical and the other a long-lived radical. The former selectively takes place in both the catalytic reaction using the slow-addition method and a stoichiometric reaction of **3** with **5**. In other words, addition of TMEDA as the additive contributes to formation of **3**, and the slow addition method plays a role in operating the catalytic cycle shown in Figure 2 with the long-lived radical pathway suppressed.

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## Presentation

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- Daisuke Noda, Takuji Hatakeyama, Yusuke Sunada, Masaharu Nakamura, Hideo Nagashima, "A Mechanistic Study of Iron Catalyzed Grignard-Coupling Reactions", 55th Symposium on Organometallic Chemistry, Sep. 2007, Ohsaka 2PC-035.
- Daisuke Noda, Takuji Hatakeyama, Yusuke Sunada, Masaharu Nakamura, Hideo Nagashima, "A Mechanistic Study of Iron Catalyzed Grignard-Coupling Reactions", 20th Seminar on Synthetic Organic Chemistry for Young Chemists (oral), Dec. 2007, Fukuoka.

## Research Report

# Development of High-Performance Materials for Eco-Friendly Energy Conversion Processes - Visible Light Responding Photocatalyst for Water Splitting -

Kyushu University Hui Liu

Nowadays, the world is facing serious environmental problems such as global warming, acid rain, photochemical pollution which mainly originate from the production and usage of fossil fuels. Therefore, it is very urgent to develop a clean and sustainable energy system to solve such problems. One possibility is photocatalysis for water splitting to produce clean hydrogen energy. In this micro review, I will introduce fundamentals and up-to-date developments of visible-light-responding photocatalysts for water splitting.

## Introduction

Nowadays, the world is facing serious environmental problem. Many environmental problems, such as green house effect, acid rain and photochemical pollution originated from the production and usage of fossil fuels. So it is very urgent to develop a clean and sustainable energy system to solve such problems. There are at least two ways to solve such problems. In one way, we have to optimize the conventional energy utilization system. For example, coal gasification by using catalysts has been developed for power plant for reducing the CO<sub>2</sub> production. In another way, we have to develop new energy systems, such as solar-hydrogen system, to substitute the fossil fuels. In both approaches of eco-friendly energy conversion, development of high-performance materials processes is very critical, and my research is concerned with (1) investigation and development of inorganic materials to facilitate coal gasification and (2) investigation and development of novel visible-light-responding photocatalysts for VOC removal and water splitting.

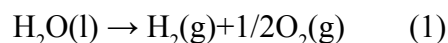
In this micro review, I will focus on visible-light-responding photocatalysts for water splitting.

## Fundamentals of photocatalytic water splitting

Photocatalytic water splitting<sup>1)</sup>, so called Honda-Fujishima effect, was discovered more

than 30 years ago. In this process, light energy is transformed to chemical energy as H<sub>2</sub> energy when H<sub>2</sub>O is decomposed to H<sub>2</sub> and O<sub>2</sub> by using light energy. So the reaction of photocatalytic water splitting is called as artificial photosynthesis.

Water splitting as shown in equation 1 is difficult to take place because of 237 kJ/mol of Gibbs free energy.



To achieve splitting water, photon of 1.23 eV, the theoretical minimum energy requirement corresponding to light of about 1100 nm, will be absorbed by photocatalysts to excite an electron from valence band to conduction band. Considering the hydrogen overpotential, 1.8 eV of photon was suggested to use for water splitting<sup>2)</sup>.

Besides, the bottom level of the conduction band has to be more negative than the redox potential of H<sup>+</sup>/H<sub>2</sub> (0 V vs. NHE), while the top level of the valence band has to be more positive than the redox potential of O<sub>2</sub>/H<sub>2</sub>O (1.23 V) as shown in Fig 1.

Main processes in a photocatalytic reaction are shown in Fig. 2. The first step (i) of the photocatalytic reaction is absorption of photons to form electron-hole pairs in the photocatalyst. The band gap of a photocatalyst should be wider than 1.8 eV to meet the requirement of water splitting as mentioned above. At the same time,

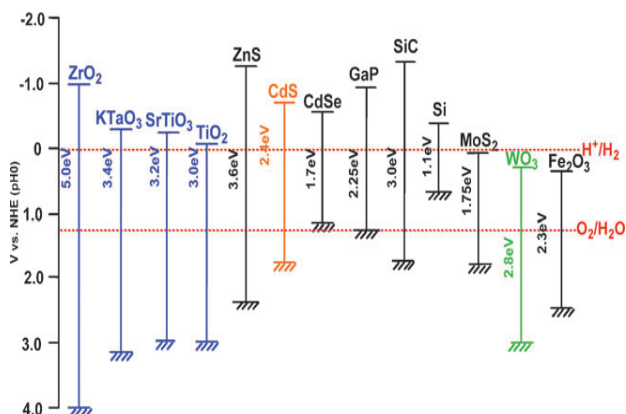


Fig. 1 Relationship between band structure of semiconductor and redox potentials of water splitting <sup>3)</sup>.

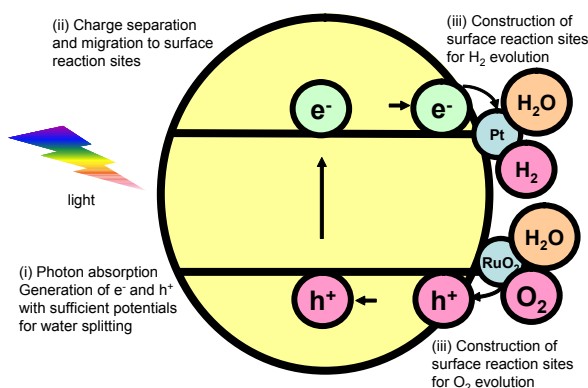


Fig. 2 Main processes in photocatalytic water splitting <sup>4)</sup>.

for visible-light-responding photocatalyst, the band gap should be narrower than 3.0 eV to absorb visible light ( $\lambda > 420$  nm). Moreover, the conduction and valence band positions should satisfy the energy requirements set by the reduction and oxidation potentials for  $\text{H}_2\text{O}$ , respectively. Therefore, it is very difficult to design photocatalysts for water splitting under visible light.

After absorbing photon, photogenerated carriers separate and migrate to surface of photocatalysts (step ii). The crystal structure and the crystallinity strongly affect these processes. The defects in the crystal work as trapping and recombination centers between photogenerated electrons and holes, resulting in a decrease in the

photocatalytic activity. Therefore, a high degree of crystallinity with a less amount of the defects, rather than a high surface area, is required of photocatalysts, especially for an uphill reaction like water splitting.

The final step (iii) consists of the surface chemical reactions. The important points for this step are surface character (active sites) and quantity (surface area). Cocatalysts such as Pt, NiO, and  $\text{RuO}_2$  are usually loaded to introduce active sites for  $\text{H}_2$  evolution because the conduction band levels of many oxide photocatalysts are not high enough to reduce  $\text{H}_2\text{O}$  to produce  $\text{H}_2$  without catalytic assistance. Active sites for 4-electron oxidation of  $\text{H}_2\text{O}$  are required for  $\text{O}_2$  evolution. Although this reaction is demanding, cocatalysts are unnecessary for oxide photocatalysts because the valence band is deep enough to oxidize  $\text{H}_2\text{O}$  to form  $\text{O}_2$ .

## Short survey of development of visible-light-responding photocatalysts

Up to date, a lot of photocatalysts were discovered by researchers, but many of them only work under UV light, which occupy only 4% of solar energy. In order to take advantage of much more solar energy, visible-light-driven photocatalysts becomes more and more important. However, a few photocatalysts can stoichiometrically split water into hydrogen and oxygen under visible light up to date. Many visible-light-driven photocatalysts produced either hydrogen or oxygen from sacrificial reagent solution due to unsuitable conduction band or valence band. So it is necessary and useful to discuss development of visible-light-responding photocatalysts for overall water splitting from a view point of designing new materials.

### 1. Synthesis of oxide photocatalysts

Recently, some new oxide photocatalysts were synthesized such as  $\text{InMO}_4$  ( $\text{M}=\text{V}^{5+}, \text{Nb}^{5+}, \text{Ta}^{5+}$ ) <sup>5-11)</sup>,  $\text{AMn}_2\text{O}_4$  ( $\text{A}=\text{Cu}, \text{Zn}$ ) <sup>12, 13)</sup>,  $\text{AlInO}_2$  ( $\text{A}=\text{Li}, \text{Na}$ ) <sup>14)</sup> and so on. However, those materials only produced  $\text{H}_2$  or  $\text{O}_2$  from sacrificial reagent solution under visible light irradiation.



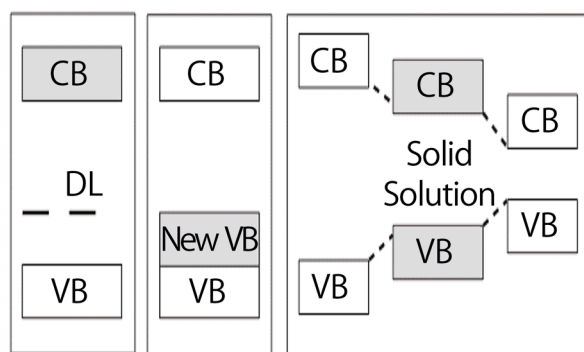


Fig. 4  
Three types of band engineering for the design of visible-light-driven photocatalysts.

solution is the most promising way to develop a new photocatalyst because the simultaneous adjustment of conduction and valence bands is possible.

## Developments of visible-light-responding photocatalysts for overall water splitting in my research

As mentioned above, many new photocatalysts were discovered to have the ability of absorbing visible light, but most of them are active to produce either  $H_2$  or  $O_2$  with sacrificial reagents. In order to split water to  $H_2$  and  $O_2$  under visible light, the conduction band and valence band of a photocatalyst should meet the potential requirements of reduction and oxidation of  $H_2O$  at the same time. Band engineering by the formation of a solid solution was reported to be a feasible and effective method to obtain suitable conduction band and valence band for splitting water<sup>16, 21)</sup>. I focused on  $BiVO_4$  and  $Bi_2WO_6$ <sup>22-24)</sup> which were reported to be visible-light responding but inactive for overall water splitting. In my study,  $BiYWO_6$  and  $Bi_{x-1-x}VO_4$  solid solutions were synthesized and found that they could split water under visible light.

$BiYWO_6$  (BYW), a solid solution of  $Bi_2WO_6$  (BW) and  $Y_2WO_6$  (YW), was found to be a new photocatalyst for overall water splitting under visible light irradiation. The band gap of BYW was 2.71 eV and it absorbed visible light up to 470 nm shown in Fig. 5. The loading of

cocatalysts such as  $RuO_2$  and  $Pt-Cr_2O_3$  was indispensable to photocatalytically split water, and the best performance was observed with 0.5 wt%  $RuO_2$ /BYW: under irradiation of visible light ( $\lambda > 420$  nm) to the reaction system of 100 mL  $H_2O$  and 0.5 g catalyst, amounts of the produced hydrogen and oxygen were about 12.3 and 5.6  $\mu\text{mol}$  in each 3 h, respectively. Since both end materials of BW and YW were inactive for the photocatalytic water splitting, the formation of the solid solution was proven to be the feasible method to obtain visible-light-driven photocatalyst through the adjustment of position of conduction and valence bands of the oxide.

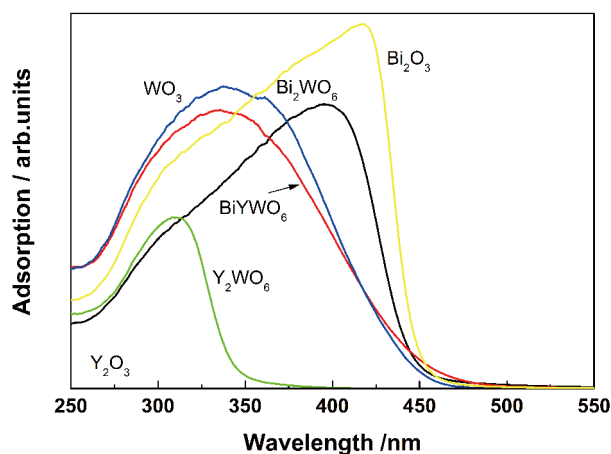


Fig. 5  
Diffuse reflection spectra of  $BiYWO_6$ ,  $Bi_2O_3$ ,  $Y_2O_3$ ,  $WO_3$ ,  $Bi_2WO_6$  and  $Y_2WO_6$ .

