航空機実験用超臨界状態光化学反応装置の開発

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Development of a Compact Photoreactor for Parabolic Flight Experiments in Supercritical Fluids

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1. Objectives

Chiral photochemistry is one of the most intriguing and challenging topics in current chemistry. We performed the enantiodifferentiating photoisomerization of (*Z*)-cyclooctene (**1Z**) to (*E*)-isomer (**1E**) sensitized by optically active menthyl (**Men**), 8-phenylmenthyl (**8Ph-Men**) and diacetone fructose (**DAF**) pyromellitates (**Pyro**) (**Fig. 1**) in organic solvents to reveal that the enantiomeric excesses (ee's) of **1E** can be controlled by temperature, pressure, and solvent. Interestingly, the product's ee showed a dramatic, discontinuous dependence on pressure when the photosensitization was carried out in near-critical (nc) and supercritical (sc) CO_2 (**Fig. 2**) [1]. The results are rationalized by the variation in CO_2 clustering around the intervening exciplex, which is affected by the density fluctuation of nc/scCO_2 and therefore expected to be exaggerated under microgravity. To verify this, a compact photoreactor for parabolic flight experiments in supercritical fluid was newly developed.

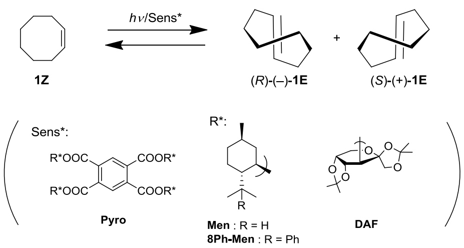
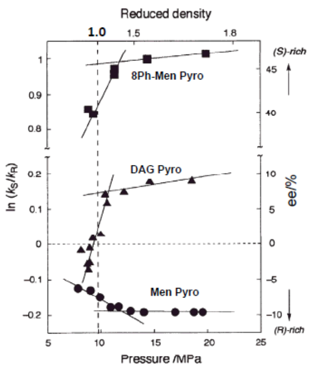


Fig. 1 Enantiodifferentiating photoisomerization of **1Z** sensitized by a variety of chiral pyromellitates.



$$ee = \frac{M_S - M_R}{M_S + M_R}$$

Fig. 2 Pressure effect on the ee of **1E**.

2. Compact Photoreactor for Parabolic Flight Experiments in Supercritical Fluids

Fig. 3 illustrates the components of the photoreactor. The reaction cells (shown as "SC-Cells" in the figure) are made of sapphire tubes to enclose the high pressure of supercritical CO_2. The internal dimension of the cell was 5.9 mm ϕ x 34 mm = 0.93 cm^3. Three identical cells surrounding a UV lamp (λ = 254 nm) were heated with silicone rubber-coated heaters up to the reaction temperature (45 °C). The temperature was controlled with a microcomputer (shown as "dsPIC" in **Fig. 3**) by monitoring the inside temperature of each cell. The UV lamp was automatically switched on/off when the z-axis G becomes smaller than a preset threshold with the microcomputer by monitoring the gravity level with a G-sensor. The experimental parameters, including acceleration (3 axes), inside temperature of each cell and photodiode output monitoring the UV intensity, were recorded with a data logger. It was verified that the temperature (fluctuation within ±1 °C) and UV illumination (**Fig. 4**) were accurately controlled by the system throughout the actual parabolic flights.

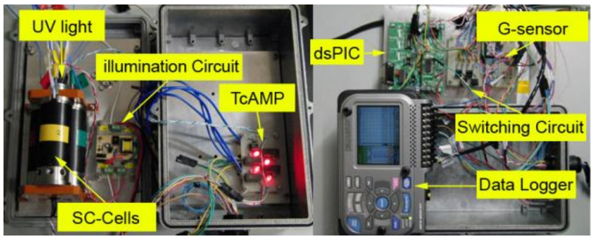


Fig. 3 Components of the photoreactor

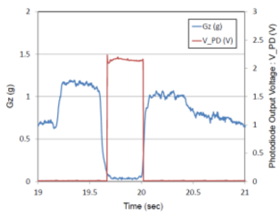


Fig. 4 Control of the llumination of UV lamp.

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航空機実験用ハニカムフィルム作製装置の開発

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Development of Honeycomb Film Fabrication Apparatus for Parabolic Flights

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1. Objectives

Shimomura et al found that fine porous polymer films ("honeycomb films") could be obtained when water vapor was added to casted polymer solutions[1,2]. Although the protocol is very simple, the uniformity and ordering of the pores are quite fine (see **Fig. 1**). Various applications have been investigated and for those larger films are desired. However unwanted domain formation (see **Fig. 2**) is often observed and preventing the honeycomb films from providing maximum capabilities to the applications. The authors speculate that this might arise from natural convections due to gravity and has tried low gravity experiments with parabolic flights to avoid the effect of the natural convections.

