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Tokushima University

Characterization and Structural Control of Synthetic Polymers

Professor Koichi Ute

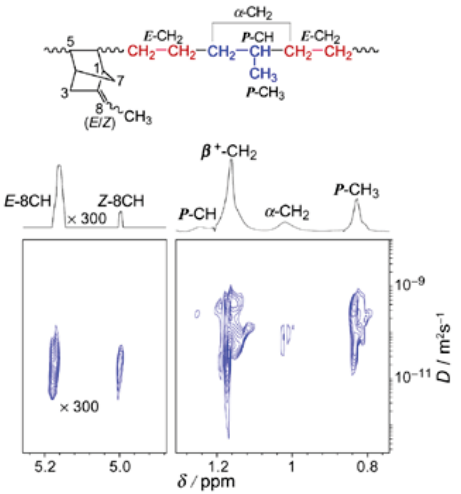


Fig. 1 Molecular weight dependence of chemical composition in an ethylene-propylene copolymer.

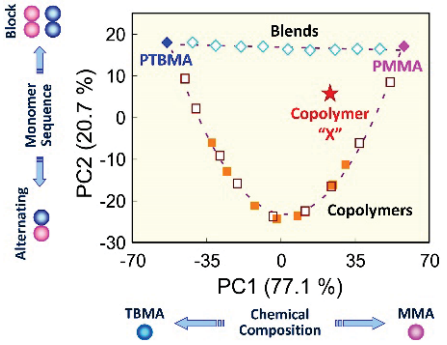


Fig. 2 Principal component score plots showing chemical composition and monomer sequence distribution in methacrylate copolymers.

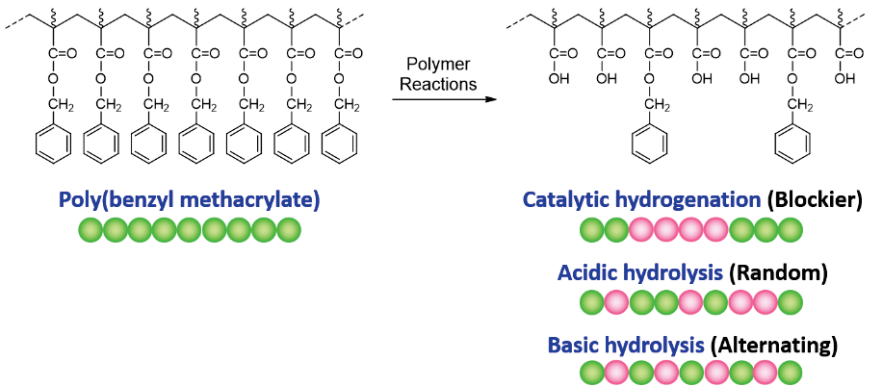


Fig. 3 Monomer sequence distributions in methacrylate copolymers prepared by polymer reactions.

Content:

Recent research and development of industrial or functional polymers increasingly require precise analysis and control of their molecular parameters (molecular weight, comonomer sequence, stereoregularity, etc.) .

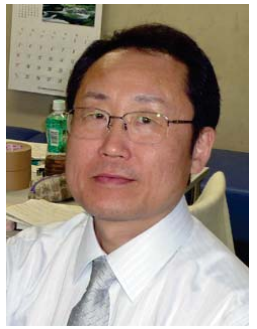
The aims of my study are to develop useful methods of polymer characterization by modern NMR (nuclear magnetic resonance) and chromatographic techniques, and to synthesize new polymer materials on the basis of the characterization.

For example, DOSY (diffusion-ordered NMR spectroscopy) is a powerful technique to measure the molecular-weight dependence of chemical composition in copolymers (**Fig. 1**).

Multivariate analysis of the NMR spectra of copolymers is another example of my approaches to precise and quantitative characterization of synthetic polymers (**Fig. 2**). The use of this multivariate approach revealed he mechanism of polymer reactions (catalytic hydrogenation, acidic/basic hydrolysis, etc.) of methacrylate copolymers (**Fig. 2**).

Keywords: polymer synthesis, NMR, chromatography, copolymers

E-mail: ute@tokushima-u.ac.jp
Tel. +81-88-656-7402
Fax: +81-88-656-7404
HP: http://poly.chem.tokushima-u.ac.jp/



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Tokushima University

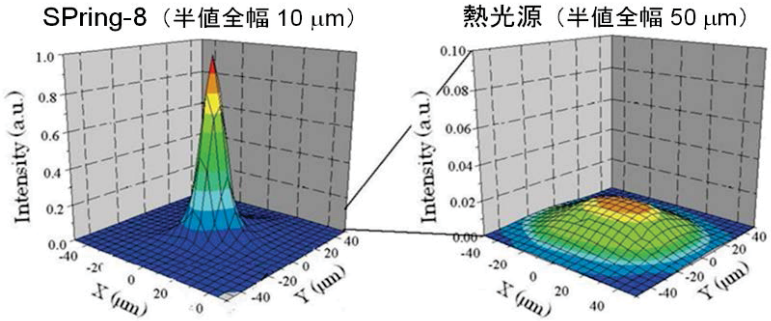
Infrared studies of materials using synchrotron radiation

Professor Hidekazu Okamura

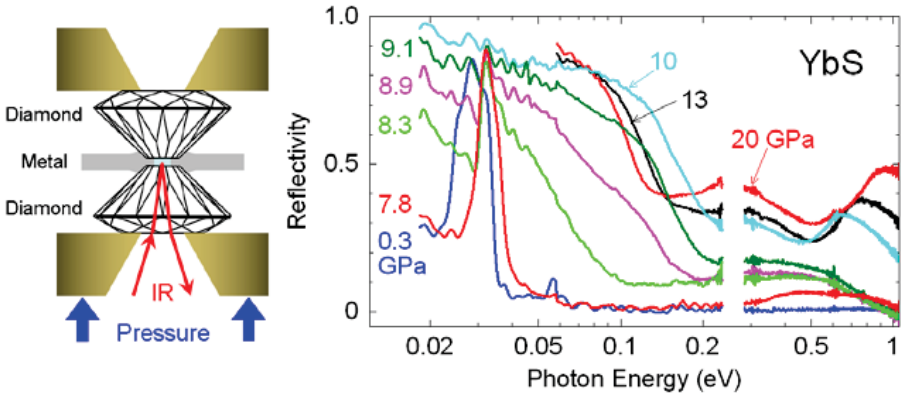
Infrared Synchrotron Radiation

- ✓ 10^2~10^3 times brighter than conventional IR source.
- ✓ Can be focused to a 10 μm diameter spot without an aperture (in the molecular vibration range).

→IR microscopy can be easily performed with a very high spatial resolution.



Comparison between SPring-8 and conventional IR source.



A high pressure IR study of YbS using SPring-8.

<Background>

- ✓ Infrared synchrotron radiation is much brighter than the conventional, black body radiation-based infrared sources. This brightness is utilized to perform infrared studies with high spatial resolution, such as micro-spectroscopy, high pressure studies using a diamond anvil cell (DAC), etc.

<Present research activities>

- ✓ Infrared studies of various materials under high pressure, using DAC and the infrared synchrotron radiation at SPring-8.
- ✓ Materials of main interest are the so-called ‘strongly correlated electron systems’, where strong electron-electron interaction results in interesting phenomena such as metal-insulator transition, heavy quasiparticle formation, superconductivity, etc.
- ✓ Development of super-spatial resolution IR microscopy using SPring-8 and near-field optics.

Keywords: Infrared spectroscopy, synchrotron radiation, high pressure, diamond anvil cell.

E-mail: ho@tokushima-u.ac.jp

Tel. 088-656-9444

Fax:

HP : http://www.chem.tokushima-u.ac.jp/B2/

Faculty of Science and Technology
Tokushima University

Development of Estimation Method of Water Adsorbents

Professor Masahiro Katoh

Fig. 1 Volumetric apparatus for measurement of adsorption & desorption velocity of water on adsorbents..

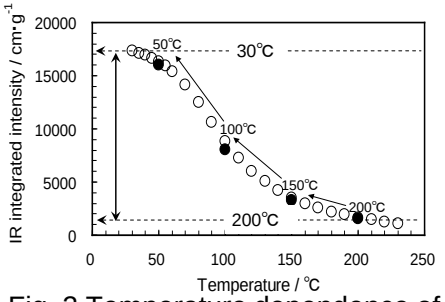


Fig. 2 Temperature dependence of IR integrated intensity of adsorbed H_2O at 10 Torr on NaY zeolite, ○: 1st, ●: 2nd.

Fig. 3 special IR cell.

Content:

The utilization of waste heat for the regeneration of desiccant material in a desiccant dehumidifier system is one of the best alternatives because regeneration cost is eliminated. However, it is only suitable for equipment which can exhaust waste heat at temperature 60 ℃ and 140 ℃. Usually, these types of equipment are only available in factories or supermarkets.

We develop estimation method of water adsorbents (desiccant materials) and propose two kinds of estimation methods for water adsorption.

(1) Estimation of adsorption and desorption velocity of water on adsorbents by volumetric apparatus (Fig .1).

(2) Estimation of temperature behavior of adsorbed water on adsorbents by IR spectroscopy.

In particular, temperature dependence (Fig. 2) of adsorbed water on desiccant can be gotten easily by using special IR cell (Fig. 3). The profile was corresponding to the equilibrium adsorption data.