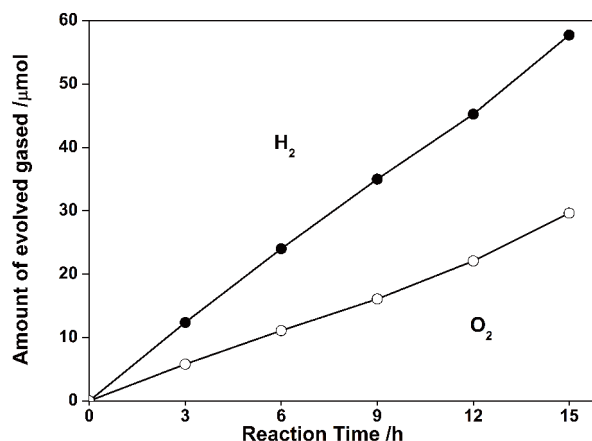


Fig. 6  
Amounts of  $H_2$  and  $O_2$  produced on 0.5 wt%  $RuO_2$ -BYW under visible light irradiation.

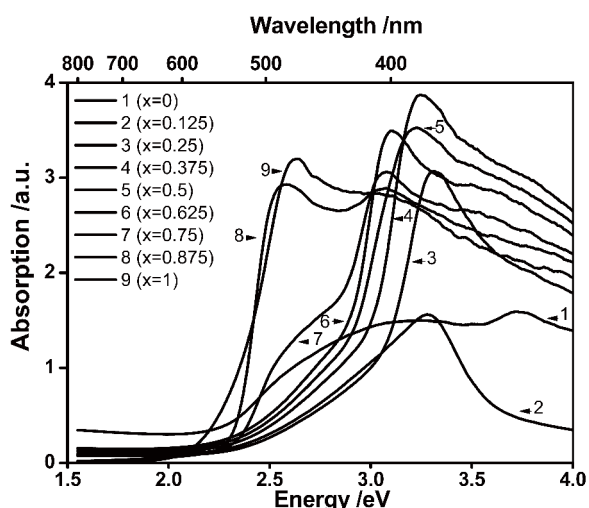


Fig. 7  
Diffuse reflectance spectra of the BYV solid solutions ( $0 < x < 1$ ).

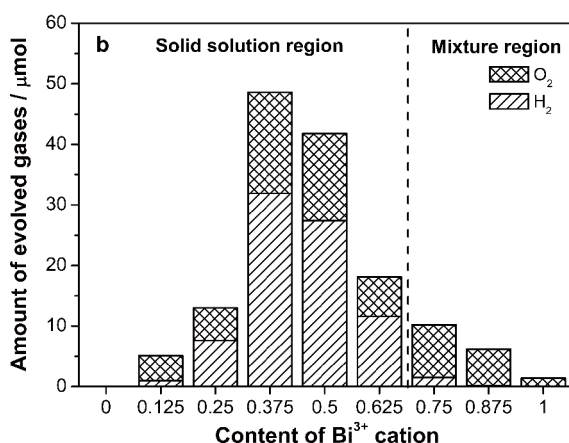


Fig. 8  
Photocatalytic activity of BYV solid solution ( $0 < x < 1$ ) loaded with 1 wt% Pt-1 wt%  $\text{Cr}_2\text{O}_3$  for water splitting under visible light ( $\lambda > 420 \text{ nm}$ ).

Besides BYW, another novel visible-light-driven  $\text{Bi}_x\text{Y}_{1-x}\text{VO}_4$  (BYV) solid solution in the tetragonal zircon type was synthesized by the solid-state reaction. The crystal structure of BYV was dependent on the  $x$  value: it was a single phase solid solution oxides with tetragonal zircon type in  $0 < x < 0.75$ ; however it was regarded as a mixture changing from tetragonal structure to monoclinic one in  $0.75 < x < 1$ . The tetragonal BYV ( $0 < x < 0.75$ ) solid solution oxides loaded with Rh (1 wt%)-CuO (1 wt%)

were discovered to split water to stoichiometric hydrogen and oxygen under visible light up to 510 nm. Among these catalysts,  $\text{Bi}_{0.375}\text{Y}_{0.625}\text{VO}_4$  showed the best photocatalytic activity for overall water splitting in all the samples under either full arc or visible light irradiation (Fig. 8), of which the apparent quantum efficiency reached 0.72% at 420 nm light irradiation. BYV solid solution was proved to remain high photocatalytic activity as well as stable crystal structure and chemical states in the surface in the repeated runs. For tetragonal BYV ( $0 < x < 0.75$ ) solid solution, Bi6s lone pair formed new valence band and increased the light absorption range to about 520 nm from the 420 nm of zircon-type  $\text{BiVO}_4$  due to the distortion of  $\text{Bi(Y)O}_8$  and  $\text{VO}_4$  polyhedrons. The photocatalytic activity of BYV for overall water splitting might be attributed to the single zircon-type structure with distorted  $\text{Bi(Y)O}_8$  dodecahedron and  $\text{VO}_4$  tetrahedron as well as the cocatalyst providing active site.

In summary, I succeeded to develop visible-light-responding photocatalysts for overall water splitting by applying the band engineering technique by the formation of solid solutions. Although the quantum efficiency of the photocatalytic overall water splitting is still low, the steady progress in the material development will lead the usage of “solar hydrogen” in the future.

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## Global Warming Issues and the Environmental Effects of Market-Based Instruments

Kyushu University Michihiro Hino

As measures for controlling global warming issues, the approach paid attention to is international environmental policies that use "Market-based instruments". In today's international situation where a WEO (world environmental organization) doesn't exist, the positive effects for the environment that exclude the cost-effectiveness of "Joint implementation" and "Expansion of the environmental industry" that are practicable and substantial measures against environmental problems are the following two points. One is the effect of the diffusion of technology; the other is the effect of an incentive on technical innovation.

International concern is being directed towards worldwide environmental issues. In particular, there are high levels of concern for global warming issues.

Global warming issues refer to the surface temperature on the Earth increasing, as well as the various problems associated with that. The source of global warming issues is the increase in the concentration of "greenhouse gases" in the atmosphere. Greenhouse gases are a collective term for those gases which absorb the heat emitted from the surface of the earth and lead to an increase in the temperature of the earth's surface. Examples include carbon dioxide (CO<sub>2</sub>) and methane gas (CH<sub>4</sub>).

The use of fossil fuels is one concrete example that can be given for activities that emit CO<sub>2</sub>. CH<sub>4</sub> is emitted from garbage and waste materials, as well as the paddy fields used to grow agricultural products. Therefore, greenhouse gas producing activities can be said to be based on the daily economic activities of firms and consumers in developed and developing countries (See Figure 1 for the state of greenhouse gas emissions in several major countries).

Due to the nature of these gases, approaches to global warming issues need to be taken within an international framework. There is also a need for a change in consumer awareness as well as changes for firms regarding this issue. However, it is not an easy task to reform the daily activities of firms and consumers worldwide. In this situation, the approach that is

attracting the most attention is an international environmental policy that takes advantage of "market-based instruments".

Market-based instruments enable the realization of specific policy goals by facilitating price mechanisms. As an example, albeit from national environmental policy in America, in order to decrease the amount of sulphur oxides (SO<sub>x</sub>) released into the atmosphere, in 1990 they implemented a plan for trading rights for SO<sub>x</sub> emissions, which lead to an actual decrease.

In today's international situation, where a WEO (World Environmental Organization) doesn't exist, the market-based instruments that can realistically be implemented at an international level are the following three. The first method is emissions trading. This is an instrument aimed at achieving an efficient decrease in pollutants by creating a new market where it is

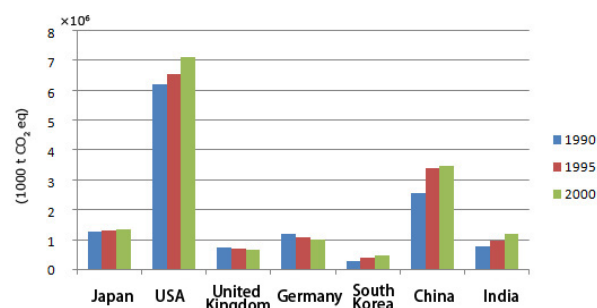


Fig. 1  
State of Emissions of Greenhouse Gases in Principal Countries.

Source) Created from OECD Environmental Data Compendium, 2007, CAIT-The Climate Analysis Indicators Tool.

possible to buy and sell the rights to emissions of pollutants. It is already a part of the Kyoto Mechanisms created by the “Kyoto Protocol”, a policy aimed at global warming issues. The second method is “Joint Implementation”. With countries that have different levels of environmental technologies, a country with relatively advanced environmental technologies could invest into a country with relatively poor environmental technologies, with the investing country gaining a number of credits equal to the amount of pollutants reduced as a result of the investment. This is included in the Kyoto Mechanisms as “Clean Development Mechanism: CDM” with developing countries as the target of investment, and “Joint Implementation” with developed and transitional countries as the target. The third method is “expansion of environmental industries”. This policy can be seen in the liberalization negotiations for the “Environmental Goods and Services: EG&S” in the WTO (World Trade Organization). EG&S are “Products with superior environmental technology being incorporated as compared to products with similar applications, or those products necessary for approaches to environmental problems”. The WTO aims to serve both free trade and environmental protection by the removal and reduction of tariff and nontariff barriers to these products. However, the conflict that exists between America, the EU and developing countries hasn’t been resolved, so results are insufficient. However, with America agreeing to the EU proposal of a “Climate-friendly goods and services” list, it was proposed in December of 2007. This list is a selection of products from EG&S that is particularly valuable or necessary for handling global warming issues.

There are two positive environmental effects aside from cost effectiveness that arise from the inevitable substantive environmental policies that come along with “Joint Implementation” and “expansion of environmental industries” besides the trading of emissions rights. The first is the “diffusion of technology”. When considering EG&S, the essential function of the policy is to achieve a price reduction in affected

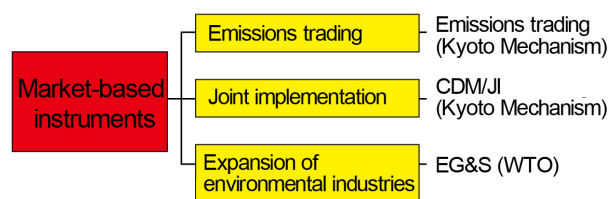


Fig. 2  
Three Market-Based Instruments which can be Implemented Internationally.

products by reducing and eliminating tariffs and nontariff barriers. By doing this the distribution of products necessary for environmental measure will be expanded, as well as improving the preference of those products with superior environmental technologies. In other words, the quality of affected products as compared to other equivalent products can be communicated via a reduction in cost. As a result, as long as there is a preference for the affected products, the environmental technologies utilized in them will end up being distributed.

The “diffusion of technology” as understood through a proposition of standard economics demonstrates the process to the market equilibrium. Market equilibrium indicates a state where the level of supply and the level of demand are equal. In other words, in the case of the price change with EG&S, it means the convergent processes of supply and demand that were heading towards a point of equilibrium. However, in theory if the flexibility (freedom of change in prices) of EG&S prices can’t be achieved, equilibrium will not be achieved.

However, in “Joint Implementation”, the cost-effectiveness is a key of measure, so a convergence towards equilibrium can be hoped for. In other words, in cases where costs for environmental measures are lower in foreign countries than costs for environmental measures in one’s own country, joint implementation projects will be implemented. By temporarily ignoring the emissions allowance of each individual country, as the number of projects increase, low cost projects will disappear, with joint implementation be utilized until costs for international projects become equivalent to costs for national

---

projects.

However, market-based instruments have one other important effect besides the “diffusion of technology”. That is an “incentive for technological innovation”. It is easily understood that the possibility for implementation of “joint implementation” depends on environmental technology necessary for that project being distributed internationally. Therefore, as the low cost projects slowly vanish, there will be an incentive for business to develop environmental technologies to make the implementation of new projects possible. For example, in CDM one technology that has been receiving attention in recent years as a way to make new projects possible are CCS (carbon capture and storage) technologies.

Effects such as these should theoretically disrupt the current equilibrium point of the market and lead it to a new equilibrium point. Joseph Schumpeter called this effect “innovation”. In the medium to long term, availability of market-based instruments is clearly reliant on the level of innovation, with it being an important activity related to the implementation of market-based instruments.

Market-based instruments fulfill an important role in regards to global warming

issues, and can be said to be an international device for the diffusion of technology and encouragement of innovation. Further, since market-based instruments don’t actually forbid or restrict economic activities, they are relatively easily accepted as a policy by developing countries with a strong desire for economic development. In fact, with CDM a certain level of results can be seen.

“Novel Carbon Resource Sciences” have the aim of understanding real countermeasures taken towards environmental issues at the global level, then forming solutions based on realistic policies. The main obstacles to realizing a policy are the following three. The first is technological issues, the second is issues of cost, and the third is political economics issues. The typical issue in the third case is achieving both economic development and environmental protection for developing countries. This is a deeply rooted problem, connected at a basic level with the universal issue of human prosperity and environmental problems. In the future, we will continue to report on the results of research related to environmental issues in current world economics and their influence on developing countries.

