Organic-bridged Allylsilane Precursors for Synthesis of Functional Organosilica Hybrids

Yoshifumi Maegawa, Norihiro Mizoshita, Minoru Waki, Takao Tani, Toyoshi Shimada and Shinji Inagaki

■**ABSTRACT**‖　Organosilica hybrid materials have received considerable attention in various research areas and are typically prepared by organoalkoxysilanes as precursors. This review describes advances in the development of organoallylsilanes as alternatives to conventional organoalkoxysilanes, which have some limitations due to their intrinsic high hydrolytic reactivity. Our group has found an alternative class of organosilane precursors, organoallylsilanes, which behave as synthetic equivalents of conventional alkoxysilanes and have sufficient stability for cross-coupling reactions and purification using silica gel chromatography. Our group proposes a general synthetic route for functional organic-bridged allylsilane precursors using a series of molecular building blocks for allylsilane sol-gel precursors (MBAS). Novel organic-bridged allylsilanes were successfully synthesized using MBAS, which were then utilized for the preparation of functional organosilica hybrids. Furthermore, the low hydrolytic reactivity of the organoallylsilanes was improved by a proper selection of the reaction solvent due to solvent effects. These findings should enable the synthesis of highly functional organosilane precursors and their conversion to organosilica hybrids, thus broadening their potential application.

■**KEYWORDS**‖　Organoallylsilane, Organosilica Hybrid Materials, Molecular Building Blocks, Functionalization, Solvent Effect

1. Introduction

Organosilica hybrid materials, typically prepared by the hydrolysis and polycondensation of organic-bridged alkoxysilanes ($R[Si(OR')_3]_n$, $n \geq 2$, R: functional organic group, R': Me, Et, etc.), have received considerable attention in various research areas (**Fig. 1**).[1] A broad spectrum of functionalities can be incorporated into the framework by proper design of the bridging organic group (R).[2] Recent demands for the development of highly functional organosilica hybrids have necessitated the use of precursors having organic groups with desired functionalities. Although a range of synthetic

methodologies for obtaining organoalkoxysilanes have been developed, conventional methods have limitations in terms of difficulties in substrate preparation and limited functional tolerance to reaction conditions. Furthermore, alkoxysilane precursors often suffer from a lack of suitable purification processes (e.g. silica gel chromatography) due to their intrinsic high hydrolytic reactivity. The purification of moisture-sensitive compounds is a critical step for non-distillable or non-crystallizable compounds. Therefore, in the further development of functional organosilica hybrids, the next challenge is to develop synthetic equivalents to alkoxysilanes that can be readily synthesized, purified by general purification processes, and sufficiently reacted in polymerization processes.

In this review, we describe advances in the development of organoallylsilanes as alternative precursors to alkoxysilanes and their conversion to organosilica hybrid materials. In section 2, we focus on synthetic methodologies for obtaining the organoallylsilane precursors and discuss the unique chemical properties of the allylsilyl group. Section 3 highlights the preparation of functional organosilica hybrids from organoallylsilane precursors. Finally, in section 4 we show the results of efforts to improve the low hydrolytic reactivity of organoallylsilanes.
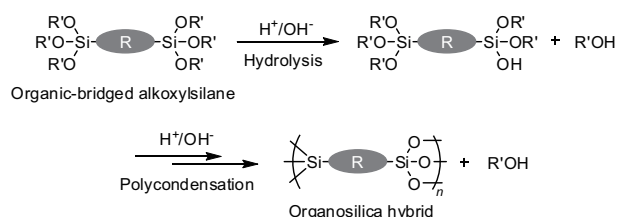

Fig. 1　Preparation of an organosilica hybrid material from an organic-bridged alkoxysilane precursor by acid- or base-catalyzed hydrolysis and polycondensation (R: functional organic group, R': Me, Et, etc.).