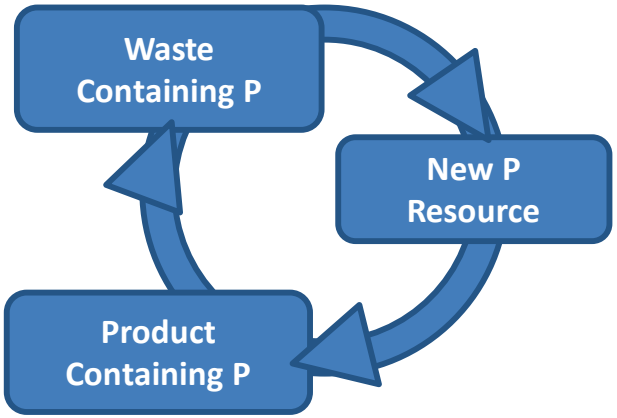
Keywords : water adsorbent, adsorption velocity, IR spectroscopy

E-mail: katoh@tokushima-u.ac.jp
Tel. +81-88-656-7429
Fax: +81-88-656-7429
HP : http://www.chem.tokushima-u.ac.jp/C3/

Faculty of Science and Technology
Tokushima University

Development of Phosphorus Resource and Catalyst Process Based on Chemical Engineering

Professor Shigeru Sugiyama



Resource Circulation Map for Phosphorus

(a) Circulation of phosphorus resource

LNG to Ethylene
= Direct Employment of LNG for Petrochemical Plants

Raw material for ethylene plant from LNG

LPG to Various Chemicals
= Development of Substituted Resources for Petroleum

Production of raw material fo MMA from LPG

(b) Various chemicals from LNG and LPG

Content:

Phosphorus is an essential element for plant growth and has no substitute in food production. Furthermore, it is used in various advanced materials. Phosphate rock as a raw material of phosphorus is finite and non-renewable. Therefore, the development of new raw materials for the rock is an urgent issue in Japan. In our group, search of new resource for the rock together with the development of the easy and economical recovery method of phosphorus from the resource is in progress.

As another topics, to prepare for the drying up of petroleum, the conversions of main products in liquefied natural gas (LNG) and liquefied petroleum gas (LPG) to various chemicals on solid catalysts are studied. Based on our earlier studies on the oxidative coupling of methane (LNG) on solid catalysts, the oxidation of C3- and C4-hydrocarbons (main components in LPG) are in progress. Recently, we have found out that oxidative dehydrogenation of isobutane (from LPG) on mesoporous silicas favorably produces isobutene, which is a raw material for methyl methacrylate (MMA); one of the most possible monomers obtained from petroleum.

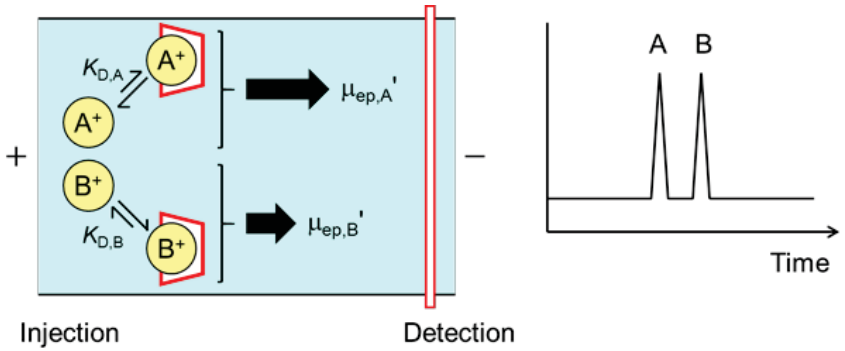
Keywords : rare resources, solid catalysts

E-mail: sugiyama@tokushima-u.ac.jp
Tel. +81-88-656-7432
Fax: +81-88-656-7432>
HP :
http://www.chem.tokushima-u.ac.jp/C3/

Faculty of Science and Technology
Tokushima University

Development of Analytical and Separation Methods with Nano-sized Molecular Assembly

Professor Toshio Takayanagi



(a) Molecular recognition with affinity (b) Chromatogram

Fig. 1 Separation improvement by affinity interaction

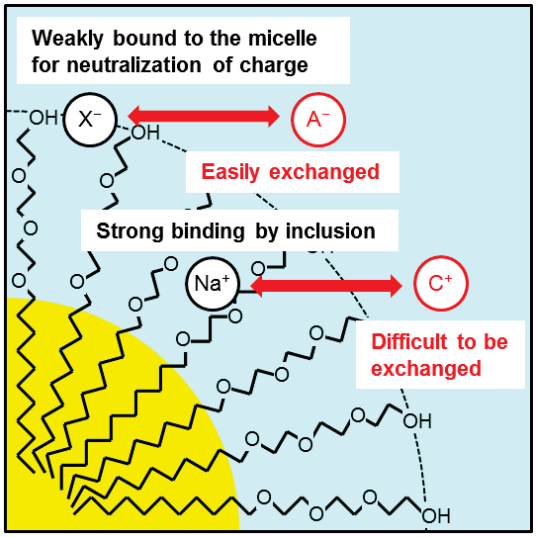


Fig. 2 Partition selectivity of ionic species toward nonionic surfactant micelle

Content:

Nano-sized molecular assemblies of surfactant micelles, vesicles, microemulsions, and polymer gels possess hydrophobic environment. Specific surface area of the molecular assemblies is greatly larger than that of bulk water-organic solvent interface. Extraction-separation with the characteristic hydrophobic environment of the molecular assemblies works in pseudo-homogeneous aqueous solution. Liquid-liquid extraction is done in the pseudo-homogeneous aqueous solution without mechanical shaking of the two phases, with fast extraction kinetics, as well as with the selectivity towards ionic substances. Functional Molecular Assembly including micelles, microemulsions, and hydrophobic matrices are to be developed.

Based on equilibria and kinetics in aqueous solution, development of affinity reagents, analysis of affinity interactions, and investigation of selectivity expression factors are studied.

Keywords : Surfactant micelle, microemulsion, hydrophobic partition, aquatic solvent, analytical separation

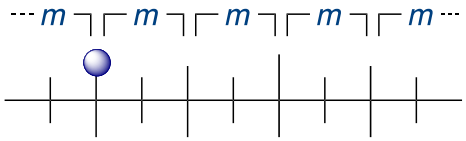
E-mail: toshio.takayanagi@tokushima-u.ac.jp
Tel. +81-88-656-7409
Fax: +81-88-656-7409
HP : http://www.chem.tokushima-u.ac.jp/B1/index.html

Faculty of Science and Technology
Tokushima University

Stereoregular thermoresponsible polymers

Professor Tomohiro Hirano

Representative stereoregular polymers

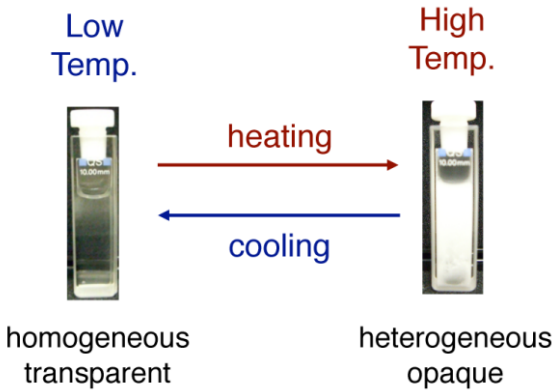


Isotactic

Syndiotactic

Heterotactic

Phase transition behavior of aqueous polymers.



Content:

Our main research interest is “synthesis of stereoregular polymers, which exhibit thermoresponsibility in aqueous solutions”. The stereospecificity of the radical polymerizations of amide-containing monomers, such as *N*-isopropylacrylamide (NIPAAm) and *N*-*n*-propylacrylamide (NNPAAm), has been successfully controlled by utilizing complex formation of monomers through hydrogen bondings.

In addition, the effect of stereoregularity (isotactic, syndiotactic and heterotactic) on the LCST (lower critical solution temperature)–type phase transition has been investigated. It has been revealed that diad tacticity plays an important role to determine the phase transition temperature in the heating process, whereas configurational sequences longer than triad do in the cooling process.

A final goal of our research is development of novel functional polymeric material by controlling the primary structures of synthetic polymers.