# Research Performance 2008

## Awards & Articles

### •Young Scientists' Prize

The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, 2008 (2008/04/15)

**Hiroki Ago**

"Development and Functionalization of Carbon Nanotube"

**Toshihiko Takemura**

"Quantitative Evaluation of the Effects of Aerosol on the Climate"

### •Sangyo Times, Inc. Award

The 6th Annual Meeting of Nano Science and Technology (2008/05/09)

**Hiroki Ago**

"Visualization of the Horizontally-aligned Growth of Single-walled Carbon Nanotubes with Carbon Isotope" and "Horizontally-aligned Growth of Single-walled Carbon Nanotubes programmed by Atomic-arrangement"

### •Contributor Award of Institute Technology Bandung (ITB)

(2009/01/08)

**Kikuo Matsui**

"Development of Environmentally-friendly Rehabilitation at Opencast Coal Mine" in Interdisciplinary Research Collaboration with Department of Environmental Development, with the Goal of Resource Development with Low Environmental Burden at Opencast Coal Mines in Indonesia.

### •The 34th Paper Award

The Mining and Materials Processing Institute of Japan, 2008 (2009/03/27)

**Keiko Sasaki, Minoru Matsuda, Tomohiro Urata, Tsuyoshi Hirajima and Hidetaka Konno**

"Sorption of  $\text{Co}^{2+}$  Ions on the Biogenic Mn Oxide Produced by a Mn-oxidizing Fungus, *Paraconiothyrium sp.* WL-2"

### •Contributor Award

Japan Society of Polymer Processing (2008/06/04)

**Toshihisa Kajiwara**

### •Award for Academic-industrial Alliance on Research

Kyushu University, 2008 (2008/05/12)

**Shigeto Okada**

**Yasutake Teraoka**

**Shiyoshi Yokoyama**

**Katsuhiko Fujita**

### •Outstanding Poster Presentation Award

ICNME2008 (2008/12/16-18)

**Shin-ichiro Inoue**

"Nonlinear Optical Responses in Polymer Two-dimensional Photonic Crystals"

### •Outstanding Paper Award of ICSST08

The 8th International Conference on Separation Science and Technology, 2008 (2008/10/03)

**Yusuke Shimoyama, Takeshi Hirayama and Yoshio Iwai**

"Gas Chromatographic Determination of Infinite Dilution Activity Coefficient of Alcohols, Ketones and Aromatic Hydrocarbons in 4-methyl-N-butylpyridinium Tetrafluoroborate and 1-butyl-3-methylimidazolium Hexafluorophosphate"

### •The 17th Technology Award of Environmental Chemistry

Japan Society for Environmental Chemistry (2008/06/12)

**Tetsuya Sawatsumashi, Chisato Tsukahara, Junko Ureshino, Tomoharu Nakao, Keigo Baba, Yoshinori Fukunaga and Norio Miura**

"Search of Liquid Chromatographic Clean-up Materials for Rapid PCB Analysis and Evaluation of their Characteristics"

### •Best Award of Outstanding Presenters at poster session

The 8th Mini International Symposium for Energy Conversion and Storage, 2009

**Sunil Park, Taishi Saito, Takayuki Doi, Y.P. Wu, Shigeto Okada and Jun-ichi Yamaki**

"Electrochemical Performance of Aqueous Rechargeable Lithium Ion Battery (ARLB) based on  $\text{LiFePO}_4$  and  $\text{LiTi}_2(\text{PO}_4)_3$ "

### •Certificate of Award for Encouragement of Research in Materials Science

The IUMRS International Conference in Asia 2008

**Masahiro Ishimaru**

(Co-researcher: Ken Itakura, Minoru Nishida)

"Microstructure Analysis of High Coercive PLD-made NdFeB Thick Improved by Tb-diffusion-coating Treatment"

### •Young Researchers' Prize (Inorganic Chemistry)

The 45th Kyushu Branch Joint Conference of Chemical Societies

**Hiroshi Ikeda**

(Co-researcher: Michitaka Ohtaki)

"Synthesis of Oxide Nano-superlattice by Electrolytic Oxidation Method with Molecular Mold and its Characteristics"

[http://kcsj.jp/award\\_y.html](http://kcsj.jp/award_y.html)



## ●Best Paper Award (DC Award)

CINEST International Symposium on Earth Science and Technology 2008

Hitoshi Takamori, Keiko Sasaki, Hitoshi Yoshizaka and Tsuyoshi Hirajima

"Role of Wood-chips in Permeable Reactive Barriers for Removal of Borate in Groundwaters"

Phung Quoc Huy, Kyuro Sasaki and Yuichi Sugai

"Effects of SO<sub>2</sub> and pH Concentration on CO<sub>2</sub> Adsorption Capacity in Coal Seams"

Ryohei Takahashi, Koichiro Watanabe, Akira Imai, Hiroharu Matsueda and Victor M. Okrugin

"Genesis and Formation of Ore Deposits in Kamchatka Peninsula, Far Eastern Russia"

## ●"Science Watch" Fast Breaking Papers 2008 (April)

<http://sciencewatch.com/dr/fbp/2008/08apr/fbp/08apr/fbpMiura/>

Norio Miura

### Interview Article

The following article topped the list of fast breaking papers (from September to December in 2007; investigated by Thomson Scientific Inc.) in the field of engineering (one of all 22 fields of science).

Recent Advancements in Surface Plasmon Resonance Immunosensors for Detection of Small Molecules of Biomedical, Food and Environmental Interest D. R. Shankaran, K. V. Gobi, N. Miura, Sensors and Actuators B, 121, 158-177 (2007).

**Knowledge Link** (Science Watch Japan Fast Breaking Papers)

<http://www.thomsonscientific.jp/knowledgelink/esi-topics/fbp/>

Knowledge Linkトップ > 日本の研究者による注目論文&インタビュー

日本の研究者による注目論文&インタビュー



統計ツール Essential Science Indicators (ESI) では、最近10年間の学術論文の引用動向データをもとに、さまざまなデータや指標を提供しています。ESI 収録の高被引用度論文 (Highly Cited Papers) の中でも特に影響度の高い論文は、弊社ウェブサイト Special Topics で著者インタビューとともに広く一般に紹介されます。

このサイトでは、Special Topics の中から、世界を舞台に活躍する日本の研究者による注目論文のみをまとめ、ご紹介しています。

**ESI SPECIAL TOPICS NEWS**

**最新情報**

2008年 4月

**Fast Breaking Papers**

工学: Recent advancements in surface plasmon resonance immunosensors for detection of small molecules of biomedical, food and environmental interest



九州大学 産学連携センター プロジェクト部門 環境・新エネルギー領域 教授  
三浦 範雄 氏

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Interviews Analysis Data & Rankings

2008 - April 2008 - Fast Breaking Papers - Norio Miura

**FAST BREAKING PAPERS - 2008**

April 2008

Norio Miura talks with ScienceWatch.com and answers a few questions about this month's Fast Breaking Paper in the field of Engineering.




**Article Title:** Recent advancements in surface plasmon resonance immunosensors for detection of small molecules of biomedical, food and environmental interest  
**Authors:** Shankaran, DR; Gobi, KV; Miura, N  
**Journal:** SENSORS ACTUATOR B-CHEM  
**Volume:** 121  
**Issue:** 1  
**Page:** 158-177  
**Year:** JAN 30 2007  
**\* Kyushu Univ, Art Sci & Technol Ctr Cooperat Res, Kasuga, Fukuoka 8168580, Japan  
\* Kyushu Univ, Art Sci & Technol Ctr Cooperat Res, Kasuga, Fukuoka 8168580, Japan  
(addresses have been truncated)**

**SW: Why do you think your paper is highly cited?**

SPR-based immunoassay is a highly demanding and rapidly growing research area around the world. Indeed, ours was an invited review paper for the special issue of the Sensors and Actuators B Journal on its celebration of its 20th year of publication. While accepting this invitation, I had a clear vision that this review paper should represent a straightforward, systematic, and well-organized information source providing a wealth of information on the state-of-the-art regarding the principle and application of SPR immunosensors.

I believe that our review article provided all the necessary information for all kinds of research conducted within this area. Through offering extensive information pertaining to the biomedical, food, and environmental applications of SPR immunosensors, this paper has received extensive attention from researchers around the world. Thus, it has been highly downloaded and cited. At this time, I'd like to thank one of my co-authors, Dr. Dinesh Ravi Shankaran, for his significant contributions to the final paper.



**SW: Does it describe a new discovery, methodology, or synthesis of knowledge?**

This review article provides the basic methodology while outlining current trends and challenges in SPR-based immunoassays across a variety of application areas.


**SW: Would you summarize the significance of your paper in layman's terms?**

SPR immunosensors offer exceptional performance capabilities with respect to sensitivity, specificity, speed, and multiplexed detection in complex analytical matrices. Advancements in the technology of antibody production and signal transduction provide a promising scope for SPR immunosensors to lead the way to the next generation of biosensors.

The important aspects investigated by the use of SPR include protein binding, association/dissociation kinetics, and affinity constants, which contribute to wider application areas such as that of molecular engineering, food analysis, clinical diagnosis, proteomics, environmental monitoring, bacteriology, virology, cell biology, drug discovery, and warfare detection.

This review highlights the current state-of-the-art in SPR immunosensors and briefly outlines important issues regarding the development of SPR immunosensors, such as the preparation of biomolecules, sensor fabrication, non-specific adsorption, surface regeneration, and detection principles.

Molecular imaging: Exciting fluorescence : research highlight : NPG Asia Materials



**research highlight**

**Molecular imaging: Exciting fluorescence**

Published online 25 November 2008

Light emission from organic molecules is promising for applications ranging from fluorescence imaging to data storage. To overcome intrinsically weak emission efficiencies, Shin-ichiro Inoue and Shiyoshi Yokoyama from Kyushu University in Japan\*, now demonstrate that photonic crystals can be used to significantly enhance non-linear optical emission from fluorescent molecules.

The advantage of non-linear optical processes compared to conventional light-emission techniques is that the intensity varies strongly with the excitation energy, which produces higher definition images. The high resolution that can be achieved is not only relevant for imaging, but can also be used in optical data storage where it allows for a higher data integration density.

One of the most widely used non-linear processes is two-photon excited fluorescence (TPEF), where the combined energy of two low-energy photons from a laser beam is used to excite an electron into an higher state. As the excited electrons relax back to the ground state, they emit the energy gained and this fluorescence is detected.

Unfortunately, "despite the important technological potential of this method, the majority of known organic molecules have very small two-photon excitation efficiencies, hampering the widespread use of TPEF applications", says Inoue. To solve the problem of low efficiencies, the researchers use a photonic crystal that is placed on top of a thin polymer layer containing the fluorescent molecules (Fig. 1).

The photonic crystal facilitates the coupling between the incident laser and the molecules. At certain laser incident angles this can lead to a strong coupling of light into the photonic crystal. This subsequently increases the light absorption by the molecules, leading to a much stronger TPEF process.

Indeed, in their experiments Inoue and Yokoyama observed a significant enhancement of TPEF at the predicted laser beam angles. These enhancements can be as high as two orders of magnitude. Therefore, much lower and less damaging incident laser powers than in conventional TPEF experiments can be used, making this technique particularly suitable for molecules with low TPEF efficiencies.

Inoue is very confident that "this dramatic improvement in performance will stimulate a number of applications, for example in optical data storage".

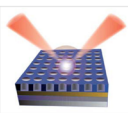


Fig. 1: The two-photon excited fluorescence process from organic molecules embedded within a polymer layer can be significantly enhanced by a photonic crystal at the surface.

**Reference**

1. Inoue, S.-I. & Yokoyama, S. Enhancement of two-photon excited fluorescence in two-dimensional nonlinear optical polymer photonic crystal waveguides. *Appl. Phys. Lett.* 93, 111110 (2008). | [article](#) |

**Author affiliation**

Shin-ichiro Inoue\* and Shiyoshi Yokoyama  
Institute for Materials Chemistry and Engineering, Kyushu University, 6-1 Kasuga Koen, Kasuga, Fukuoka 816-8580, Japan. \* [inoue@om.kyushu-u.ac.jp](mailto:inoue@om.kyushu-u.ac.jp)

This research highlight has been approved by the author of the original article and all empirical data contained within has been provided by said author.

**NPG Asia Materials**

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## ●Research Highlight Nature Publishing Group (NPG) Asia Materials (Published: 25 November 2008)

Shin-ichiro Inoue, Shiyoshi Yokoyama

Enhancement of two-photon excited fluorescence in two-dimensional nonlinear optical polymer photonic crystal waveguides. S.-I. Inoue, S. Yokoyama: *Appl. Phys. Lett.*, Vol. 93, pp. 111110, 2008.