2. Synthetic Route of Organoallylsilane as Synthetic Equivalent of Organoalkoxysilane

In 2003, our group found the first alternative class of silane coupling reagents, organoallylsilanes, suitable for functionalization on a silica gel surface. Organoallylsilanes were shown to behave as synthetic equivalents to conventional alkoxysilane coupling reagents and demonstrated sufficient stability for cross-coupling reactions and purification using silica gel column chromatography.[3] In 2005, our group reported an alternative route for the preparation of benzene-bridged periodic mesoporous organosilica (PMO) with crystal-like pore walls starting from the corresponding organic-bridged allylsilane precursors.[4] These pioneer works clearly showed that allylsilyl groups could be hydrolyzed and polycondensed to form silanol groups and/or siloxane bonds under acidic or basic hydrolytic conditions through the elimination of propene (deallylation) (**Fig. 2**). These innovations encouraged us to synthesize a variety of functional organoallylsilane precursors for the preparation of highly functional organosilica hybrid materials.

Allylsilyl groups can be easily prepared from the corresponding alkoxysilyl groups by treatment with allyl metal reagents. This transformation can be useful for the preparation of hydrolytically stable sol-gel precursors with high purity from unstable alkoxy- and chlorosilane precursors which cannot be purified by silica gel column chromatography. However, the use of the highly reactive allyl metal reagents does not tolerate the presence of functional groups (e.g. carbonyl groups). To overcome this limitation, our group recently proposed a general synthetic route for obtaining functional organoallylsilanes using a series of molecular building 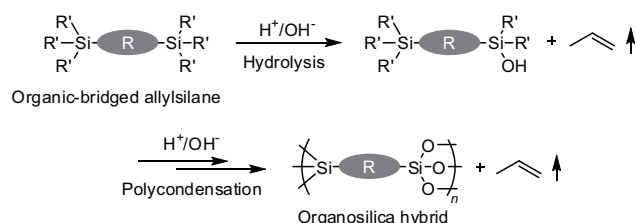blocks containing an allylsilyl group (**Fig. 3**(a)).[5] This strategy is a versatile and promising approach which overcomes the limitations of conventional routes using unstable organosilane substrates. We synthesized three types of molecular building blocks for allylsilane sol-gel precursors (MBAS) (Fig. 3(b)). These MBAS can be employed in Suzuki-Miyaura, Stille, Sonogashira, Grignard cross-coupling and Buchwald-Hartwig amination reactions, as well as in Wittig olefination. The reagents are robust and their allylsilyl groups remain unchanged over the course of the cross-coupling reactions. These findings enabled us to design and synthesize a variety of functional organic-bridged allylsilane precursors by cross-coupling reactions.

Our group synthesized novel functional organic-bridged allylsilanes by cross-coupling using MBAS. For example, Sonogashira coupling of MBAS **1j** with 2,2',7,7'-tertraiodo-9,9'-spirobifluorene (**2a**) in the presence of $Pd_2(dba)_3$ as a catalyst in triethylamine/toluene afforded a highly fluorescent spirobifluorene (SBF)-bridged allylsilane precursor **SBF-Si** (**Fig. 4**).[6] The obtained precursor was successfully used for the preparation of an emissive periodic mesostructured organosilica hybrid film (see
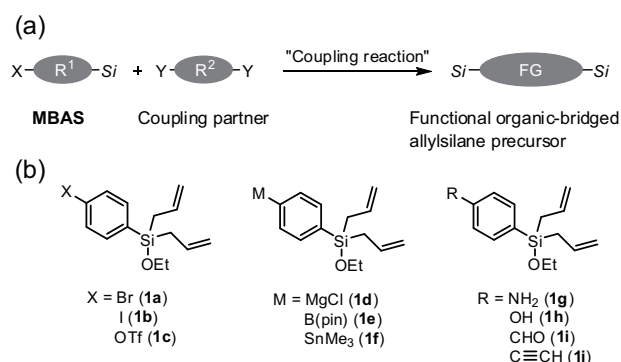