Keywords : radical polymerization, stereoregularity, LCST

E-mail: hirano@tokushima-u.ac.jp

Tel. 088-656-7403

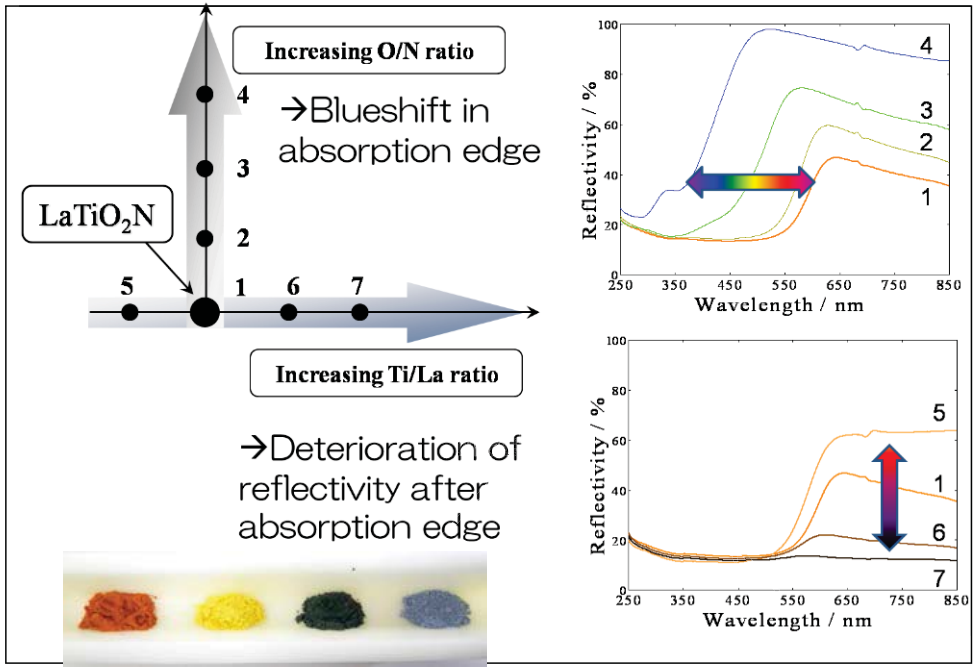
Fax: 088-656-7404

HP : http://poly.chem.tokushima-u.ac.jp

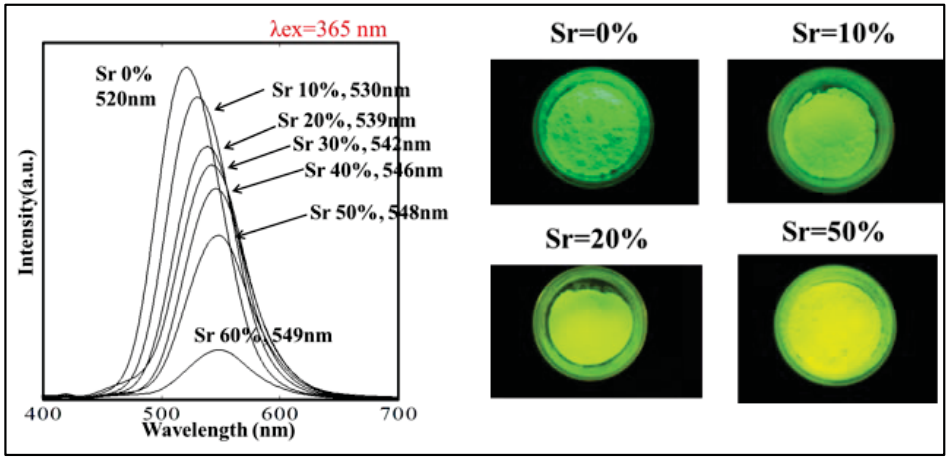
Optimization of Optical Properties of Eco-friendly Oxynitrides through control of Stoichiometries

Professor, Toshihiro MORIGA

Faculty of Science and Technology
Tokushima University



Figs. 1 Color tuning in $LaTiO_2N$ via control of anion and cation stoichiometries



Figs. 2 Redshift of emission for $Ba_3Si_6O_{12}N_2$:Eu-type phosphors by substitution of Ba by Sr.

We have demonstrated that a color of the perovskite-type $LaTiO_2N$ oxynitride could be tuned from orange through yellow and green to pale gray or white by proper adjustment of the O/N ratio. (Moriga et al., *phys. stat. sol.* (a), 203, 2818 (2006)), whereas increasing Ti/La ratio deteriorates the reflectivity after the absorption edge (Moriga et al., *J. Ceram. Soc. Jpn.*, 115, 637 (2007)). We are now trying to make a redder or bluer oxynitride powders by partial substitution of the constituent cations, and by controlling of the cation and/or anion stoichiometries as well.

Oxynitride phosphors are recently spotlighted as yellow or red phosphors for white LEDs because oxynitrides have no toxicity, blue light are available for excitation source and oxynitrides possess low thermal quenching behavior, compared with oxide phosphors. We have found that $Ba_3Si_6O_{12}N_2$:Eu-type phosphors showed considerable redshift in emission wavelengths from 520nm for the Sr-free oxynitride up to 550nm for 50%-substituted oxynitride by Sr, with increasing Sr content (Sarda, Moriga et al., *J. Nano Res.*, 36, 1 (2016)).

Keywords : oxynitrides, eco-friendly pigment/phosphors,

E-mail: moriga@tokushima-u.ac.jp
Tel. +81-88-656-7423
Fax: +81-88-655-7025

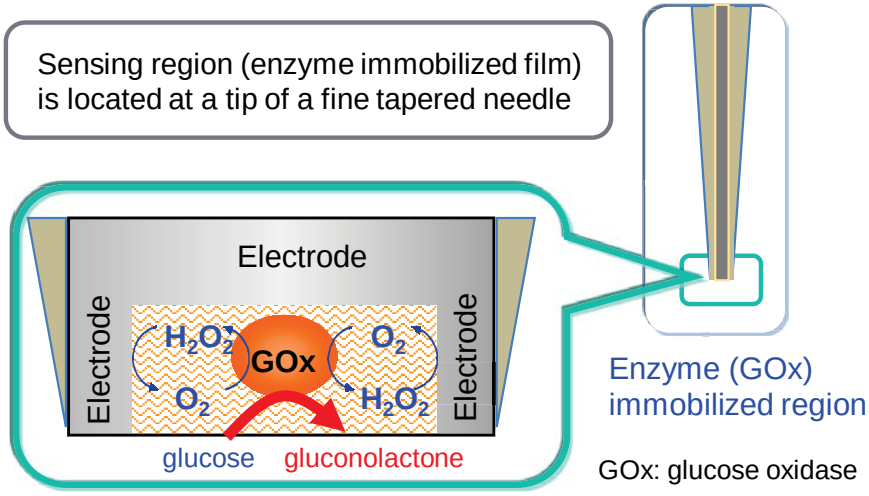
Faculty of Science and Technology
Tokushima University

Development of Minimally Invasive Type Biosensor for Continuous Glucose Monitoring

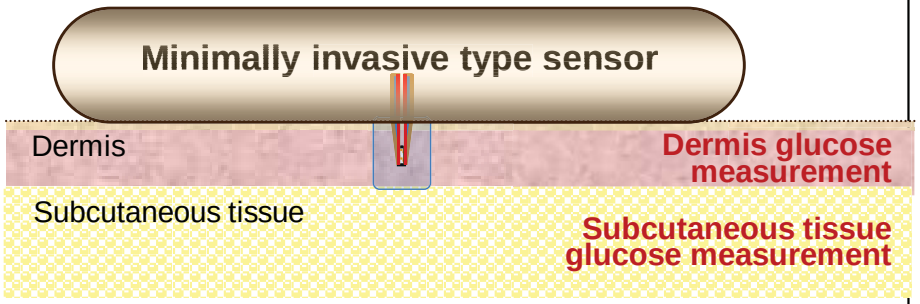
Professor Mikito Yasuzawa

Minimally invasive type glucose sensor

Sensing region (enzyme immobilized film) is located at a tip of a fine tapered needle



Only the most tip of a fine needle (less than 1.0 mm in length) must be inserted in the skin.



Sensor placement

Conventional sensor → **"Inserting"**

Minimally invasive type sensor → **"Sticking"**

Content:

Diabetes is a leading cause of morbidity and mortality and a major health problem around the world. It is well known that keeping good control of the blood glucose degree can prevent the onset and progression of serious diabetes complications. Therefore, it is important to accurately recognize the blood glucose degree and provide appropriate treatments. Daily self-monitoring of blood glucose (SMBG) is the essential procedure for blood glucose level recognition. However, it may require stressful action even after midnight and the observed value is a point without direction. Recently, implantable glucose sensors for continuous glucose monitoring system (CGMS) for diabetes patients have been developed and is now available on the market. They can provide useful information to predict the upcoming situation such as hyperglycemia and hypoglycaemia. However, they require the device to be inserted about 1 cm in length inside the skin. Therefore, the development of lower invasive CGMS is expected for the improvement of diabetic patients "quality of life (QOL)". We have recently developed a low invasive type glucose sensor, which has a sensing region at the tip of a fine pointed electrode. A clear sensor response correlative with the trend of blood glucose was obtained using a devise inserted in skin no more than 1 mm in length.

Keywords : Electrochemistry, biosensor, continuous glucose monitoring system, biocompatible material, eco-friendly water purification

E-mail: yasuzawa@tokushima-u.ac.jp

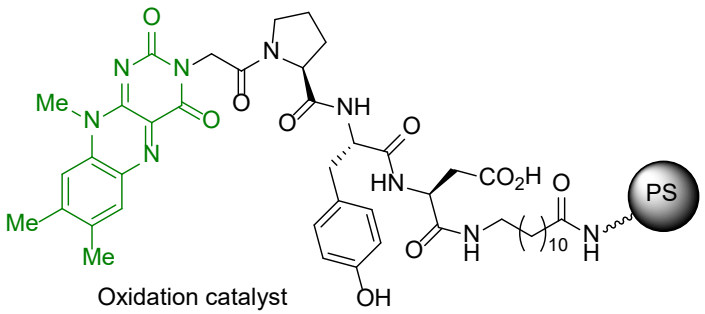
Tel. 088-656-7410

Fax: 088-655-7025

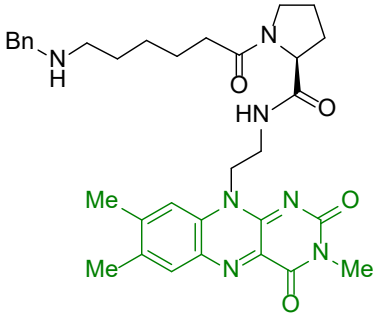
Faculty of Science and Technology
Tokushima University

Organic Molecules and Polymers with Catalytic Function

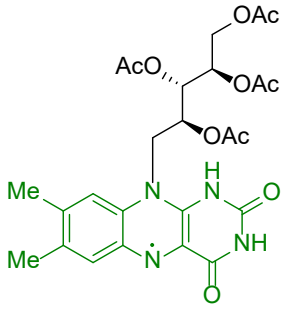
Associate Professor Yukihiro Arakawa



Oxidation catalyst
Chem. Sci. **2017**, *8*, 5468

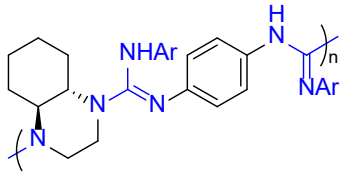


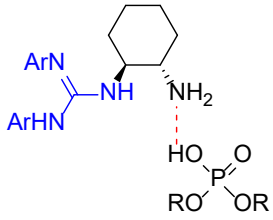
Photoredox catalyst
Org. Lett. **2019**, *21*, 6978



Brønsted acid catalyst
Chem. Commun. **2020**, *56*, 5661

Chiral Brønsted base catalysts





ACS Omega **2021**, *6*, 33215

Content:

A central theme of our research is to design and provide new organic synthetic methods that contribute to the green and sustainable chemistry, which includes the development of organic molecules and polymers with catalytic function (especially for asymmetric synthesis), environmentally friendly and metal-free syntheses, visible-light-driven organic reactions, and molecular transformations utilizing a flow microreactor.