**Research Highlights** is an attempt to highlight and introduce the world's most advanced research results selected by the international editorial committee of Nature Publishing Group (NPG), known for publishing of *Nature*.

**Kyuro Sasaki, Yuichi Sugai**

NEWS

## By Erica Vargas

Dr. Tayfun Babadagli, a Petroleum Engineering professor at the University of Alberta, visited Japan in 2006 through the Japan Society for the Promotion of Science (JSPS) Post doctoral Fellowship Program, an idea sparked to provide a number of other researchers an opportunity to be involved in international collaborations.

During his visit to Kyushu University, he met with Dr. Kyuro Sasaki, who had spent his post doctoral period at the University of Alberta more than 10 years ago.

When the two professors met at a Calgary conference in 2007, they decided to create a departmental exchange program. By early July 2008, papers were signed and the five year exchange program between the University of Alberta and Kyushu University became official. "The exchange of technology and ideas are always good, not only for students but also for professors," says Babudzeli.

The program is open to senior graduate students, post doctoral fellows, and faculty members to conduct joint research. Each year two students from Kyushu and two students from Alberta will stay at the partner department.

for a period of under 10 months.

The program has already started enhancing the perspective of a young Japanese researcher.

Dr. Yuichi Sugai, the first participant in the program, arrived with in Edmonton his family on July 21st, 2008 and stayed at the University of Alberta until the end of September 2008. Already, he has delved into his research, and even enjoyed visiting scene of Alberta's natural sights on the weekends.

Under the supervision of Babadagli, Sugai is researching Enhanced Oil Recovery (EOR) using microorganisms. He will investigate the behavior and growth of effective microorganisms that are injected into an oil reservoir, and the byproducts that they produce such as polymers, gases and surfactant, which help enhanced oil recovery. One of his masters students from Japan, Machiko Oka, will also be joining him in his research for a month this summer.

"Collaborations like this one are very important for young researchers especially. The Japanese government puts a very high importance on education and so we know the theory behind petroleum engineering very well. But

being a country without many natural resources like oil, gas, gold, or copper, we don't always get the chance to put this knowledge into practice as much as we would like to. This increasing consumption of energy and resources presents a threat

to the human activities in Japan. We need to learn how to obtain and work with these resources effectively to sustain development in our country," he exclaimed.

The University of Alberta is one of four international universities that collaborate with Kyushu University's engineering program.

Bubadigli is pleased with the scope of program agreement and its potential for creating solutions both in Kyushu and Alberta.

"Our agreement covers not only



Dr. Yuiei Sugan, Dr. Kyuro Sasaki and Akito Matsunaga tour the university of Alberta Campus, meeting with residence services and library staff to ensure a comfortable stay for future exchange participants.

petroleum but also other disciplines in our department. Documents were signed by three departments at Kyushu University: the Department of Earth Resource Engineering, the Department of Civil and Structural Engineering, and Department of Urban and Environmental Engineering. At the University of Alberta, the Department Civil and Environmental Engineering signed it representing all of its eight disciplines. So, the coverage is widespread and almost all disciplines in our department can participate and benefit from this program."

## Hideo Nagashima

## Iron Catalyst Used for Organic Synthesis

Expected to cut production cost of electronic materials and medicine

## 鉄触媒、有機物合成に活用

電子・医薬材料 製造安く  
高価な貴金属不要に

[illegible]

「D-1Cは電力に劣らず、電圧降下を抑制し、電圧変動を少なくし、電圧変動に耐性がある。また、酸、鹼に、反応を示さず、腐食に耐性がある。また、酸、鹼に、反応を示さず、腐食に耐性がある。また、酸、鹼に、反応を示さず、腐食に耐性がある。」

[illegible]

## Kyuro Sasaki

## Inactive Tunnel Transformed to Refrigerator

Experimental test was open to the public



# SYMPOSIUM & WORKSHOP

## Hosting



### The First International Symposium of "Novel Carbon Resource Sciences" Global COE of Kyushu University - The Kick-off Symposium -

**Date: October 26, 2008**

**Venue: Grand Hyatt Fukuoka**

**Chair: Hideo Nagashima, Hirotsugu Kikuchi, Shigeto Okada**

#### Opening Remarks

Hideo Nagashima (Leader of the G-COE "Novel Carbon Resource Sciences")

Setsuo Arikawa (President of Kyushu University)

Hirota Tani (Ministry of Education, Culture, Sports, Science and Technology)

Kimihsa Kittaka (Ministry of Economy, Trade and Industry)

#### Introduction of G-COE Program

Hideo Nagashima (Leader of the G-COE "Novel Carbon Resource Sciences")

Yasutake Teraoka (Sub-Leader & Cluster Leader of the G-COE "Novel Carbon Resource Sciences")

Tsuyoshi Hirajima (Cluster Leader of the G-COE "Novel Carbon Resource Sciences")

#### Lectures

Seong-Ho Yoon (Institute for Materials Chemistry and Engineering, Kyushu University)

"Carbon Materials for Energy and Environmental Devices"

Mikio Sato (Central Research Institute of Electric Power Industry)

"Fossil Fuel Energy Outlook and Engineering Solutions for Climate Change in Electric Power Sector"

Doo-hwan Jung (Korea Institute of Energy Research, Korea)

"Current Situation of Energy in Korea"

Yanqing Wu (Shanghai Jiao Tong University, China)

"The Global COE for Novel Carbon Resource Sciences: Geological Storage of CO<sub>2</sub>"

Sudarto Notosiswoyo (Institute of Technology Bandung, Indonesia)

"Research Activities Related to Conventional Energy (Oil, Gas, and Coal) in Institute Technology Bandung, Indonesia"

Chun-Zhu Li (Monash University, Australia)

"Energy Research in Curtin University of Technology Australia"



### Earth Resource Science and Technology

- 2nd International Symposium of Novel Carbon Resource Sciences -

**Date: March 10-11, 2009**

**Venue: Institute of Technology Bandung, Indonesia**

**Chair: Sudarto Notosiswoyo (ITB), Budi Sulistianto (ITB), Hideo Nagashima, Kikuo Matsui, Tsuyoshi Hirajima, Kyuro Sasaki**

#### Keynote Speeches

Kikuo Matsui (Faculty of Engineering, Kyushu University)

"Development of Eco-friendly Coal Mines in Overseas Countries Considering Environmental Issues"

Kyuro Sasaki (Faculty of Engineering, Kyushu University)

"Two Major Problems of Japanese CO<sub>2</sub> ECBM Test Project at Yubari, Japan"

Yanqing Wu (Shanghai Jiao Tong University, China)

"Modeling and Remedation with Permeable Reactive Barriers in Groundwater Contaminated by Perchloroethylene"

Chun-Zhu Li (Curtin University, Australia)

"Catalytic Effects of Alkali and Alkaline Earth Metallic Species during the Gasification of Brown Coal"

Dwiwahju Sasongko (Institute of Technology Bandung, Indonesia)

"Coal Gasification and Liquefaction: a Brief Review"

Bukin Daulay (Mineral and Coal Technology Research and Development Center, Indonesia)

"Low Rank Coal Upgrading"

#### Special Lectures

Shigeto Okada, Takayuki Doi and Jun-ichi Yamaki (Institute for Materials Chemistry and Engineering, Kyushu University)

"Cathode Active Materials for Post Lithium-Ion Battery"

Jun Fukai and Koichi Nakaso (Faculty of Engineering, Kyushu University)

"Application of Carbon Fibers to Thermal Engineering"

Ken Kuwahara and Shigeru Koyama (Interdisciplinary Graduate School of Engineering Sciences, Kyushu University)

"Researches on Improving the Performance of Refrigeration/Air-conditioning System in Our Laboratory Related to the Energy Saving/Environmental Protection Technology"

Hajime Kusaba, Hisahiro Einaga, Yasutake Teraoka (Interdisciplinary Graduate School of Engineering Sciences, Kyushu University) and Hironobu Shimokawa (Faculty of Engineering Sciences, Kyushu University)

"Development of Catalyst for the Removal of Particulate Matter from Diesel Exhausts"

Takeshi Tsuji, Masaharu Tsuji, Takayuki Doi, Jun-ichi Yamaki (Institute for Materials Chemistry and Engineering, Kyushu University), Masataka Nakanishi, Takeshi Mizuki (Graduate School of Engineering Science, Kyushu University)

"Preparation of Nano-sized Functional Materials Using Laser Ablation in Liquids"

## Public Program / Lecture Meeting

### GCOE "Novel Carbon Resource Sciences"

### Public Program and Lecture Meeting on Environmental Economics

**Date: March 25, 2009**

**Venue: International Conference Hall, Across Fukuoka 3F**

**Organizer: Toshiyuki Fujita, Nobuhiro Horii, Michihiro Hino**

#### Public Program

Hideo Nagashima (Institute for Materials Chemistry and Engineering, Kyushu University)

"What is happening globally now: Energy, environment and global warming"

Tadakatsu Ohnaka (Faculty of Human Environmental Science, Fukuoka Women's University)

"Global warming people feel inside the house: Can you sleep well?"

Chang-Jin Ma (Faculty of Human Environmental Science, Fukuoka Women's University)

"Characteristics of carbon particles and air pollutants attributed to vehicle exhaust"

Shiro Hori (Art, Science and Technology Center for Cooperative Research, Kyushu University)

"Steering next-generation Japan: Energy-environment policy"

#### Lecture Meeting

Hideo Nagashima (Institute for Materials Chemistry and Engineering, Kyushu University)

"Brief overview of the project of Novel Carbon Resource Sciences: Challenge of Kyushu University"

Nobuhiro Horii (Faculty of Economics, Kyushu University)

"Chinese energy-environment problems and their impact on the world"

#### Part 1: Current Situation of Energy Utilization and Challenge to Sustainability of Energy in China

Hongying Wang (Energy Economic Institute of Shanxi Academy of Social Sciences)

"Coal industry reform and development of clean coal technology in China"

Nobuhiro Horii (Faculty of Economics, Kyushu University)

"Energy-saving strategies and environmental measures in Chinese power industry: Diffusion of exhaust gas desulfurizer in China and its backgrounds"

Xiliang Zhang (Institute of Energy, Environment, and Economy, Tsinghua University)

"Rapid growth of Chinese renewable energy industry: Competitiveness analysis of enterprises"

#### Part 2: How to promote Japanese energy-conservation and environmental technologies throughout China

Tatsuro Harada (Research Department, Kyushu Electric Power Co. Inc.)

"Situations of clean energy technologies in Japan: A case of electric power"

Toshiyuki Fujita (Faculty of Economics, Kyushu University)

"The necessity of Kyoto mechanism"

#### Panel Discussion: "How to break into the turning point of Chinese energy and environmental problems"

Facilitator: Toshiyuki Fujita (Faculty of Economics, Kyushu University)

Panelists:

Hongying Wang (Energy Economic Institute of Shanxi Academy of Social Sciences)

Xiliang Zhang (Institute of Energy, Environment, and Economy, Tsinghua University)

Masaki Takahashi (Senior Electric Power Engineer, World Bank)

Tatsuro Harada (Research Department, Kyushu Electric Power Co. Inc.)

