Joint Studies Programs

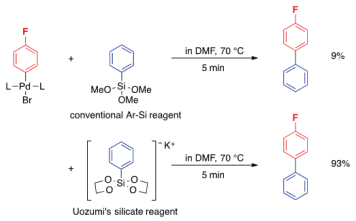
As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

(a) *Operando* Structural Studies on the Reacting Species of the Cross-Coupling Catalysis

FUJIKAWA, Shigenori (*Kyushu Univ.*)
TAKAYA, Hikaru (*Teikyo Univ. Sci. and IMS (concurrent)*)
NAGASAKA, Masanari (*IMS*)
OKUMURA, Shintaro (*IMS*)
UOZUMI, Yasuhiro (*IMS*)

The palladium-catalyzed cross-coupling reactions have been recognized as the most powerful synthetic means of carbon–carbon bond formation. Coupling of aryl halides and organosilicon reagents, the so-called Hiyama coupling, is one of the representatives. Recently, Uozumi at IMS developed aryl silicate reagents which exhibited remarkably high reactivity toward the Hiyama coupling with aryl halides (Scheme 1). These observations prompted us to the joint project that examines the *operando* structural studies on the aryl silicates as well as conventional aryl silyl reagents under the actual coupling reaction conditions by *in situ* NEXAFS measurements. Figure 1 shows the carbon K-edge NEXAFS spectrum of 100 mM trimethoxy(phenyl)silane (Ph-Si(OMe)$_3$) in tetrahydrofuran (THF) measured at BL3U of UVSOR-III Synchrotron (by Okumura, Nagasaka, Uozumi). The C=C π* peak of phenyl groups in Ph-Si(OMe)$_3$ is observed even in organic solvent containing carbon atoms since the peaks of THF exist at the higher energy side. We have investigated the C–Si bond length of several organosilicon compounds by C K-edge NEXAFS experiments and inner-shell quantum chemical calculations and have discussed the relation of the reaction mechanism of Hiyama coupling reaction. This project also aims to achieve the Si L-edge NEXAFS measurements of organosilicon compounds under the actual reaction conditions by the combination of (1) a new coupling reaction (by Uozumi, Okumura) and (2) an ultrathin liquid cell that achieves the 2.6 mm optical length of argon gas (by Nagasaka, Takaya) including novel Si-free nanomembranes developed by Fujikawa (Figure 2). In the present status, we have tested the ultrathin liquid cell including Si-free nanomembranes by using a conventional FT-IR system (by Nagasaka) and will apply the Si L-edge NEXAFS measurements at BL3U of UVSOR-III in this year.



Scheme 1. The Hiyama Coupling Reactions with Uozumi's Aryl Silicate.

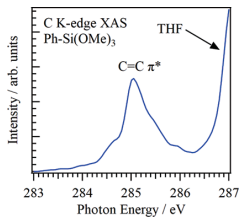


Figure 1. C K-edge NEXAFS spectrum of 100 mM Ph-Si(OMe)$_3$ in THF.

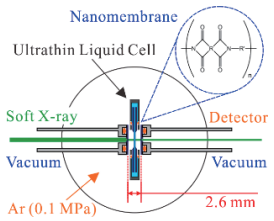


Figure 2. The schematic of an ultrathin liquid cell including Si-free nanomembranes.

(b) Analysis and Elucidation of Deactivation Mechanism for High Durability of Metal Complex-Carbon Electrodes for Electroreduction of CO_2 in Water

SAITO, Susumu (*Nagoya Univ.*)
SATO, Shyunsuke (*Toyota Central R&D Labs., Inc.*)
SUGIMOTO, Toshiki (*IMS*)

In order to investigate the cause of the performance degradation of the cathode electrode during the ongoing electroreduction of CO_2 in water using a complex-carbon electrode,[1] *in-situ* observations of the cathode electrode are performed using third-order nonlinear vibrational spectroscopy. We have jointly constructed an electrolysis cell for spectroscopy equipped with an anhydrous quartz window, which is the most suitable material for measurement. Using this spectroscopic cell, we first optimized the optical system for third-order nonlinear spectroscopic measurement for the complex-carbon electrode installed in the reaction cell. As the next step, we are going to conduct third-order nonlinear vibrational spectroscopy to identify the cause of the deterioration of the electrode performance, while systematically changing the reaction conditions such as the temperature, pH, applied voltage, and CO_2 concentration of the aqueous solution.

Reference

1) M. Yamauchi, H. Saito, T. Sugimoto, S. Mori and S. Saito, *Coord. Chem. Rev.* **472**, 214773 (2022).

(2) Research Symposia

(From Oct. 2021 to Sep. 2022)

Dates	Theme	Chair
Feb. 28–Mar. 1, 2022	Current Status and Future Prospects for Attosecond Laser Facility (ALFA)	**YAMANOUCHI, Kaoru** **OKAMOTO, Hiromi**
Mar. 8, 2022	Frontiers in Energy Science: Towards Cross-Hierarchical Understanding	**NAKAMURA, Toshikazu** **YAMAMOTO, Hiroshi**
Sep. 7, 9, Nov. 8–17, 2021	Study of Spin Transport Unique to Chiral Materials	**SUZUKI, Yuta** **YAMAMOTO, Hiroshi**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2021–Mar. 2022			Apr. 2022–Sep. 2022		Total			
		Regular	NanoPlat	NMRPlat	Regular	ARIM	Regular	NanoPlat/ ARIM	NMRPlat	Sum
Special Projects		1			1		2			2
Research Symposia		2			3		5			5
Research Symposia for Young Researchers		0			1		1			1
Cooperative Research		27	36	1	22	14	49	50	1	100
Use of Facility	Instrument Center		78			59		137		137
	Equipment Development Center	0	4		0	4	0	8		8
	UVSOR	110	2		103	2	213	4		217
Use of Facility Program of the Computer Center							278*			278*

* from April 2021 to March 2022