As for the catalyst development, we have recently reported a flavin-based oxidation catalyst (*Chem. Sci*., **2017**, *8*, 5468), photoredox catalyst (*Org. Lett*., **2019**, *21*, 6978), and Brønsted acid catalyst (*Chem. Commun*., **2020**, *56*, 5661). In addition, we are also interested in developing the synthesis of chiral polymers bearing guanidines in the main chain and their application as asymmetric catalysts (*ACS Omega*, **2021**, *6*, 33215).

Keywords : organocatalyst, polymeric catalyst, photoredox catalyst, asymmetric catalyst

E-mail: arakawa.yukihiro@tokushima-u.ac.jp

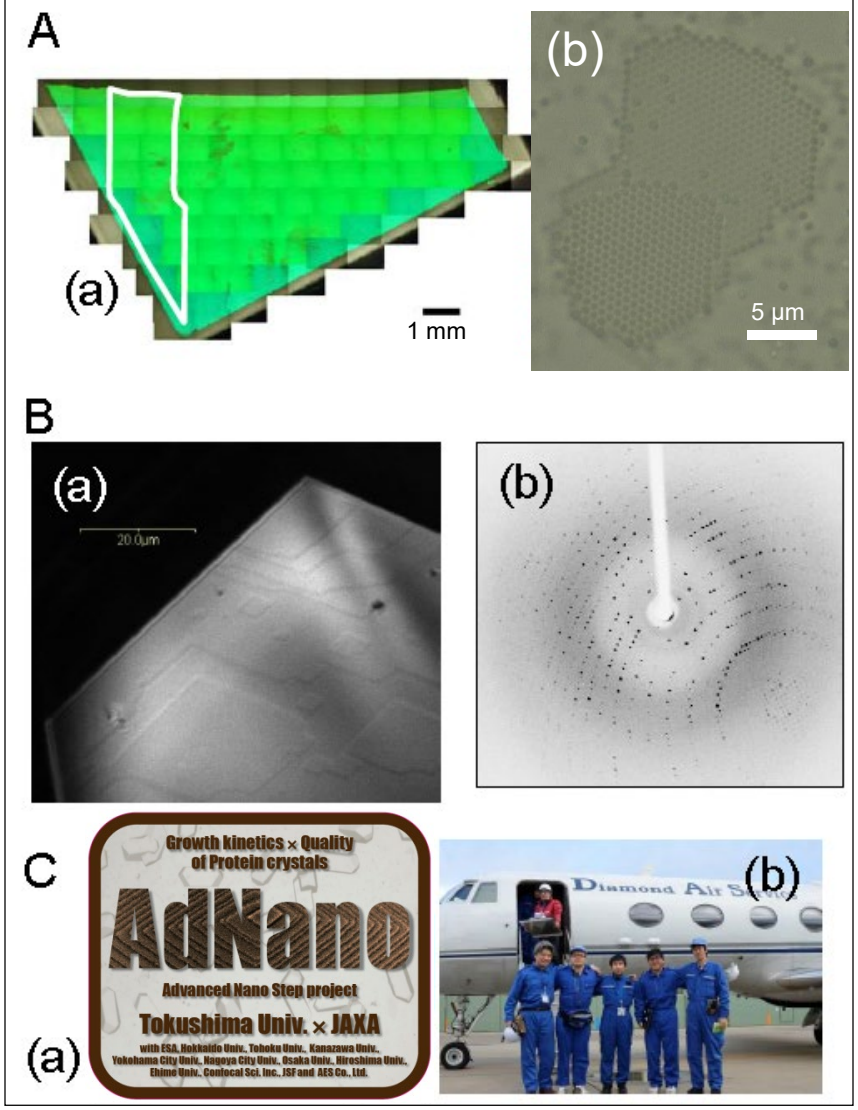
Tel. +81-88-656-9704

HP : http://www.chem.tokushima-u.ac.jp/A3/

Faculty of Science and Technology
Tokushima University

Fundamentals of Crystal Growth of Nano-Submicron Particles

Associate Professor Yoshihisa Suzuki



Content:

A. **Colloidal crystallization**: Colloidal crystals are hoping materials for optical circuits and optical computer in the future. We have successfully fabricated bulky grains (~ 6.1 mm^3) of a close-packed polystyrene colloidal crystal ((a)) by centrifugation. Recently, we have also studied dynamical crystallization processes at a single particle level using colloidal crystals with depletion attractions (b).

B. **In situ observation of molecular steps on protein crystal surfaces and novel crystallization techniques without any precipitants**: Fundamental studies and developments of novel techniques of protein crystallization are important for obtaining high quality crystals, which are prerequisites of genomic drug discovery. We are now studying kinetic bahaviors of molecular steps on the surface of a glucose isomerase crystal ((a)). We have also succeeded in fabricating high quality lysozyme crystals without using any precipitants ((b)) for the first time.

C. **Precise growth mechanisms of protein crystals under microgravity**: Microgravity is known to be a good environment for obtaining high quality protein crystals. Our Advanced Nano Step (AdNano) mission ((a)) in the international space station (ISS) is currently underway. Now, we analyze growth rates of glucose isomerase crystals during the fifth flight of AdNano mission in ISS. We have also used parabolic flight opportunities ((b)).

Keywords : Crystal Growth, Protein, Colloid, Microgravity

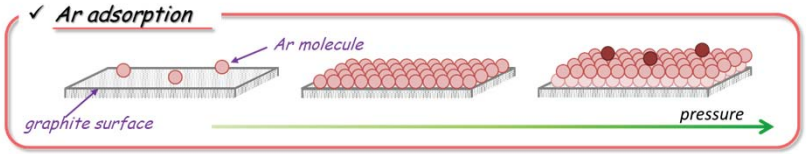
E-mail: yoshis@tokushima-u.ac.jp
Tel. +81-88-656-7415
Fax: +81-88-655-7025
HP : https://www.researchgate.net/profile/Yoshihisa_Suzuki/

Faculty of Science and Technology
Tokushima University

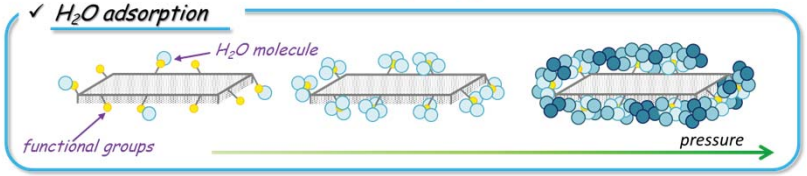
Elucidating the gas adsorption mechanism and developing its applications

Associate Professor Toshihide HORIKAWA

Non-polar vs. polar molecules adsorption on graphite surface

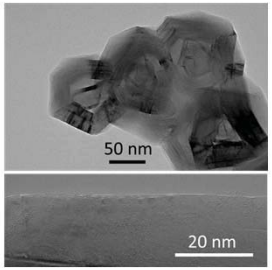


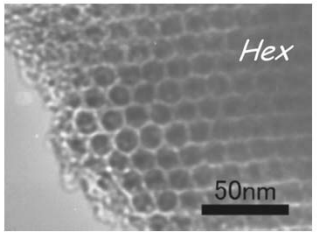
: layering adsorption mechanism



: clustering adsorption mechanism

● Non-porous graphite ● Highly ordered mesoporous carbon





* J. Phys. Chem. C (2011), pp. 2720–2726

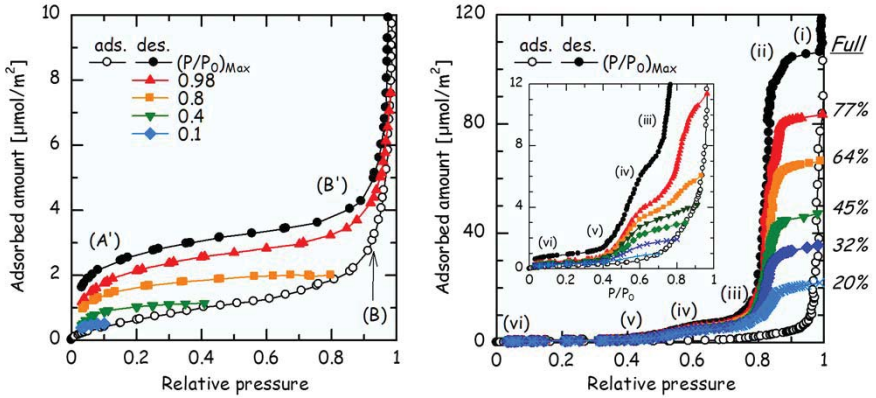


Fig. Water desorption scanning curves on (a) Carbopack F and (b) Hex at 273K [1].

Content:

Adsorption phenomena is applied many separation technologies, e.g. gas separation, environmental purification. When you use those technologies, you need to choose a suitable adsorbent from many types of adsorbents. If you could choose right one from those, you can save energy, time and cost. Therefore, it is very important to choose an optimized adsorbent.