Nobuhiro Horii (Faculty of Economics, Kyushu University)

## Joint Hosting

### The First KU-SJTU Joint Workshop on Environment and Energy Issues in Relation with Novel Carbon Resource Sciences

**Date: November 12, 2008**

**Venue: Chikushi Campus, Kyushu University**

**Chair: Yasutake Teraoka**

**Discussion by Students of Kyushu University & Shanghai Jiao Tong University**

**"Is coal more useful energy resource instead of oil?"**

**Participants: 28**



### International Symposium on Earth Science and Technology 2008

**Date: December 1-2, 2008**

**Venue: Nishijin Plaza, Kyushu University**

**Chair: Kikuo Matsui, Tsuyoshi Hirajima, Kyuro Sasaki, Rudy Sayoga Gautama (ITB), Vladimir Kebo (VSB)**

**Plenary Lectures**

Rudy Sayoga Gautama (Institute of Technology Bandung, Indonesia)

"On the Issue of Acid Mine Drainage in Indonesian Mines"

Tayfun Babadagli (University of Alberta, Canada)

"Evaluation of the Critical Parameters Affecting CO<sub>2</sub> Sequestration Performance During Enhanced Oil Recovery"

Suseno Kramadibrata (Institute of Technology Bandung, Indonesia)

"Failure Criteria Development Using Triaxial Test Multistage and Conventional"



**Oral Presentation: 62**

**Poster Presentation: 33**

### The 1st International Workshop on Energy and Environment in Chemical Engineering

**Date: December 5, 2008**

**Venue: C-CUBE at Chikushi Campus, Kyushu University**

**Chair: Jun Fukai**

**Lectures**

Sang Done Kim (KAIST, Korea)

"Current Status of Clean Fossil Energy Technology in Korea"

Doo Hwan Jung (KIER, Korea)

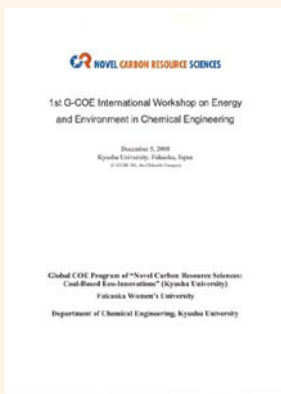
"Application of Carbon Materials in Fuel Cell Industry"

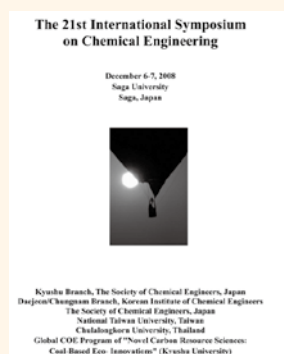
Tharapong Vitidsant (Chulalongkorn Univ., Korea)

"Catalytic Cracking of Waste Plastics and Used Vegetable Oil to Liquid Fuel"

Yongtaek Lee (Chungnam National Univ., Korea)

"Application of Zeolite Membranes for Preparation of Bioethanol"





## The 21st International Workshop on Chemical Engineering

**Date: December 6-7, 2008**  
**Venue: Saga University**  
**Chair: Katsuki Kusakabe**

Oral Presentation: 146  
 Poster Presentation: 99



## Chemistry of Organic & Polymer Materials for Ubiquitous ICT

**Date: December 19-20, 2008**  
**Venue: C-CUBE at Chikushi Campus, Kyushu University**  
**Chair: Shiyouji Yokoyama, Katsuhiko Tomooka, Hirotosugu Kikuchi**

### Lectures

#### Part 1: Session for Optoelectronics Applications

Shiyouji Yokoyama (Kyushu University)

"Smart Polymers for Optoelectronic Applications"

Larry Dalton (University of Washington)

"Organic Nonlinear Optical Materials, Silicon Photonics, and Plasmonics"

Dong Hoon Choi (Korea University)

"Stability Control of Electro-optic Effect Using New Maleimide Copolymers

Containing Photoreactive Tricyanopyrrolidene-based Chromophores"

Soo Young Park (Seoul National University)

"Highly Fluorescent and Semiconducting Organic Nanostructures: Nanoparticle"

Akira Otomo (Nat. Inst. Info. & Commun. Tech)

"Molecular-scale Photonic Devices for Energy Saving Information Technology"

Hirotosugu Kikuchi (Kyushu University)

"Electro-optics of Nano-structured Liquid Crystals"

#### Part 2: Session for Synthetic Organic Chemistry

Ryo Irie (Kumamoto University)

"Development of Chiral 2, 6-trans-1, 2, 6-Trisubstituted Piperidine and its Metal Complexes for Asymmetric Catalyses"

Toshiyuki Hamura (Kwansei Gakuin University)

"Synthesis, Reactivity, and Structure of Strained Aromatic Compounds"

Kazunobu Igawa (Kyushu University)

"Enantioselective Synthesis of Chiral Silanol: Asymmetric Nucleophilic Substitution Reaction of Achiral Dialkoxysilane"

Young-Ger Suh (Seoul National University)

"Total Syntheses and Synthesis-based Structure Elucidation and Biological Activity of Macrophelides"

Masato Ito (Tokyo Institute of Technology)

"Design of Bifunctional Cp\*Ru Catalysts for Asymmetric Synthesis"

Masanari Kimura (Nagasaki University)

"Transition Metal Catalyzed C-C Bond Formation and Cleavage Reaction Utilizing Organoborane"

Tatsuya Uchida (Kyushu University)

"Unique Catalysis of Ru(salen) Complexes: Aerobic OH-oxidation under Irradiated and Non-irradiated Conditions"

Yoshihiko Yamamoto (Tokyo Institute Technology)

"Cu-catalyzed Hydroarylation of Electron-deficient Alkynes"

Mitsuru Shindo (Kyushu University)

"Stereoselective Olefination of Carbonyl Compounds Controlled by Torquoselectivity"

Poster Presentation: 16



## International Workshop on "Recent Advances in Science and Technology for Exhaust Treatments of Mobile Sources"

**Date:** February 13, 2009

**Venue:** C-CUBE at Chikushi Campus, Kyushu University

**Chair:** Yasutake Teraoka

### Lectures

Nitin Labhsetwar (National Environmental Engineering Research Institute, India)

"Non-noble Metal Based Catalysts: Possibilities for Their Applications in Exhaust Treatments of Mobile Sources"

Vito Specchia (Politecnico di Torino, Italy)

"Vehicle Emissions Control via Catalytic Reaction Engineering: State-of-the-art at Politecnico di Torino"

Koji Takasaki and Hiroshi Tajima (Kyushu University, Japan)

"Marine Exhaust Emission Regulation and Control"

Hideaki Hamada (National Institute of Advanced Industrial Science and Technology, Japan)

"Development of Ir/silica-based Catalysts for the Selective Reduction of NO with CO Applied to Diesel Exhaust"

Hong He (Research Center for Eco-Environmental Sciences, CAS, China)

"Selective Catalytic Reduction of NO<sub>x</sub> by Ethanol over Precipitable Silver Compound Catalysts and the Application of AgCl/Al<sub>2</sub>O<sub>3</sub> to Diesel Exhaust Treatment"

Norio Miura (Kyushu University, Japan)

"Zirconia-based Gas Sensors Aiming at Monitoring of Automotive Exhaust"

Masato Machida (Kumamoto University, Japan)

"Catalytic Applications of Large-capacity Oxygen Storage Materials"



## Fourth International Conference of The Yellow Sea Rim International Exchange Meeting on Building Environment and Energy (YSRIM 2009)

**Date:** January 29-30, 2009

**Venue:** Mielparque-Kumamoto

**Chair:** Tetsuo Hayashi, Kazuhide Ito

### Special Lecture

Shuichi Torii (Kumamoto University, Japan)

"Thermal Fluid-flow Control in Opened or Closed Indoor with Injection and Suction Ducts by Using Vertical Partition Plate"

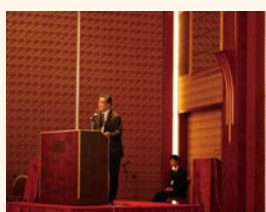
### Keynote Lecture

Hidetoshi Nakagami (Jyukankyo Research Institute, Japan)

"Current and Future Status of ESCO in Asia"

**Oral Presentation:** 15

**Poster Presentation:** 25



## G-COE Novel Carbon Resource Sciences Seminar

| Date       | Seminar   | Lecturer  |
|------------|---|---|
| 2008/7/17  | <b>Production Optimization for Developing Thin Oilsands Layers</b><br>【Venue】<br>W2-517, Ito Campus, Kyushu University  | <b>Bae, Wisup</b><br>(Sejong University, Korea)   |
| 2008/9/11  | <b>Antimicrobial Polymers Today: The Chemistry and Applications</b><br>【Venue】<br>C-Cube 303, Chikushi Campus, Kyushu University Research, Chikushi Campus, Kyushu University   | <b>El-Refaie Kenawy</b><br>(Tanta University, Arab Republic of Egypt)   |
| 2008/11/17 | <b>Nanomanufacturing with Colloids of Nanoparticles and Carbon Nanotubes : Fluid and Heat Transfer Physics</b><br>【Venue】<br>W4-732, Ito Campus, Kyushu University  | <b>Dimos Poulikakos</b><br>(Swiss Federal Institute of Technology Zurich)   |
| 2008/11/21 | <b>The 129th KASTEC Seminar</b><br>【Venue】<br>3F Learning Room,<br>Art, Science and Technology Center for Cooperative Research, Chikushi Campus, Kyushu University  | <b>Jun Izumi</b><br>(Art, Science and Technology Center for Cooperative Research, Kyushu University, Adsorption Technology Industries Ltd.)<br><b>Masahiro Uchiyama</b><br>(Art, Science and Technology Center for Cooperative Research, Kyushu University, National Institute for Environmental Studies) |
| 2008/12/1  | <b>Researches &amp; Developments at Business Enterprises: An Example of R&amp;D at Mitsubishi Chemical Cooperation</b><br>【Venue】<br>South-112, Institute for Materials Chemistry and Engineering, Chikushi Campus, Kyushu University | <b>Hisao Urata</b><br>(Mitsubishi Chemical Holdings Corporation)  |
| 2008/12/16 | <b>Organometallic Seminar XXXVI<br/>"New Paradigm of Molecular Catalytic Chemistry"</b><br>【Venue】<br>International Hall, Kyushu University   | <b>Hiroto Yoshida</b> (Hiroshima University)<br><b>Susumu Saito</b> (Nagoya University)<br><b>Makoto Tokunaga</b><br>(Faculty of Science, Kyushu University)<br><b>Kazuhiko Takai</b> (Okayama University)<br><b>Yoichiro Kuninobu</b> (Okayama University)   |



## 01 The 1st International Symposium of Novel Carbon Resource Sciences

We held our kickoff symposium, "The First International Symposium of Novel Carbon Resource Sciences", at Grand Hyatt Fukuoka on October 26, 2008.

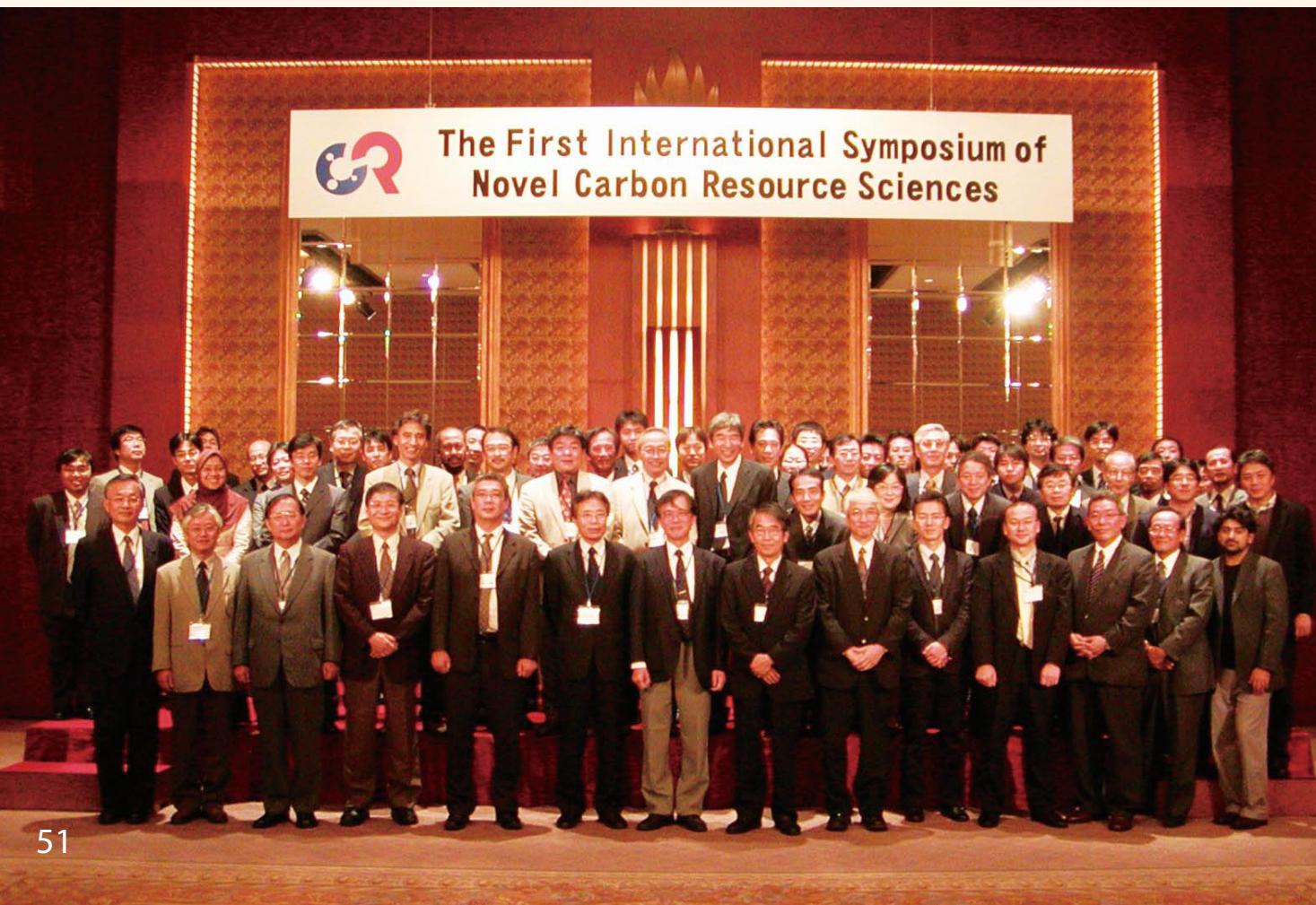
Opening remarks were stated by Prof. Hideo Nagashima (Leader of G-COE), Dr. Setsuo Arikawa (President of Kyushu University), Mr. Hirota Tani (Ministry of Education, Culture, Sports, Science and Technology), and Mr. Kimihisa Kittaka (Ministry of Economy, Trade and Industry) respectively. After that, Prof. Nagashima, Prof. Yasutake Teraoka and Prof. Tsuyoshi Hirajima

presented the outline of our G-COE program (its background, aims, plans, education program and partnership). The representative lecture from our G-COE was presented by Prof. Seong-Ho Yoon, which was about the significance and possibility of carbon materials in the research field of energy and environmental technology.