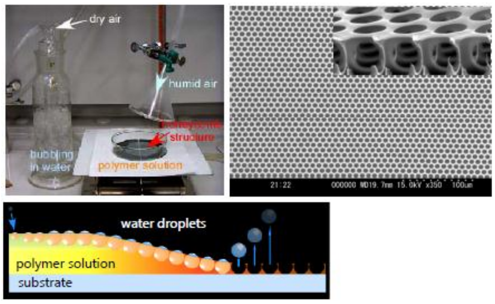

Fig. 1 Fabrication of a honey comb film

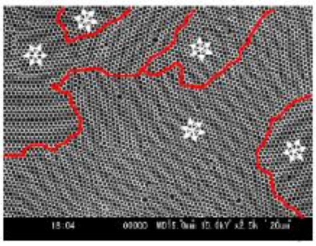

Fig. 2 Domain formation

2. Parabolic Flight Experiments

The components of the honeycomb film fabrication apparatus for parabolic flights are shown in **Fig. 3**. A honeycomb film is fabricated by casting a polymer solution (polystyrene + chloroform + surfactant). The polymer solution poured in a cell made of PTFE is initially confined in a cell with electrical valves as shown in **Fig. 4**. When the solenoid valve controller having a G-sensor detects low gravity less than a threshold value, the solenoid valve inserted in the exhausted line will be opened to start casting and then, a few seconds after, another electrical valve inserted in the water vapor line will be opened to start vapor condensation onto the surface of the casted polymer solution. The process of the film formation is recorded with a video camera. The first parabolic flight experiments were tried in May, 2011, but acceleration just before a microgravity period and an air flow to the exhaust and from water vapor lines deformed the surface of the solutions. To avoid this, the new apparatus employed a swing arm mechanism and a novel design for the cell part. The second parabolic flights were carried out in Dec. 2011 and the new apparatus succeed to eliminate the surface deformation.

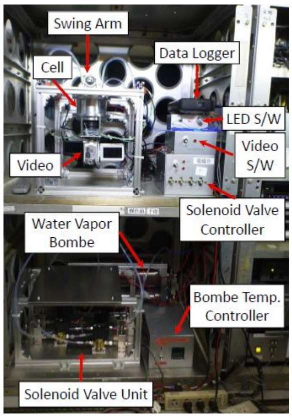

Fig. 3 Honeycomb film fabrication apparatus

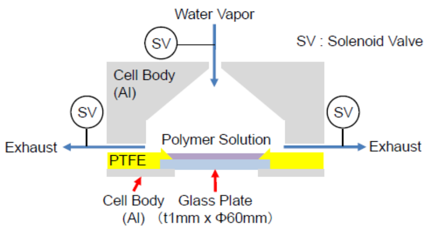

Fig. 4 Schematic representation of the cell

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宇宙実験支援のための熱物性計測

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Thermal Property Measurement for Support of Microgravity Experiment in JAXA

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1. Introduction

Utilization of the space environment, especially utilization of microgravity are greatly expected to be available to produce the new or high-quality material which can't be gotten on the ground. On the other hand, it is clear that solidification and crystallization of materials are affected by Marangoni flow or wettability of container even they don't matter on the ground.

In JAXA, we have developed the evaluation technology of wettability since 1990[1]. And we have supported the microgravity experiments by these evaluation technology on the ground. These measurement data are opened to the public in JAXA Web pages as opened data base[2].

2. Experiment Support Systems

Table 1 shows our support system which can be used for decision of the microgravity experimental condition. All systems are set in Tsukuba Space Center. Especially, Wettability/Surface tension Measurement Device (shown in **Fig. 1**) was developed by JAXA. Its specification is shown in **Table 2**.

Table 1 Experiment support systems

No.	System	Measured Value
1	Wettability / Surface tension Measurement Device	Contact Angle, Surface Tension
2	Thermal Diffusivity Measurement Device by Laser Flash Method	Thermal diffusivity, Specific Heat, Thermal Conductivity
3	High Temperature Oscillating Viscometer	Coefficient of Viscosity