However, sometimes there are no suitable or optimized adsorbents for the process, so we might need to develop an optimized adsorbent. When you develop a new material, you must understand what kind properties you want for the process according to the adsorption phenomena. I can help you to develop the material using my adsorption knowledge.

E-mail C-2 lab HP EDB

Keywords: gas adsorption
carbon materials
adsorption mechanism

E-mail: horikawa@tokushima-u.ac.jp
Tel. +81-88-656-7426
Fax: +81-88-656-7426
HP : http://www.chem.tokushima-u.ac.jp/C2/

Electroanalytical systems using track-etched microporous membrane electrodes

Faculty of Science and Technology
Tokushima University

Associate Professor Hitoshi Mizuguchi

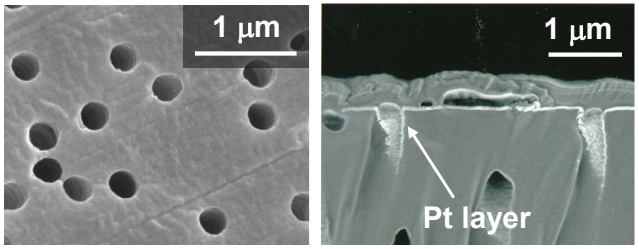


Fig.1 SEM images of track-etched microporous membrane electrode. Surface of the electrode (left), and. cross sectional view (right).

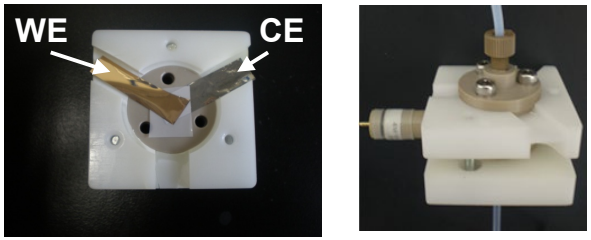


Fig.2 Structure of the proposed flow cell

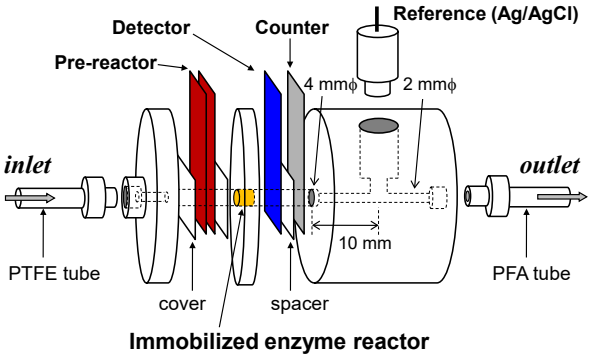


Fig.3 Amperometric enzyme biosensor

Content:

We recently reported an electrochemical flow cell in which the track-etched microporous membrane electrodes had been mounted. The electrode was prepared by sputter deposition of platinum or gold on the track-etched microporous membrane filters. The coatings were produced on the smooth flat surface and entrance of the cylindrical pores. Sample solution flows through the membrane filter while performing electrolysis. In this case, the sample solution flows through the cylindrical pores of the electrodes (Fig.1). The electrode enables efficient electrolysis in a flow condition. This property would be attributed to the limitation of growth of the diffusion layer at the entrances of pores. Various analytical systems can be built merely by piling up the track-etched microporous membrane electrodes which have a 10 μm thickness (see Fig.3). Although many researchers have investigated for quantitative electrolysis, the simplicity and flexibility of arrangement of electrodes as well as high efficiency of electrolysis is the greatest feature of the track-etched microporous membrane electrodes.

Keywords: track-etched membrane, biosensor, flow-based analysis

E-mail: mizu@tokushima-u.ac.jp

Tel. +81-88-656-7419

HP : http://www.chem.tokushima-u.ac.jp/B1/index.html

Faculty of Science and Technology
Tokushima University

Development of Advanced Inorganic Materials

Associate Professor Kei-ichiro, Murai

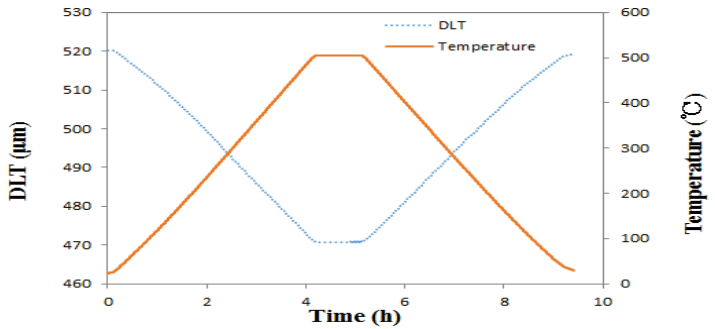


Fig.1. Diagram for dilatometry of $Zr_2(WO_4)(PO_4)_2$.

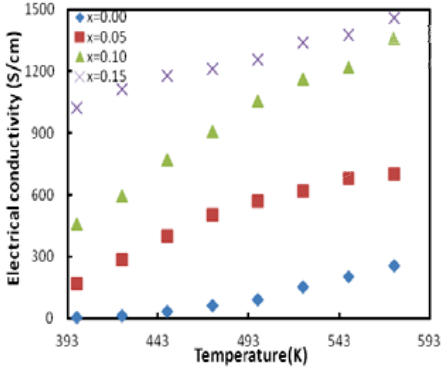


Fig. 2. Electric conductivities of $La_{1-x}Ca_xCoO_3$ (x = 0.00, 0.05, 0.10, 0.15)

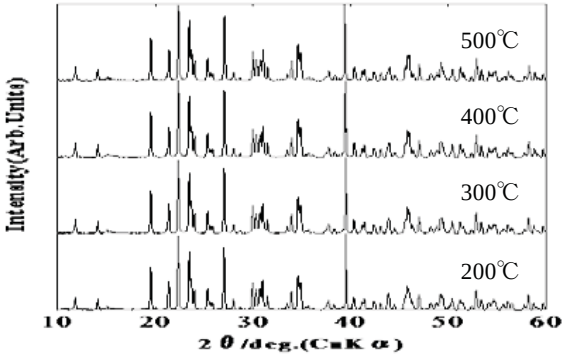


Fig. 3. Variation of in-situ XRD patterns for $Zr_2(WO_4)(PO_4)_2$ at the given temperatures.

Content:

The research work is developments of advanced inorganic materials such as negative thermal expansion materials (Fig. 1) or thermoelectric materials (Fig.2) made of oxides which is low in price, harmless and stable from physical and chemical viewpoint. X-ray diffraction (XRD) techniques are also used in materials characterization in our lab (Fig. 3). Crystal structure of materials has a close connection with its properties.

Negative thermal expansion oxide have a range of potential engineering, photonic, electronic, and structural applications. If a negative thermal expansion material is mixed with a "normal" material which expands on heating, it could be possible to make a zero expansion composite material.

Today, some alloys are in practical use as thermoelectric materials. However, Perovskite-type materials are more stable in high temperature region. In our lab., it was found that some cation-doping oxides had higher values than non-doped materials in thermoelectric properties.

Crystal structures of materials above mentioned are investigated by XRD and Rietvelt analysis.

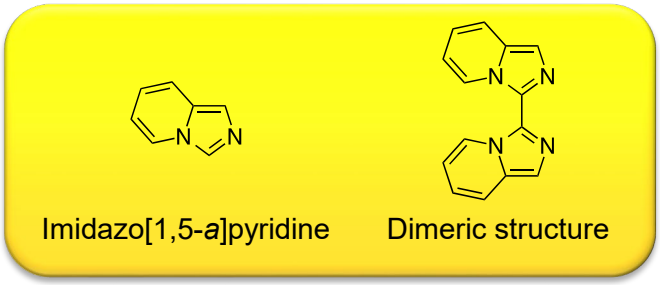
Keywords : Advanced Materials, Crystallography

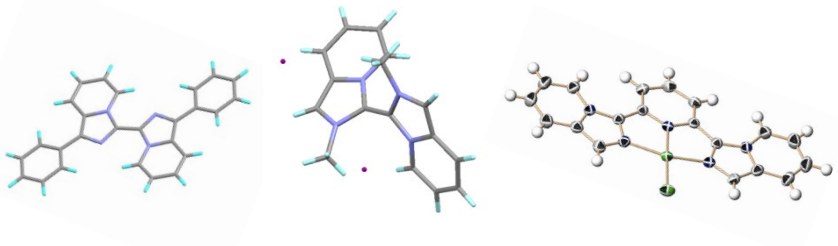
E-mail: keimurai@tokushima-u.ac.jp
Tel. +81-88-656-7424
Fax:+81-88-655-7025

Faculty of Science and Technology
Tokushima University

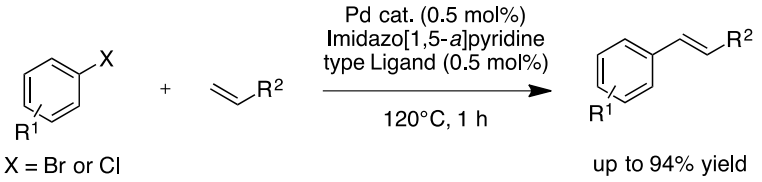
Synthesis and Functionalization of Heterocycles

Associate Professor Fumitoshi, Yagishita





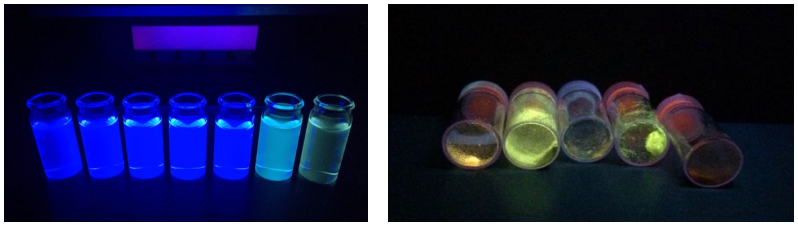
<Application as Ligands to Mizoroki–Heck Reaction>



X = Br or Cl

up to 94% yield

<Fluorescence in solution and in the solid state>



Content:

Imidazo[1,5-*a*]pyridine derivatives have been drawn considerable attention because of their potential application as pharmaceutical agents and functional materials. Therefore, various molecules featuring imidazo[1,5-*a*]pyridine skelton have been synthesized and characterized.