We also invited lecturers from our partner institutions. As a representative of our academia-industry collaboration partner, Dr. Mikio Sato (Central Research Institute of Electric Power Industry) talked

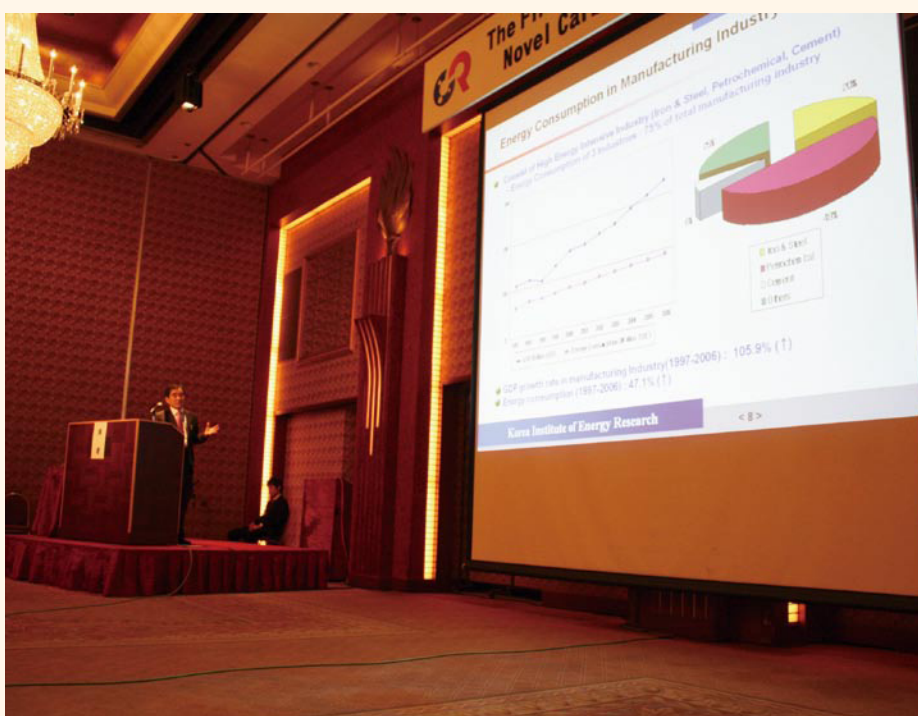
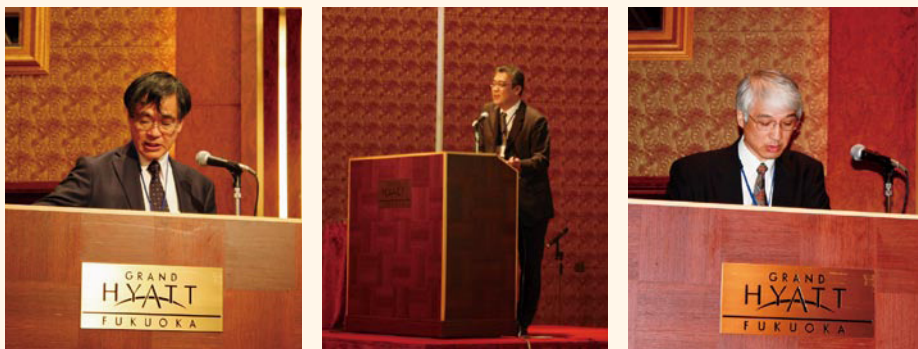


Mr. Kimihisa Kittaka



about the engineering solutions for climate change in electric power sector. As representatives of our international collaboration partners, Prof. Yanqing Wu (Shanghai Jiao Tong University, China), Prof. Sudarto Notosiswoyo (Institute of Technology Bandung, Indonesia), Prof. Doo-hwan Jung (Korea Institute of Energy Research), and Prof. Chun-Zhu Li (Monash University, Australia) reported the situation of energy and environmental issues in each country and of researches concerning them at each institution.

The symposium had 171 participants, and was closed successfully after active discussions on the future of our energy resources and environment. The closing remark was given by Dr. Makoto Takagi, the President of Fukuoka Women's University. We had a friendly banquet after the symposium.



|   |   |   |
|---|---|---|
| 1 | 2 | 3 |
| 4 | 5 |   |
| 6 |   |   |
| 7 | 8 | 9 |

1. Prof. Hideo Nagashima 2. Prof. Yasutake Teraoka  
3. Prof. Tsuyoshi Hirajima 4. Prof. Seong-Ho Yoon  
5. Dr. Mikio Sato 6. Prof. Doo-hwan Jung  
7. Prof. Yanqing Wu 8. Prof. Sudarto Notosiswoyo  
9. Prof. Chun-Zhu Li



# 02 The 2nd International Symposium of Novel Carbon Resource Sciences



We held the Second International Symposium of Novel Carbon Resource Sciences (NCRS) from March 10 to 11 at Institute of Technology Bandung (ITB), Indonesia.

On the first day, opening remarks were stated by Prof. Sudarto Notosiswoyo, Dean of Faculty of Mining and Petroleum Engineering, ITB, Prof. Hideo Nagashima, Leader of our COE, and Prof. Djoko Santoso, Rector of ITB, respectively. Next, keynote lectures were presented; 'groundwater pollution problem' by Prof. Yanqing Wu from Shanghai Jiao Tong University, China, 'utilization of brown coal' Prof. Chun-Zhu Li from Curtin University of Technology, Australia, and 'coal gasification' Prof. Dwiwahju Sasongko, Dean of Faculty of Industrial Technology, ITB. After that, a series of separate sessions on Environmental Science, New Materi-

als related to Carbon Resources, Thermal Energy, Policy and Novel Carbon Technology were held in two rooms. From Kyushu University, 4 COE members including Prof. Jun Fukai and Prof. Shigeto Okada delivered special lectures on carbon fiber in thermal engineering, post lithium-ion battery, preparation of nano-sized functional materials, improvement in performance of refrigeration/ air conditioning system in these sessions. 4 other researchers and 11 students made oral presentations as well.

The second day of the symposium focused on earth resource science, one of the important areas of NCRS. Keynote lectures were presented by Prof. Kikuo Matsui and Prof. Kyuro Sasaki who are our COE members and Dr. Bukin Daulay, Head of Mineral and Coal Technology Center, ITB. These subjects were devel-

opment of eco-friendly coal mines, CO<sub>2</sub> storage technology at Yubari, and low rank coal upgrading, respectively. Then, five sessions on Earth Resources, Coal Mining Science and Technology, Coal Resource Utilization, Thermal Energy, and Petroleum Engineering were held at two rooms, for which 4 researchers and 11 students from Kyushu University made oral presentations. In these sessions, important issues for novel carbon resource sciences were actively discussed, such as CO<sub>2</sub> storage, effective utilization and depollution of low rank coal (brown coal, sub-bituminous coal, etc) which is substantially distributed in Indonesia, and environmental problems concerning development of strip mines of Indonesia.

The symposium had 174 entries except 50 organizing staff members from 9 Asian and other countries and success-



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- 1-3. Institute of Technology Bandung (ITB), Indonesia
- 4-6. The 1st Day of the Symposium
- 7-8. The 2nd Day of the Symposium
- 9-10. Banquet
- 11. Geysers in Kamojang Craters National Park
- 12. Pongkor Gold Mine in Bogor
- 13. Meeting for Assessment of our Activities



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11



13

fully ended with interactive discussions. While 37 people from Kyusyu University including researchers, students and staff participated in the symposium, 35 of them made oral presentations. It is also worthy of special mention that each of students from our COE helped organize the program as an assistant of each session. At the banquet on the first evening, participants deepened their exchanges playing music with Indonesian traditional instruments together.

On the next day of the symposium, some participants made an excursion to Kamojang geothermal power station or Pongkor gold mine, which represent Indonesia as a resources and energy power. About 20 researchers and students from Kyushu University participated in the excursion. Kamojang geothermal power plant located in Garut, West java has world's top-class

energy reserve. After they received explanations of facilities, electric-generating capacity and locational conditions of the plant, they made an inspection of the facilities such as steam turbines and the geysers in Kamojang Craters National Park. Pongkor gold mine, which is located in Bogor, West Java is one of the largest gold mines in Indonesia. As the theme of excursion was aeration control in the pit, the participants observed its faces and aeration facilities, and asked questions about the advantage and the validation method of new pits under construction. In addition, some participants of the symposium visited ITB laboratories related to their own field of expertise.

On the day before the symposium, Prof. Nagashima and 5 other members of the COE visited ITB to express our gratitude to Prof. Djoko Santoso, Rector of ITB,

and Dr. Indratmo Sukarno, Vice-Rector of ITB. At the same time, we held a meeting for assessment of our activities with 6 researchers of ITB and Prof. Wu from China and Prof. Li from Australia. We reported our activities of FY 2008, exchanged opinions on academic and educational exchanges between our COE and partner institutions and discussed the plan for our next international symposiums.

The symposium of this time became very fruitful for researchers and students of our COE in all respects such as broadening our views, promoting academic exchange and building human network. We are also planning to hold our symposiums in China, Australia, and other Asian countries in the future.

# 03 G-COE NOVEL CARBON RESOURCE SCIENCES Public Program and Lecture Meeting on Environmental Economics, Kyushu University

On March 25th NOVEL CARBON RESOURCE SCIENCES public program and lecture meeting was held at ACROS Fukuoka in Tenjin.

The first half of the symposium was the public program aiming to deepen both expert's and general public's understanding of the significance of NOVEL CARBON RESOURCE SCIENCES (NCRS). Lectures and discussions took place from society's perspective during the program.

First of all, Assoc. Prof. Toshiyuki Fujita delivered an opening address. Then, the group leader of Prof. Hideo Nagashima, Prof. Tadakatsu Ohnaka and Prof. Chang-Jin Ma and Prof. Shiro Hori gave lectures.

The latter half of the symposium was the lecture meeting. The main theme was the situation in China that has played a central role in resolving global energy

and environmental issues. With guests speakers from overseas including Prof. Zhang Xiliang, who was engaged in writing Intergovernmental Panel on Climate Change (IPCC) Fourth Report awarded Nobel Peace Prize 2007 and a senior power engineer Takahashi Masaki at World Bank, lectures and discussions were carried out from more professional point of view. First, Prof. Youichi Kawanami delivered the opening address. The keynote speaker was Prof. Nagashima, followed by the brief introduction of the lecture from Assoc. Prof. Nobuhiro Horii.

In the first session; 'Current situation of energy utilization in China and challenge to sustainability of energy' Wang Hongying, Assoc. Prof. Horii and Prof. Zhang gave lectures on the reality of energy measures in China which is not widely known throughout Japan.

In the second session; 'How to promote

Japanese energy-conservation and environmental technologies throughout China', Tatsuro Harada, and Assoc. Prof. Fujita delivered lectures on Japanese technology and a prospect of its expansion.

Finally, a comprehensive discussion was carried out by Director Wang, Prof. Zhang, Mr. Harada, Assoc. Prof. Fujita, Assoc. Prof. Horii and Mr. Takahashi. They actively exchanged opinions regarding sharing how China is evaluating its measures of environmental issues, and problems and outlook for measures of environmental issues in both Japan and China.

A total of 162 participants joined the symposium including 45 of the general public. The lecturer received a number of questions and opinions from the audience and it led to vigorous discussions. After the lecture meeting, a get-together was held including the



invited guests.

This public program made the audience aware of issues and provided information by reviewing NCRS from whole society's point of view.