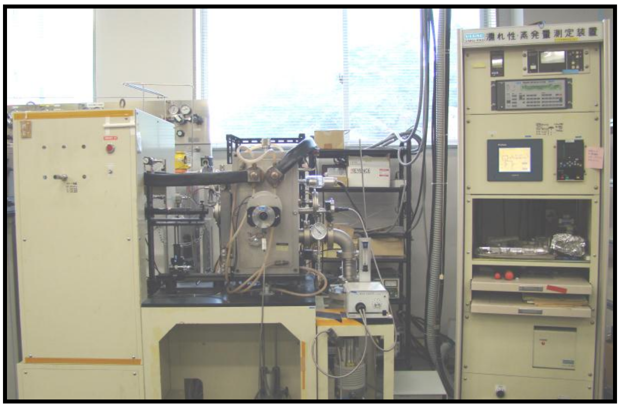

Fig.1 Wettability / Surface tension Measurement Device

Table 2 Specification of Wettability/Surface tension Measurement Device

Temperature range	Room temperature – 1500 degree C.
Temperature monitor	R-type(B-type) thermocouple
Atmosphere	Vacuum, Inactive gas and Low concentration reducing gas
Pressure	0.01Pa – atmosphere pressure
Heating Method	Tungsten mesh heater
Vacuum pump	Dry pump and turbo molecular pump
Image acquisition	Two axes CCD camera
Sample holdings	Static drop method, Extrusion method

3. Support Results

Many measurement cases are related to experiments in ISS or discussion in ground for ISS experiment. For Example, "Hicari" Experiment which aims to make the high-quality SiGe semiconductor crystal in microgravity received the support by our systems on ahead. The data which was measured by our system have served as a useful reference.

In addition to this, some themes which use the "Gradient Heating Furnace (GHF)", "Electrostatics Levitation Furnace (ELF)" or "Multi-purpose Small Payload Rack (MSPR)" were supported as well as Hicari. Not only the crystal growth experiment but also the combustion experiment is included in these supported cases.

4. Future Prospects

Researchers which aim the ISS experiment can use our systems for decision of the experiment condition on the ground. In addition our data base can be the reference for many potential users in the future. In these ways, the result of experiment in ISS will be maximized.

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ジルコニア式酸素ポンプを用いた低酸素分圧下における金属高温融体の表面張力測定

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渡辺直行（首都大），渡邊匡人（学習院大）

Surface Tension Measurement of High Temperature Molten Metal under Low Oxygen Partial Pressure Atmosphere using Zirconia Oxygen Pump

1. Introduction

The ability to measure accurate surface tension of molten metals is important for reliable numerical calculation of high temperature melt processes such as welding and casting. One such promising technique is the oscillating droplet technique using electromagnetic levitation (EML). When this technique is employed on the ground, theoretically-derived Cummings and Blackburn calibration [1] is required because the levitated droplet is deformed from a spherical shape due to the gravitational acceleration and magnetic force from a levitation coil. However this calibration has not been confirmed by experiment completely. However this calibration has not been validated by an experiment completely because the influence of the Po_2 on surface tension has not been considered in the experiment; oxygen is strong surfactant for molten metals.

In order to validate the Cummings and Blackburn calibration properly, a long microgravity experiment in consideration of the influence of the Po_2 is expected at the International Space Station (ISS). One possibility for the Po_2 control at the ISS experiment is to employ a zirconia oxygen pump.

A zirconia oxygen pump was used to control the oxygen partial pressure of atmospheric gas during surface tension measurement of molten nickel by oscillating droplet method using EML on the ground. The purpose of this study was to investigate the effectiveness of the oxygen pump for the Po2 control in the surface tension measurement at the ISS.

2. Experimental procedure

High purity nickel (provided from Dr. K. Tanaka, Sumitomo Metal Mining Co., Ltd.) was electromagnetically levitated and then melted under flow condition (2L/min) of Ar-He mixed gas. The Po_2 of the gas was maintained to 3.8×10^{-19} Pa by the oxygen pump (ULOCE-500, Canon Machinery Inc) operated at 873K. The oscillation behavior and the temperature of the droplet were monitored from above using a high speed video camera and a single color pyrometer. The surface tension of molten samples was calculated from the frequencies of m=0, ±1, and ±2 for l=2 mode of the droplet using Rayleigh equation [2] calibrated by Cummings and Blackburn [1].

3. Results and Discussions

Figure 1 shows surface tension of molten nickel under the flow condition of Ar-He gas processed by the oxygen pump. Also shown is the surface tension of molten nickel measured under the Ar-He-5vol.%H_2 gas with the moisture content of 2.66 ppm[3]. We successfully measured the surface tension of molten nickel over the very wide temperature range of 750K including undercooling conditions. The temperature dependence of the surface tension of molten nickel exhibited a kink due to competition between the temperature dependence of the Po_2 and that of the oxygen adsorption equilibrium constant as in the case of the surface tension measured under the Ar-He-5vol.%H_2 gas. The kink is observed at higher temperature under the gas processed by the oxygen pump because of higher Po_2. Even though the Po_2 is different between these experiments, almost the same surface tension is observed at low temperature. This result implies that the influence of dissociation of H_2O should be considered for accurate evaluation of the Po_2 of atmospheric gas prepared by oxygen pump during surface tension measurement.