Recently, we have synthesized the novel dimeric imidazo[1,5-*a*]pyridine. These compounds have been examined to apply as the ligand in catalytic systems and functional materials such as sensing molecules and high efficient light emitting molecules. For example, the palladium-catalyzed Mizoroki–Heck reaction of aryl bromides and chlorides with alkenes using our imidazo[1,5-*a*]pyridine-$PdCl_2$ system afforded the desired products in good-to-high yields with the low palladium loadings and short reaction times. On the other hand, the substituted dimeric imidazo[1,5-*a*]pyridines exhibited relatively strong emissions.

Keywords : Heterocycle, Functionalized molecule

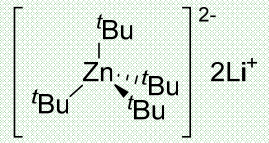
E-mail: yagishitaf@tokushima-u.ac.jp
Tel. +81-88-656-7405
Fax: +81-88-655-7025

Faculty of Science and Technology
Tokushima University

Chemoselective Transesterification and Polymer Synthesis Using Zinc Art Complex

Senior Lecturer Miyuki Oshimura

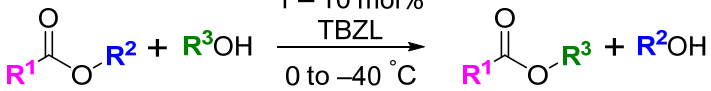
dilithium tetra-*tert*-butylzincate (**TBZL**)



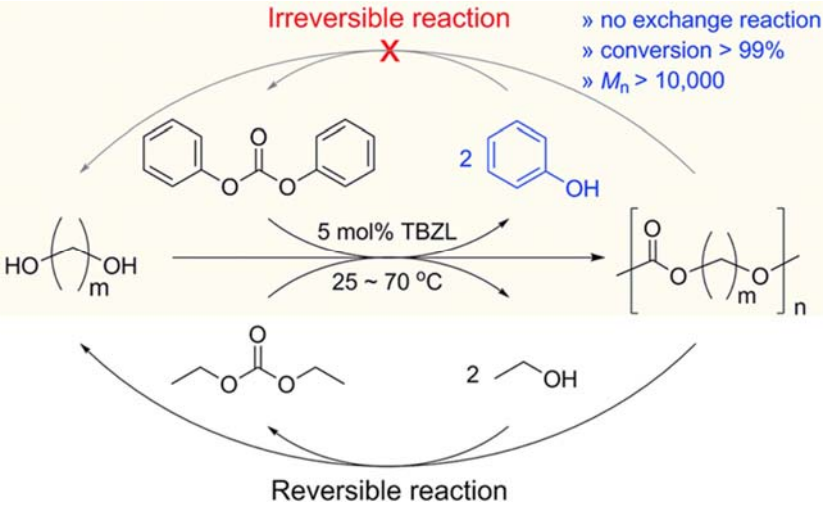
» easy to prepare
» low basicity, high nucleophlicity
» tolerance to H_2O

1. Transesterifications under mild conditions

» at low temperature
» tolerance to H_2O and amines



2. Synthesis of Aliphatic polycarbonates



Content:

I am doing research using zinc art complex, $^tBu_4ZnLi_2$ (TBZL), based on polymer synthesis having biodegradability and biocompatibility.

1. Transesterifications under mild conditions

Transesterification is a useful method for preparing various esters. However, strong acid/base and severe conditions are generally required. The transesterification of alcohols with carboxylic esters were investigated in the presence of a catalytic amount of TBZL as a catalyst. The transesterification occurred at low temperature. In addition, the transesterification proceeded even in the presence of H_2O and amines.

2. Synthesis of Aliphatic polycarbonates

The polycondensation of diphenyl carbonate with diols catalyzed by TBZL were carried out. The irreversible polycondensations proceeded under moderate polymerization temperature and atmospheric pressure. This polymerization system is a useful to obtain aliphatic polycarbonates without requiring a tedious procedure.

Keywords : high-functional materials, biodegradable polymer

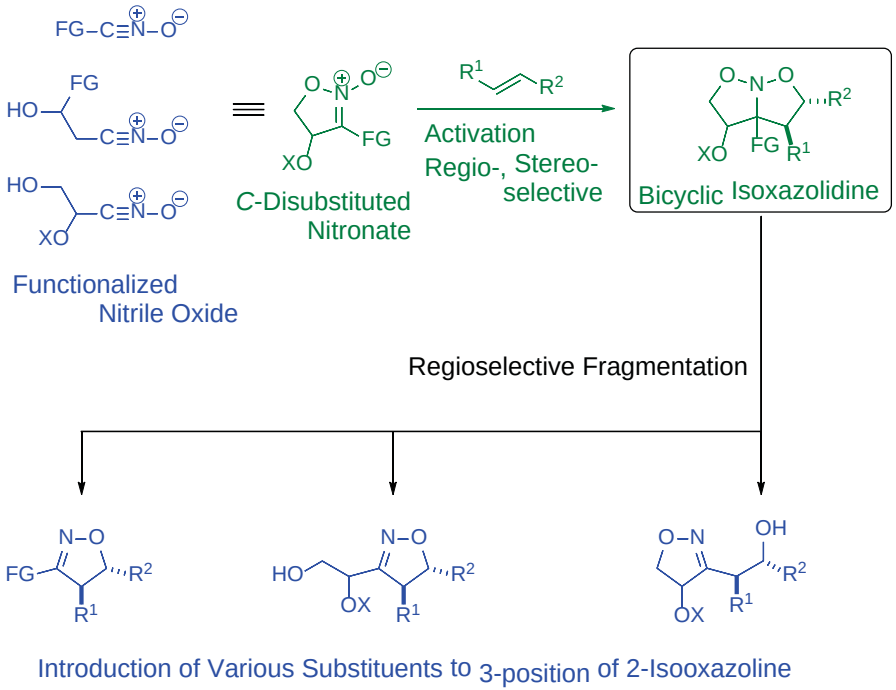
E-mail: oshimura@tokushima-u.ac.jp
Tel: +81-88-656-7404
Fax: +81-88-656-7404
HP : http://poly.chem.tokushima-u.ac.jp/

Faculty of Engineering
The University of Tokushima

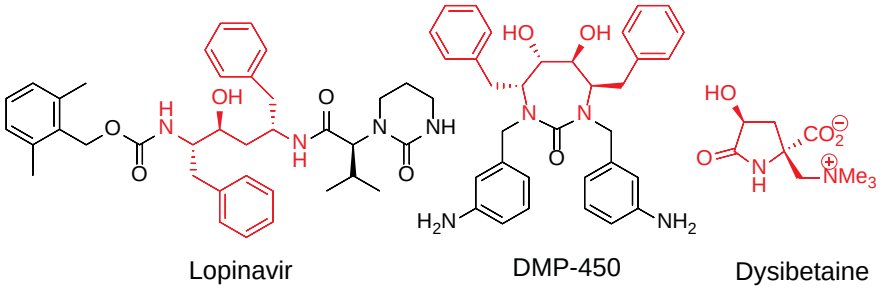
Research on synthesis of heterocycles

Associate Professor Masaki Nishiuchi

C-Disubstituted Nitronates as a Synthetic Equivalent of Functionalized Nitrile Oxides



Application to Biologically Active Substance



I research on the development of the selective and effective synthetic method of the heterocycle compound that the application to biologically active substance (medicine, agricultural chemicals, etc.) is expected. Mainly, about the synthetic method of the hetero five-membered rings compounds containing nitrogen, oxygen using 1,3-dipolar cycloaddition reactions :

1) Activation of 1,3-DC reaction by catalyst
2) Development of regio- and stereoselective reaction
3) Synthesis of biologically active substance

I have accomplished the following matters so far:

1) Development of high-rate acceleration and regio- and stereocontrol of nitrile oxide cycloadditions by Lewis acid.
2) Development of *C*-disubstituted nitronates as a synthetic equivalent of functionalized nitrile oxides.
3) Formal synthesis of dysibetaine and synthesis of core structure of lopinavir (HIV-prtease inhibitor).

Keywords : biologically active substance, stereoselective, regioselective, catalytic reaction

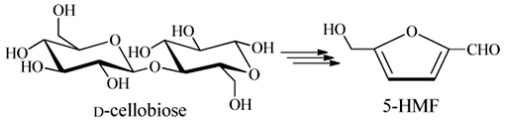
E-mail: nishiuchi@tokushima-u.ac.jp
Tel. +81-88-656-7400
Fax: +81-88-655-7025
HP :

Faculty of Science and Technology
Tokushima University

In situ NMR monitoring of Conversion of Polysaccharides into Value-Added Chemicals

Associate Professor Ken Yoshida

<図表>



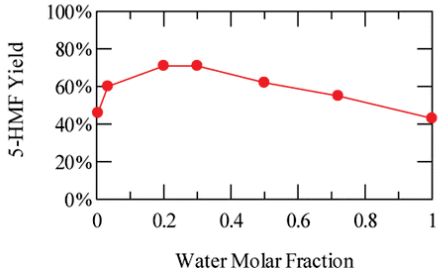


Fig. 1. 5-HMF yield in the cellobiose decomposition in DMSO/water mixture solvent.