In addition to that, it gave the G-COE members and its students a great opportunity to understand their research in a broader context. Moreover, the lecture meeting became a valuable opportunity to provide the latest knowledge of top-rated experts, who are leading this field, to the G-COE members and other people. G-COE group is looking forward to holding next public programs and lecture meetings with a broader, international, social and interdisciplinary point of view.



1. Prof. Hideo Nagashima, Group Leader, Institute for Materials Chemistry and Engineering, Kyushu University
2. Prof. Tadakatsu Ohnaka, Faculty of Human Environmental Science, Fukuoka Women's University
3. Assoc. Prof. Chang-Jin Ma, Faculty of Human Environmental Science, Fukuoka Women's University
4. Prof. Shiro Hori, Art, Science and Technology Center for Cooperative Research, Kyushu University
5. Prof. Youichi Kawanami, Dean of Graduate School of Economics and Faculty of Economics, Kyushu University
6. Assoc. Prof. Nobuhiro Horii, Faculty of Economics, Kyushu University
7. Director Wang Hongying, Government Allowanced Expert granted by the State Council, Energy Economic Institute of Shanxi Academy of Social Sciences, China
8. Prof. Zhang Xiliang, Deputy Director of Institute of Energy, Environment and Economy in Tsinghua University, China
9. Assoc. Prof. Tatsuro Harada, Kyushu University, Research Laboratory Kyushu Electric Power Co., Inc
10. Comprehensive Discussion: Facilitator; Assoc. Prof. Toshiyuki Fujita, Faculty of Economics, Kyushu University



# 04 10th Cross Straits Symposium on Materials, Energy and Environmental Sciences (CSS10)

Faculty of Engineering Sciences, Kyushu University

**Yasutake Teraoka**



Poster Presentation

## About CSS

In 1998, The Interdisciplinary Graduate School of Engineering Sciences, Kyushu University (KU-IGSES) made a proposition to the Pusan National University (PNU) and the Pohang University of Science and Technology (POSTECH) to establish a forum for students to interact with one another through "presenting research that integrates materials, energy and environment in English". The two universities, PNU and POSTECH, were chosen because of not only their long standing relationship of academic and student exchanges with KU-IGSES but also their relative proximity to Fukuoka. The symposium was named Cross Straits Symposium on Materials, Energy and Environmental Sciences (CSS) with the wish to deepen friendship across the straits between Kyushu Island and South Korea. The first symposium (CSS1) was held at the Chikushi Campus of KU under the sponsorship of KU-IGSES on November 1-2, 1999, which was followed by CSS2 (PNU, November 2-3, 2000) and CSS3 (POSTECH, November

15-16, 2001) under rotation system. As the first symposium in the 4th cycle, CSS10 was organized by KU-IGSES on November 13-14, 2008.

The CSS is originally and basically organized by three universities (schools), so that it is briefly called as "Three-University Seminar". The CSS has been open to invite another university: for example, Shanghai Jiao Tong University (SJTU) was invited at CSS7 and CSS10 organized by KU-IGSES.

## CSS and education in the era of globalization

The aim of the CSS is to provide graduate students of PNU, POSTECH and KU-IGSES with the opportunity to present their scientific findings to overseas counterparts in English and exchange opinions not only on their research but also on mutual interests. The graduate students will be exposed to many different viewpoints, thus providing them with much broader perspectives. This event is hoped to be

very helpful in promoting friendship among graduate students from different countries. The CSS has been considered to be very important for the practical education in the era of globalization because the graduate students play substantially roles not only in planning and management but also in academic activity. In 2005 and 2006, KU-IGSES implemented "Program for the Strategic Education of Material Science Oriented Creative Young Researchers" under the project of Initiative for Attractive Education in Graduate Schools, Ministry of Education, Culture, Sports, Science and Technology, Japan. In the program, CSS was regarded as important, and invitation of SJTU to CSS7 and sending students of KU-IGSES to CSS8 resulted in practical effects in cultivation of international sensitivity. CSS is also an important educational event in the G-COE program of Novel Carbon Resource Sciences (NCRS). Organizing and active participating in CSS are compulsory for students in KU-IGSES as a part of the subject "International Exercises in Novel

| Number of papers |        | POSTEC | PNU | SJTU | KU | Total |
|------------------|--------|--------|-----|------|----|-------|
| Plenary          |        | 1      | 1   | 1    | 1  | 4     |
| Oral             | Mater. | 2      | 2   |      | 3  | 7     |
|                  | Envi.  | 2      | 2   | 1    | 2  | 7     |
|                  | Energy | 2      | 2   | 1    | 2  | 7     |
| Poster           | Mater. | 3      | 7   | 2    | 30 | 42    |
|                  | Envi.  | 4      | 2   | 2    | 9  | 17    |
|                  | Energy | 6      | 8   | 1    | 36 | 51    |
| Total            |        | 19     | 23  | 7    | 82 | 135   |

Number of Presenters

Carbon Resource Sciences”.

### About CSS10

The memorial CSS10, which was the first symposium in the 4th cycle, was organized by KU-IGSES and held at the Chikushi Campus on November 13-14, 2008. Numbers of student participants were about 40 from South Korea (PNU and POSTEC), 8 from China (SJTU) and about 80 from Japan (KU-IGSES), and they gave oral or poster presentation about their research in fields of materials, energy and environment. They have deepened mutual understanding and friendship through scientific discussion as well as activities in students’ session, which is expected to contribute to the promotion of their scientific achievements by encouraging each other as well as to exchanges of academic and personal activities in the future.

The number of papers presented in CSS10 is listed in the table. One professor from each university gave a plenary lecture. Each lecture was well prepared for the purpose of graduate-level education with rich content and simple expression. 21 oral papers and 10 poster papers by students were selected as awarded papers.

The continuation of CSS has been agreed by three universities because it is significant in graduate education in each university, and CSS11 will be organized by PNU in the next fall.

18 students of KU-IGSES were given 1 credit of “International Exercises in Novel Carbon Resource Sciences” as a result of activities in CSS10 and the below-mentioned KU-SJTU joint workshop.

### The First KU-SJTU Joint Workshop on Environment and Energy Issues in Relation with Novel Carbon Resource Sciences

SJTU is one of core international partners of the global COE program of NCRS, so that students and staffs of SJTU were invited by the COE program to participate in the CSS10. By taking this opportunity, the COE program organized the titled joint workshop in the afternoon of November 12th, 2008 as a kickoff of student-level exchange event between two universities.

The workshop started with the brief introduction to NCRS by Prof. Nagashima, followed by introduction and discussion of KU-SJTU collaboration presided by Prof. Teraoka, and debate by

students.

The theme of the debate “the use of coal as energy source instead of oil” was set up by the representative student group in KU and announced to participants in advance so as to make own idea from “yes” and “no” standpoints. The student representative of KU (coordinator of the debate) surveyed the present situation of global energy and then active debate started between “yes” and “no” groups each of which consisted Chinese and Japanese students. The theme is deeply related with the concept of NCRS and it is natural that one cannot reach a definite answer. Opinions from the both groups were convincing, and the discussion in each group and debate between groups were found to be very significant. Due to the time limitation, we could spare only one and a half hours for the debate. Participants from both universities were convinced that the improvement of English ability of students is indispensable to achieve more practical effects and that the debate event with longer time and with the participation of both students and staffs should be planned in the future.

#### ◆Program for discussion the “Selected Topics” by students

1. Introductions of students (Name, Major, ...)
2. Discussion the “Selected Topics” by students

We will debate about

**the use of coal as energy source instead of oil.**

- 2-1 Introduction of actual situation in general
- 2-2 Discussion on the use of coal based on three points (price, the amount of deposit, air pollution)
- 2-3 Opinion from professor

3. Closing this session



Debate by Students

# 05 International Symposium on Earth Science and Technology 2008

Faculty of Engineering, Kyushu University

## Kyuro Sasaki

International symposium on earth science and technology 2008 was held at Nishijin Plaza, Fukuoka, Japan on December 1st and 2nd. 102 persons including 48 overseas students attended the symposium from 8 domestic institutions, as well as 27 persons from 8 overseas institutions. There were oral sessions and a poster session and topics of resources, environments and earth sciences were discussed lively in each session. Plenary lectures were presented by Professor Rudy Sayoga Gautama (Institut Teknologi Bandung, Indonesia), Professor Tayfun Babadagli (University of Alberta, Canada) and Professor Suseno Kramadibrata

(Institut Teknologi Bandung, Indonesia) who were eminent researchers of earth science and technology at the first day of the symposium.

Professor Rudy Sayoga Gautama who is one of the specialists in treatment of acid mine drainage in coal mine lectured on the present conditions of environment-conscious development of coal mine and resources processing concretely.

Professor Tayfun Babadagli who carries out the advanced researches of Enhancing Oil Recovery (EOR) by using CO<sub>2</sub> lectured on the utilization of CO<sub>2</sub> for the

production of heavy oil and future outlook of CO<sub>2</sub>-EOR which is one of Carbon Capture and Storages (CCS).

Professor Suseno Kramadibrata who is one of the specialists in safety engineering for development of coal mine lectured on recent research situations of environment safety and health in underground coal mine.



Prof. Rudy Sayoga Gautama



Prof. Tayfun Babadagli



Prof. Suseno Kramadibrata



Oral Presentation



Q&A Session



Poster Presentation

# 06 1st G-COE International Workshop on Energy and Environment in Chemical Engineering

The workshop on energy and environment was held on 5 December 2008 in Chemical Engineering Department. Three first-class-honors invited speakers from overseas gave the lectures in the workshop.

First, Professor Sang Done Kim from KAIST - South Korea gave the lecture regarding the structure of energy consumption from primary energy in South Korea and CO<sub>2</sub> emission from power generation plant. In his lecture, he also explained the current state for developing the clean power generation plant from mineral resource. Then, Dr.

Doo Hwan Jung - the Director of South Korea Energy Resources Research Institute, gave the lecture to explain the current development of fuel cell, the anode catalyst development using porous carbon fiber, and the experiment to develop cathode catalyst using carbon nano fiber. At the last lecture, after explaining the fund, demand forecast and so on related to bio-ethanol purpose in Asia especially South Korea, Professor Yongtaek Lee from Chungnam National University gave the lecture of the bio-ethanol manufacturing by membrane separation and the zeolite membrane performance.

Faculty of Engineering,  
Kyushu University

**Jun Fukai**

The workshop was attended by graduate students. There were some questions and active discussion after each session of the lectures.



Situation of the Lecture



Prof. Sang Done Kim



Dr. Doo Hwan Jung



Prof. Yongtaek Lee

# 07 The 21st International Symposium on Chemical Engineering

Faculty of Human Environmental Science, Fukuoka Women's University

**Katsuki Kusakabe**

The 21st International Symposium on Chemical Engineering was held at Saga University on December 6th and 7th, 2008. The main purpose of the symposium is to educate graduate students and therefore all the presentation of the symposium is carried out by the students in English. The symposium served this purpose for the past 21 years. As a result, large proportion of young professor who is attending the symposium has had experiences where he has made a presentation in the past symposium.

Although the participation of the 21st symposium from Japan, Korea, Taiwan and Thailand was scheduled, it was very regrettable that Thai students could not attend the symposium due to the groundstop order in Thailand International Airport. In this year, the number of

participants was 314 including 72 professors and 242 students. Many topics regarding energy, environment, reaction and reactor were related to the G-COE program for Novel Carbon Resource Sciences. Among them, many students belonging to G-COE program participated in the newly established session for Novel Carbon Resource Sciences. Even though the student was nervous about English presentation and the content of the presentation was incomplete result in some cases, this experience had a great worth for them. The students, who made an excellent presentation and discussion, received the student awards in the banquet of the symposium.



Speech of Korean Student Who Received the Student Award

# 08 The 1st International Symposium on Light Using Organic and High Polymer Chemistry in Ubiquitous Information Society

Institute for Materials Chemistry and Engineering, Kyushu University

## Shiyoshi Yokoyama, Katsuhiko Tomooka



1st Part: Keynote Lecture



2nd Part: Invited Lecture



2nd Part: Q&A Session by Students



Chairs & Lecturers



Poster Presentation

Our G-COE and Institute for Materials Chemistry and Engineering (IMCE) have jointly organized the titled symposium on December 19 and 20 in 2008. The oral presentation of this symposium was divided into two parts. In the first part (Dec. 19), three distinguished foreign researchers provided their recent topics on the development of new materials for optical network and organic light emitting display (OLED). In the second part (Dec. 20), nine researchers provided their recent topics on the development of new synthetic organic chemistry for the creation of a diversity of functional molecules and physiologically active compounds. In addition, recent results in both areas were disclosed by graduate students on poster presentation at Dec. 20.