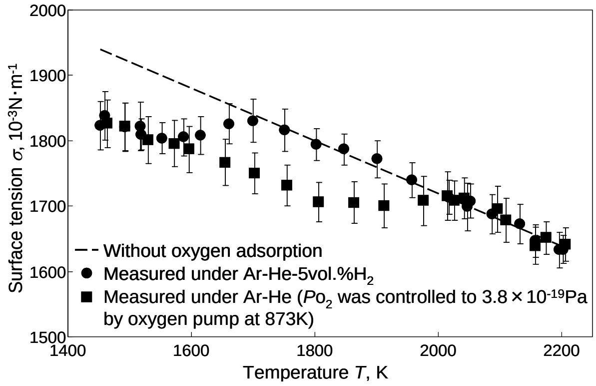

Fig. 1 Surface tension of molten nickel measured under Ar-He gas processed by oxygen pump and under Ar-He-5vol.%H_2 gas. The surface tension of pure state is expected from the plots as a dashed line

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液滴振動法による高温融体熱物性計測

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Thermophysical Properties Measurement of High-Temperature Liquids by Oscillating Drop Technique under Microgravity

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Oscillating drop method with levitation technique under the microgravity conditions has advantage of thermophysical properties measurements high-temperature liquids. Thermophysical properties of high-temperature melts are indispensable for numerical simulations of materials processing. Accurate data are necessary to improve the process modeling, which leads to cost-effective production of high-quality products. From the requirements the levitation technique, which provides containerless conditions during the measurements, is progressed for accurate measurements of the thermophysical properties of high-temperature liquids. Therefore, we are planning thermophysical properties of high-temperature melts in the International Space Station (ISS) [1,2] using the materials-science laboratory-electromagnetic levitator (MSL-EML)[3]. On this basis JAXA and ESA together with national space agencies in Europe has set up a strong scientific collaboration programmed to utilize space as a complementary crucial tool to ease and accelerate the development of new products through knowledge-based designs using the timely fundamental advances acquired from in the near future, the ISS. Using MSL-EML we obtain the surface tension from the surface oscillation frequency and also the viscosity from the dumping time of the surface oscillations under the microgravity conditions. However, analysis of oscillating drop method in EML must be improved even in the microgravity conditions, because on the EML conditions the electromagnetic force (EMF) cannot generate the surface oscillation with discretely oscillation mode. Since under microgravity the levitated droplet shape is completely spherical, the surface oscillation frequency with different oscillation modes degenerates into the single frequency. However, if sample position moves close to the coils, droplet shape is modulated by the EMF even in small electric current case. The droplet shape modulation changes the oscillation mode and then cause to the oscillation frequency separation. Therefore, for our project purpose of precise surface tension measurements under the controlled oxygen atmospheric conditions we must clarify the droplet shape modulation effects on the surface oscillation frequency shifts. Because if oscillation frequency is shifted by droplet shape modulation, we miss understanding of how the oxygen atmospheric condition affects on the surface tension. Moreover, for the viscosity measurements we also care of the different oscillation mode by the droplet shape modulations. Because dumping time of surface oscillation of liquid droplets depends on the oscillation modes, the case of surface oscillation including multi oscillation modes the viscosity values obtained from dumping time will be modified from the correct viscosity. Therefore, we investigate the dumping time of surface oscillation of levitated droplets with different oscillation modes and also with including multi oscillation modes using electrostatic levitation (ESL) on ground and EML under microgravity conditions by the parabolic flight of airplane. The ESL can discretely generate the surface oscillation with different oscillation modes by the change of generation frequency of surface oscillation, so we can obtain dumping time of surface oscillation with discrete oscillation mode. We obtained the dumping time of surface oscillation with different EMF conditions by EML under microgravity using parabolic flight of airplane operated by Diamond Air Service [4]. The different EMF conditions generated the different surface oscillations with multi oscillation modes. From both levitation experiments, we obtained the different dumping time depending on the external force conditions. From the precise analysis of the dumping time difference, we discuss about that how does the dumping time modification by the oscillation mode conditions affect on the viscosity values from the Rayleigh's relations [5]. We also discuss the collection model of surface oscillation dumping for the case of multi oscillation modes generated in droplets. In the presentation, we also introduce the task and future plan of this international collaboration projects.

Acknowledgments

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