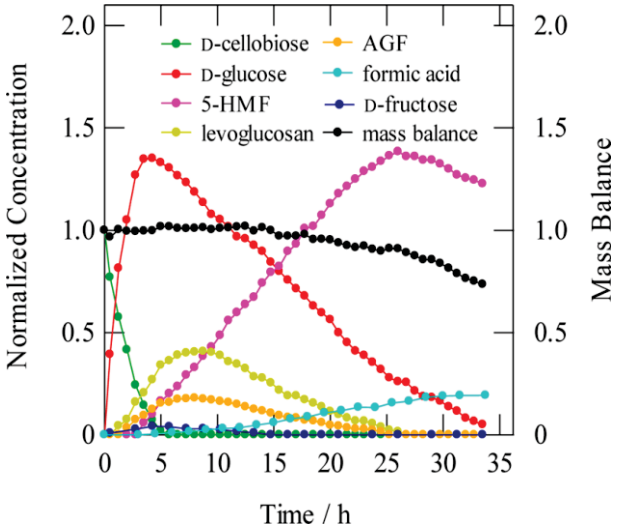


Fig. 2. Time course of the reactant and product of the decomoposition of cellobiose determined by using ^{13}C in situ NMR monitoring.

Content:

Biomass-derived poly-saccharides have attracted attentions as the novel renewable sources. Recently we succeeded in the production of 5-hydroxymethyl-2-furaldehyde (5-HMF) from cellobiose, the model disaccharide for cellulose (H. Kimura et al., J. Phys. Chem. A, 117, 10987 (2013); Fig. 1). 5-HMF is a center of focus today as a biomass-derived valuable that can be converted into biofuels, fine chemicals, and polymers.

In the decomposition reaction steps of saccharides, a variety of isomers, tautomers, and precursors are generated as intermediate products. Solution NMR spectroscopy is a powerful method to monitor all of those species involved in the reactions. By using ^{13}C NMR, each of the individual species can be distinguished from each other. The positions of the glucose units in the oligomers can be specified. The in situ NMR method allows us to determine the time course of the product and reactant species. As shown in Fig. 2, reliable data are obtained with a single setup of the in-situ experiment. The best conditions for the target species can be determined on the basis of the reaction kinetics.

Keywords : saccharides, in situ NMR, 5-HMF

E-mail: yoshida.ken@tokushima-u.ac.jp
Tel. +81-88-656-7669
Fax: +81-88-655-7025
HP : http://www.chem.tokushima-u.ac.jp/B2/

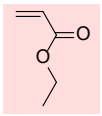
Faculty of Science and Technology
Tokushima University

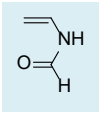
Development of Though Hydrogels by Focusing on Monomer Structure and Polymerization Mechanism

Assist. Prof. Ryo Kawatani

PR: Polymerization Rate

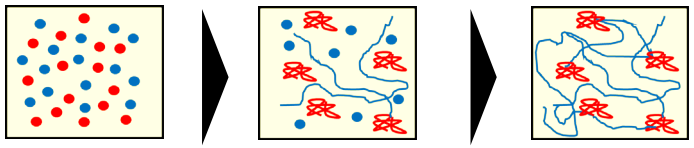
①





Hydrophobicity Hydrophilicity

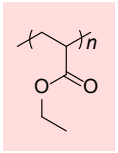
PR	Fast	Slow
Intermol. Interaction	Hydrophobic interaction	Hydrogen bonding

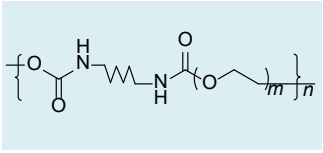


Before Early Stage Later Stage

Homogenous	Entanglement network with hydrophilic monomers	Entanglement network with hydrophilic networks

②





Hydrophobicity Hydrophilicity

Type	Radical	Polyaddition
PR	Fast	Slow
Intermol. Interaction	Hydrophobic Interaction	Hydrogen bonding

Content:

Development of Tough Hydrogels

By introducing intermolecular interactions into the gel, molecular interactions can preferentially fragmentation when mechanical loads are applied, allowing for the consumption of mechanical energy. Intermolecular interactions in the gel is key point.

Two methods have been employed to develop tough hydrogels, with the aim of efficiently introducing intermolecular interactions into the gel:

①Exploiting Differences in Polymerization Reactivity (Radical Polymerization)

Radical polymerization is carried out using two monomers with significantly different polarities and polymerization rates simultaneously. This leads to the preparation of a hydrogel where molecular entanglement is promoted, resulting in a tough hydrogel.

②Combination of Two Polymerization Mechanisms

Combining a monomer that undergoes radical polymerization and a monomer that undergoes addition polymerization, both polymerization mechanisms are employed simultaneously to prepare the hydrogel. This approach results in a tough hydrogel.

Keywords : Hydrogel, Radical Polymerization, Polyaddition

E-mail: kawatani.ryo@tokushima-u.ac.jp

Tel. 088-656-7401

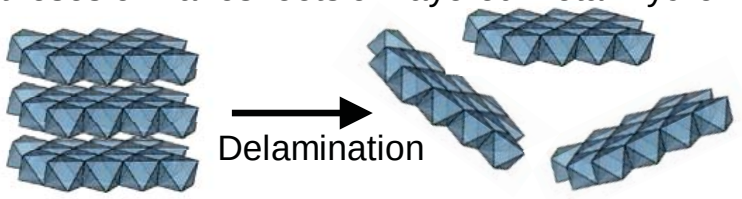
HP : https://poly.chem.tokushima-u.ac.jp

Faculty of Science and Technology
Tokushima University

Syntheses and Applications of Layered Metal Hydroxides

Assistant Professor Masashi Kurashina

I. Syntheses of Nanosheets of Layered Metal Hydroxides



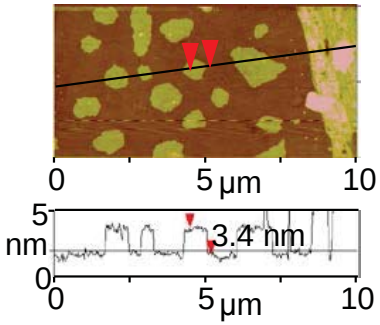


Fig. 1 AFM image of cobalt hydroxide nanosheets

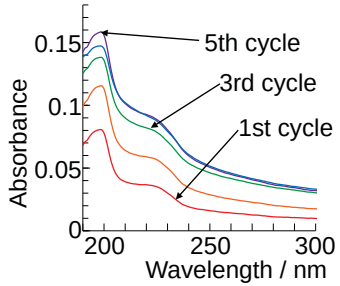
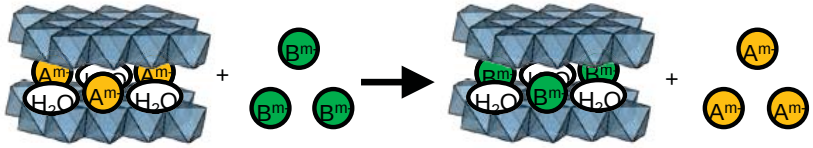


Fig. 2 UV absorption spectra of restacking of nickel hydroxide nanosheets

II. Control of Interlayer ions in Layered Metal Hydroxides



- Adsorption of polyoxomolybdate and borate
- Control of elution of phosphate

Fig. 3 Growing tests of Japanese mustard spinach using a Mg/Fe-type layered double hydroxide

Content:

The layered metal hydroxide is a layered compound consisted of repeating stacking of nano-meter-sized metal hydroxides. This compound is mainly synthesized by addition of base into the metal solution.

Inorganic nanosheets have been prepared by delamination of layered materials. Nanosheet has an ultimate two-dimensional anisotropy and manifests unique physical properties arising from size effects. We have synthesized nickel and cobalt hydroxides nanosheets (Fig. 1) and assembled these nanosheets by stacking on the glass slide to make new lamella structure(Fig. 2).

Layered double hydroxide is a layered compound that contains divalent and trivalent metal ions. It consist of hydroxide layer and interlayer anion, and the interlayer anion is captured and able to exchange. We use this property for adsorption and controlled-release of anions. Adsorption of polyoxomolybdate and borate control of elution of phosphate have been investigated and try to apply it to fertilizer(Fig. 3).