The speakers of the first part included Prof. Larry Dalton (Washington University), who has been one of the leading experts in the field of organic non-linear optical materials and devices, as well as Prof. Dong Hoon Choi (Korea University)

and Prof. Soo Young Park (Seoul National University), both of whom have been leading Korean researchers in the field of optical electronics. Since all of their researches cover a broad range of interdisciplinary scientific areas from materials chemistry, electronic engineering to optical electronics, the organizing committee in advance had asked these speakers to give a talk on the chemical aspect of their research in order to attract the audience, most of which were graduate students in chemistry. Prof. Dalton's lecture focused on the property of new non-linear optical materials for the ultrahigh-speed optical modulator and on their orientational dynamics in the polymer matrix. The lectures of two Korean researchers featured the recent topic on the development of OLED and solar battery, which were familiar to researchers and students at IMCE.

The speakers of the second part included Prof. Young-Ger Suh (Seoul University) and eight up-and-coming

domestic researchers, three of which were invited from Kyushu University and five of which were invited from outside of Kyushu University. Their topics were ranging from the development of new asymmetric synthesis and novel carbon-carbon coupling method to the synthesis of highly strained molecules and physiologically active compounds as well as the elucidation of their reactivity.

More than a hundred participants from Kyushu University as well as nine other universities and colleges discussed hot issues at this symposium actively. As a result, this international symposium offered an excellent opportunity for the smooth communication on the latest results in "Advanced Technological Development for Low Energy Consuming Society", which constitutes one of the most important objectives of our G-COE program. Finally, fruitful discussions among graduate students were greatly encouraged by the educational program of our G-COE.

# 09 International Workshop on "Recent Advances in Science and Technology for Exhaust Treatments of Mobile Sources" (NCRS G-COE Symposium/Workshop Series 2008-VIII)

Faculty of Engineering Sciences, Kyushu University

**Yasutake Teraoka**



1. Prof. Specchia
2. Prof. Miura
3. Dr. Labhsetwar
4. Prof. Teraoka
5. Dr. Hamada
6. Prof. Machida
7. Mr. Shimokawa
8. Prof. He
9. Prof. Wu (Shanghai Jiao Tong Univ.)

The titled workshop was held at Chikushi Campus, Kyushu University on February 13, 2009. The purpose of this workshop is to discuss the current status, to point out the current problems, to exchange ideas and to suggest the future direction of development in the field of science and technology for exhaust treatments of mobile sources among leading researchers.

After an opening remark by Prof. Nagashima (Leader of G-COE) and brief introduction of the G-COE and workshop by Prof. Teraoka, the following scientific lectures were given.

Dr. Nitin Labhsetwar (National Environmental Engineering Research Institute, India); "Non-noble metal based catalysts: Possibilities for their applications in exhaust treatments of mobile sources"

Prof. Vito Specchia (Politecnico di Torino, Italy); "Vehicle emissions control via catalytic reaction engineering: State-of-

the-art at Politecnico of Turin"

Prof. Koji Takasaki and Prof. Hiroshi Tajima (Kyushu University, Japan); "Marine exhaust emission regulation and control"

Dr. Hideaki Hamada (National Institute of Advanced Industrial Science and Technology, Japan); "Development of Ir/silica-based catalysts for the selective reduction of NO with CO applied to diesel exhaust"

Prof. Hong He (Research Center for Eco-Environmental Sciences, CAS, China); "Selective catalytic reduction of NO<sub>x</sub> by ethanol over precipitable silver compound catalysts and the application of AgCl/Al<sub>2</sub>O<sub>3</sub> to diesel exhaust treatment"

Prof. Norio Miura (Kyushu University, Japan); "Zirconia-based gas sensors aiming at monitoring of automotive exhaust"

Mr. Hironobu Shimokawa and Prof. Yasutake Teraoka (Kyushu University, Japan); "Catalyst development and catalysis of diesel particulate removal"

Prof. Masato Machida (Kumamoto University, Japan); "Catalytic applications of large-capacity oxygen storage materials"

After finishing the workshop, the organizer received the following comments from invited speakers which clearly indicated the successful workshop; "The workshop was well organized in scientific sense, and it should be open to researchers and students working in related fields." One of doctor-course student in G-COE (Mr. Shimokawa) confidently presented and discussed his research. This must be a good example of the realization of the purpose of G-COE in education and internationalization of young researchers.

# 10 Fourth International Conference of The Yellow Sea Rim International Exchange Meeting on Building Environment and Energy ( YSRIM 2009 )

Faculty of Engineering Sciences, Kyushu University

**Kazuhide Ito**

SYMPOSIUM  
&  
WORKSHOP  
REPORT

Fourth International Conference of The Yellow Sea Rim International Exchange Meeting on Building Environment and Energy (YSRIM 2009) was held in Mielparque-Kumamoto, Kumamoto, Japan from 29th to 30th January 2009. This conference was chaired by Prof. Tetsuo Hayashi (Kyushu University) and organized by Kyushu Branch of The Society of Heating, Air-conditioning and Sanitary Engineers of Japan, Yeongnam Chapter of Korea Institute of Architectural Sustainable Environment and Building Systems, Shanghai Society of Refrigeration and Kyushu University G-COE program "Novel Carbon Resource Sciences".

This symposium focused on sustainable development in Asia countries in both research and practical business. More than 100 people participated, and 2 keynote lectures and 40 technical papers (15 oral presentations and 25 poster presentations) were presented during the symposium.

The titles of the keynote lectures were: Prof. Shu-ichi Torii, "Thermal Fluid-Flow Control in Opened or Closed Indoor with Injection and Suction Ducts by Using Vertical Partition Plate"  
Prof. Hidetoshi Nakagami, "Current and Future Status of ESCO in Asia"

## Special lecture

Shuichi Torii, Kumamoto Univ., JP

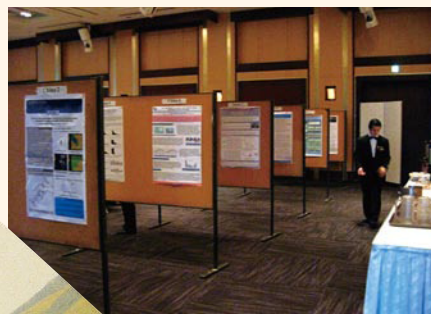
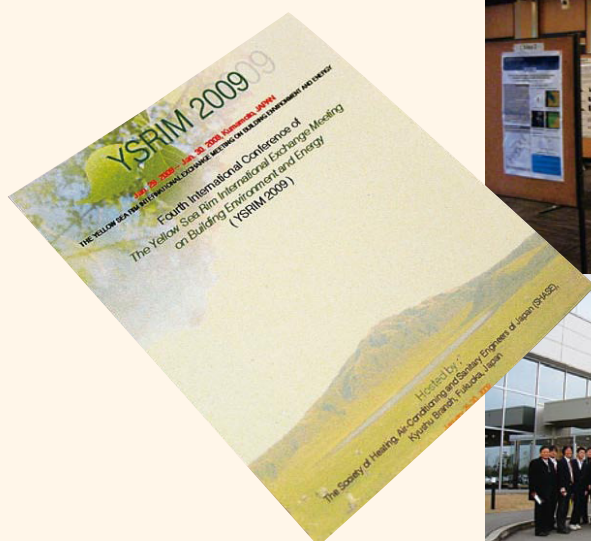
"Thermal Fluid-Flow Control in Opened or Closed Indoor with Injection and Suction Ducts by Using Vertical Partition Plate"



## Keynote lecture

Hidetoshi Nakagami, Jyukankyo Research Institute, JP

"Current and Future Status of ESCO in Asia"



- 1.2. Oral Presentation
3. Poster Presentation
4. Technical Tour to Sony Semiconductor Kyushu Corporation Kumamoto Technology Center
5. Banquet

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# Research and Educational Center of Carbon Resources



The Research and Educational Center of Carbon Resources (hereafter referred to as the Carbon Center) was founded in April 2008 with the aim of tackling the challenges for development and effective utilization of carbon resources and solution of energy problems. It has its office in Chikushi Campus, Kyushu University, and its brief overview is introduced on our home page (<http://cr.cm.kyushu-u.ac.jp>). The Carbon Center is building up a new academic system which encompasses whole issues related to carbon resources, as well as promoting development of human resources, innovative and progressive research and development in collaboration with industrial sector, and network construction concerning carbon resources.

Behind the background of the center's foundation, there was global shortage of carbon resources such as coal and petroleum since early 2007, which boosted the prices of them and caused anxiety about exhaustion of resources. Under the leadership of then President Kajiyama of Kyushu University, and with a support and advice of Emeritus Isao Mochida, who is currently a Research Professor of the Carbon Center, a Research Core (an inter-disciplinary organization of researchers at Kyushu University which aims at providing a basis for formation of a global educational and research center) was founded in August 2007. (Its representative was Prof. Hideo Nagashima, Dean of Institute for Materials Chemistry and Engineering.) The researchers who were members of the Research Core took a leading part in launching a project of Ministry of Economy, Trade and Industry (FY2007-2009), with the objective of human resource development related to fossil resources in collaboration with industry. With the growing interest in this project among industrial sectors, as well as increasing public concern over the problems of resources, energy, environment and global warming, we reached the conclusion that our university needed to establish a center which would address such problems related to carbon resources professionally and comprehensively. In response, Kyushu University proceeded with the preparations for establishment of the center at a high pace, so by the end of 2007 the Carbon Center already awaited its start in April 2008. Its first approach to competitive project was application for the Global COE program.

The Carbon Center plays a role as a medium of Global COE program. Although COE itself is formally an organization directly supervised by the President of the university, its activity is actually a part of the operation of the Carbon Center. The employment of Research Professor, Visiting Professor and Postdoctoral Fellow is discussed at COE and announced by the head of the Carbon Center after the approval of its committee. Two important projects of the Carbon Center, which are shown below, are being implemented in close cooperation with COE. We will introduce two main activities of us briefly here, and the next issue of News Letter will cover more details of our activities. For up-to-date information, please refer to our homepage.

## Advanced Education Program for Effective Utilization of Fossil Fuels

This project, which was adopted in 2007 as a part of the

sponsored project (Project of Academic-Industrial Partnership for Human Resource Development) of Ministry of Economy, Trade and Industry, is preparing educational materials related to the subject of utilization of coal till March 2010. Faculties of Kyushu University (Institute for Materials Chemistry and Engineering, Faculties of Engineering, Science, Engineering Sciences, Agriculture, Economics, and Art, Science and Technology Center for Cooperative Research), public institutes, and industrial sectors are jointly developing educational materials such as textbooks and holding experimental lectures. In experimental lectures announced on our homepage, we use the textbooks developed in the same year and verify their effectiveness. Graduate students of Kyushu University can acquire credits corresponding to each lecture. The lectures are also open to other persons from industries or other universities. As practice is of importance for the research fields, we hold not only lectures but also internship programs of visiting companies (including on-the-job training) and seminars for solution of practical problems. These curricula enable students to have great variety of experiences from basic research to its application in business situations through instructors with multiple backgrounds. This program will be succeeded as another project with university's own budget in FY 2010. We are currently in the process of developing educational materials for the last financial year of this project and arranging English version of some materials for encouraging students' future success in Asia. The experimental lecture of this program is recommended to take by COE as one of the subjects related to carbon resources.

## Kyushu Society for Low-Carbon Systems ([http://cr.cm.kyushu-u.ac.jp/eng/?page\\_id=32](http://cr.cm.kyushu-u.ac.jp/eng/?page_id=32))

Kyushu Society for Low-Carbon Systems was organized mainly by Kyushu Bureau of Economy, Trade and Industry and Kyushu University in September 2008 as a society in northern Kyushu area for study and information exchange among business organizations which pursue the goal of environmentally-friendly utilization of coal and other fossil resources as well as researchers engaged in the development of coal industry. It focuses its attention on the possibility of "low-carbon systems" as a solution to the problems of energy resources and environment, and aspires for earlier realization of environmentally-friendly and sustainable low-carbon society, and formation of the center for research, human resource development, personnel exchange, and overseas advancement. The Society aims at building a center for human resources development and research related to coal and other fossil resources, equipped with a function as a center for researchers exchange and technological transfer concerning CCT (Clean Coal Technology). The founding members are 17 business organizations, 7 universities, and 13 administrative agencies, and the number of members is increasing more and more. The Society had its meetings three times in FY 2008.



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**Kyushu University G-COE program “Novel Carbon Sciences” secretariat**

6-1 Kasuga-Koen, Kasuga, Fukuoka, 816-8580 Japan

TEL: 092-583-7616 FAX: 092-583-7619

Email: [ncrs@cm.kyushu-u.ac.jp](mailto:ncrs@cm.kyushu-u.ac.jp)

URL: <http://ncrs.cm.kyushu-u.ac.jp>