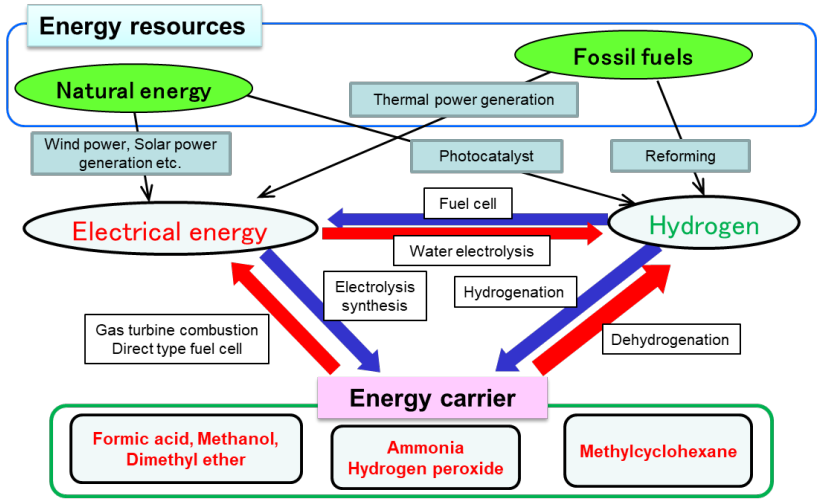
Keywords: layered compound, metal hydroxide, nanosheet, ion exchange

E-mail: kurashina.masashi@tokushima-u.ac.jp
Tel. +81-88-656-7418
Fax: +81-88-655-7025

Faculty of Science and Technology
Tokushima University

Development of Heterogenous Catalysts for Synthesis and Utilization of Hydrogen Energy Carrier

Assistant Professor Naohiro, Shimoda

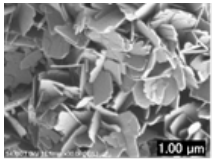


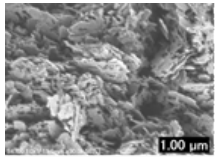
- Supply Instability in power generation from natural energy
- "Green hydrogen" synthesis from water using surplus electricity
- Portability and storability issues in hydrogen utilization

⇒ Utilization of hydrogen energy carrier substances

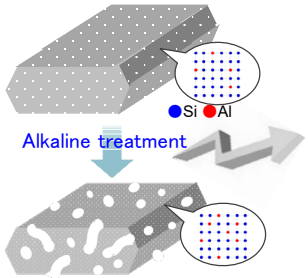
Research

Dimethyl ether synthesis from methanol over zeolite catalyst

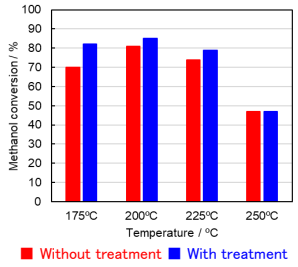




FER type zeolite



Catalytic reaction test of Methanol dehydration



☑ Formation of meso-pores ➢Improvement of MeOH conversion
☑ Reduction of Si/Al ratio ➢Suppression of carbon deposition

Content:

Toward the realization of a hydrogen energy society

In order to efficiently use the limited fossil fuel resources as energy, it is important to build a hydrogen energy society centered on the fuel cell power generation system. In addition, electric energy produced from natural energy such as wind power and solar power is inefficient in transportation and storage. Therefore, the problem is that the supply and demand peaks of electricity do not match. Under such circumstances, hydrogen energy has been attracting attention as an energy storage medium in recent years. However, hydrogen alone is a substance that is difficult to handle due to its poor storability and transportability. Therefore, it is desired to convert and handle hydrogen as another chemical substance that can easily extract and store hydrogen, so-called hydrogen energy carrier.

Development of solid-sate catalyst

In our laboratory, we are focusing on ammonia, methane, methanol, and dimethyl ether, which are candidate materials for hydrogen carrier substances. We are also developing solid catalyst materials such as supported metal catalysts and zeolite catalysts to efficiently proceed various heterogeneous reactions of synthesizing hydrogen carrier substances and of extracting hydrogen from them.

Keywords: Hydrogen, Solid-state catalyst, C1 chemistry

E-mail: shimoda@tokushima-u.ac.jp
Tel.: +81-88-656-7430
Fax: +81-88-656-7432
HP : http://www.chem.tokushima-u.ac.jp/C3/

Faculty of Science and Technology
Tokushima University

Molecular and Electron Dynamics in Materials under High Pressure

Assistant Professor Naoki Noguchi

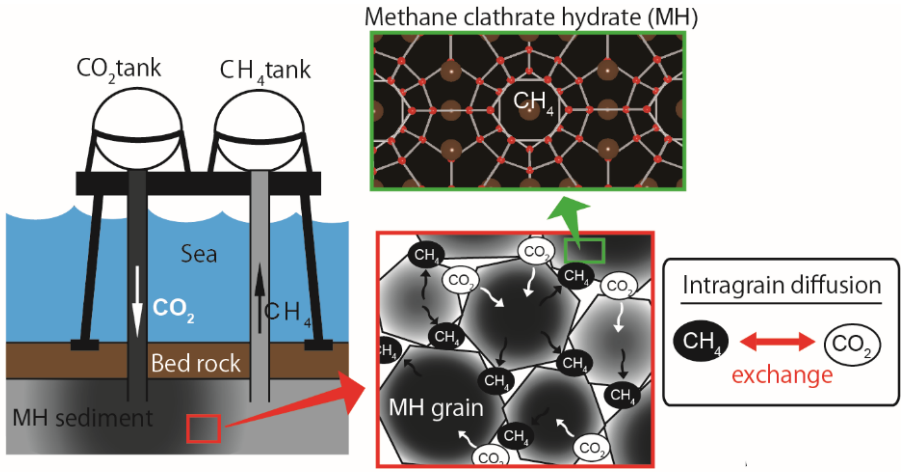


Fig.1. CH_4-CO_2 replacement in CH_4 clathrate hydrate (MH) bearing sediments below seafloor

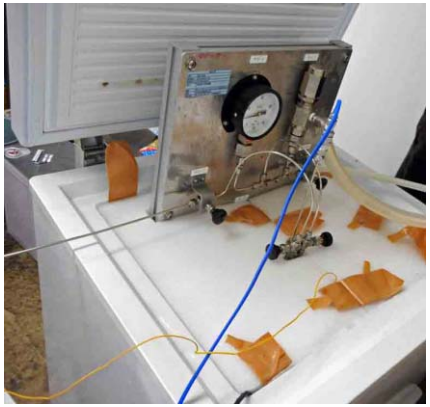


Fig.2. High-pressure reactor

Fig.3. Crystal of $FeGa_3$

Content:

Dynamics of molecules and electrons in materials controls transport properties such as conductivity, thermal and mass diffusivities. Investigations for the dynamics will contribute to better knowledges for the elemental processes of the transport phenomena.

Our research subjects are (1) the proton and molecular dynamics in ice and gas clathrate hydrates, and (2) the electron dynamics in thermoelectric materials. For the first subject, we investigate the CH_4-CO_2 replacement reaction in CH_4 hydrate (MH) using infrared (IR) spectroscopy and diamond anvil cell. This study will help realize the recovery of CH_4 from MH bearing sediments below seafloor (Fig. 1). A high-pressure reactor dedicated to the synthesis of MH has been constructed for this subject (Fig. 2). For the second subject, the electron dynamics near the Fermi level in a thermoelectric material, $FeGa_3$ (Fig. 3), is investigated using IR spectroscopy and He cryostat.

Keywords : proton dynamics, IR spectroscopy, high pressure, diamond anvil cell

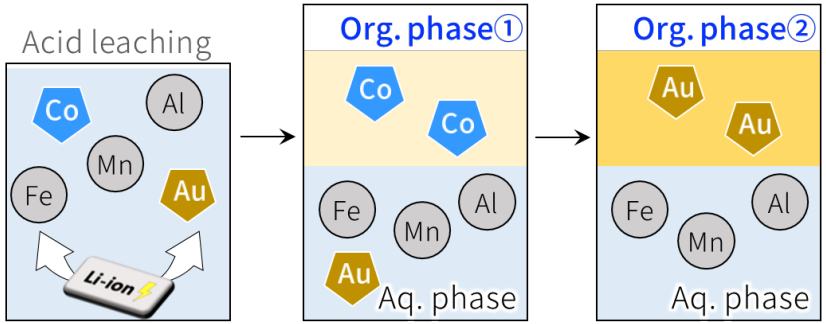
E-mail: noguchi.naoki@tokushima-u.ac.jp
Tel. +81-88-656-9977
HP : http://www.chem.tokushima-u.ac.jp/B2/

Faculty of Science and Technology
Tokushima University

Deep Eutectic Solvents for Critical Metal Refining and Recycling

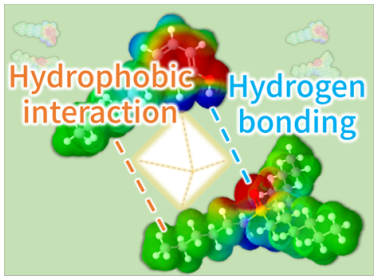
Assistant Professor Takafumi Hanada

A) Conventional method: Solvent extraction process



✓ Rapid & High purity ✘ Harmful chemicals

B) Green alternative：deep eutectic solvents (DESs)



✓ Less volatile & easy preparation

▶ Environmentally benign separation system

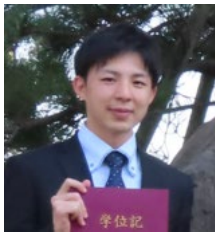
Content:

The solvent extraction method, which is one of the rare metal separation techniques, is a practical process that allows for rapid and high-purity separation and recovery of target metals. However, concerns about environmental pollution arise from the use of inorganic acids and organic solvents in the leaching and extraction stages.

In recent years, deep eutectic solvents (DESs) have gained attention as alternative solvents to inorganic acids and organic solvents. DES is a mixture that becomes a liquid simply by combining hydrogen bond donor and acceptor compounds. It was first reported in 2003 as a new solvent of the 21st century (Abbott *et al., Chem. Commun.*). DES is known as an environmentally friendly solvent due to its low volatility and low toxicity. However, most existing DESs are hydrophilic, making it difficult to apply them to separation techniques such as solvent extraction.

Therefore, this study focuses on hydrophobic DES, which are immiscible with water, with the aim of applying them to the solvent extraction process for rare metals. Furthermore, by utilizing the unique intermolecular interactions between the hydrogen bond donor and acceptor compounds that constitute DES, the study aims to develop advanced rare metal separation systems.

Keywords：Deep eutectic solvents, critical metals, extraction, separation



E-mail: hanada@tokushima-u.ac.jp
Tel. +81-88-615-8604
HP https://www.chem.tokushima-u.ac.jp/C4/