Fig. 3 (a) Proposed general synthetic route for obtaining functional organic-bridged allylsilane precursors. (b) Examples of molecular building blocks for allylsilane sol-gel precursors (MBAS).
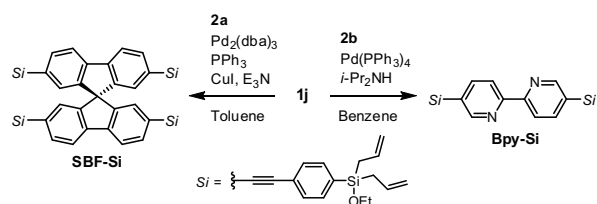

Fig. 2 Preparation of an organosilica hybrid material from an organic-bridged allylsilane precursor by acid- or base-catalyzed hydrolysis and polycondensation (R: functional organic group, R': allyl (-CH$_2$-CH=CH$_2$) group).

Fig. 4 Synthesis of spirobifluorene-bridged allylsilane precursor **SBF-Si** from **1j** and **2a**, and bipyridine-bridged allylsilane precursor **Bpy-Si** from **1j** and **2b**.

section 3.1). Our group also synthesized a bipyridine (Bpy)-bridged allylsilane precursor **Bpy-Si** via coupling of MBAS **1j** and 5,5'-dibromo-2,2'-bipyridine (**2b**) in the presence of $Pd(PPh_3)_4$ as a catalyst in benzene (Fig. 4).[7] The precursor **Bpy-Si** was utilized for preferential functionalization of the inner pore surface of the biphenyl (Bp)-PMO by means of a covalent immobilization protocol (see section 3.2).

3. Preparation of Functional Organosilicas from Organic-bridged Allylsilane Precursors

3. 1 Synthesis of Functional PMO by Surfactant-Directed Polycondensation

Among the various types of organic-inorganic hybrid materials reported, periodic mesostructured or mesoporous organosilicas (PMOs), prepared by surfactant-directed polycondensation of organic-bridged alkoxysilane precursors, offer considerable promise as functional materials having organic-inorganic hybrid frameworks and well-defined mesochannels (**Fig. 5**).[8] In PMOs, both the organosilica framework and the inner parts of the mesochannels are available for functional design, which broadens the potential application of PMOs as solid photocatalysts,[9] adsorbents,[10] sensing systems,[11] and optical and electronic devices.[12,13]

Recently, much attention has been focused on fluorescent PMO films due to their transparency (no light scattering losses), flexibility in shaping, high fluorescence quantum yields and tunability in emission color arising from their unique light-harvesting antenna property.[14] We synthesized a novel fluorescent PMO film bearing spirobifluorene (SBF) groups from an allylsilane precursor **SBF-Si** by surfactant-directed polycondensation (**Fig. 6**(a)).[6] Acid-catalyzed hydrolysis and polycondensation of **SBF-Si** in the presence of the nonionic template surfactant Brij76 ($C_{18}H_{37}(OCH_2CH_2)_{10}OH$) successfully gave an organosilica film, **SBF-Si-F**, with a mesoscale periodic structure. The film showed a single intense diffraction peak at $d = 5.52$ nm without any higher-order peaks (Fig. 6(b), black), which implies the formation of a wormhole-like array of mesochannels despite the bulky structure of the SBF bridge. The periodic mesostructure was retained after extraction of the template surfactant. The XRD pattern of the extracted film showed a broad diffraction peak at $d = 5.39$ nm (Fig. 6(b), grey). The obtained PMO film showed a strong fluorescence emission with a quantum yield (Φ_F) of 0.59 upon excitation at $\lambda = 360$ nm (Φ_F of a solution of **SBF-Si** in 2-propanol: 0.92) and exhibited vibronic structure in the spectrum (Fig. 6(c)). These results indicate that the bulky structure of the SBF bridge is effective in suppressing strong aggregation of the fluorene chromophores and thereby limiting the decrease in Φ_F. The resulting highly emissive PMO film has potential for various applications, including white-LEDs and fluorescence chemosensors.
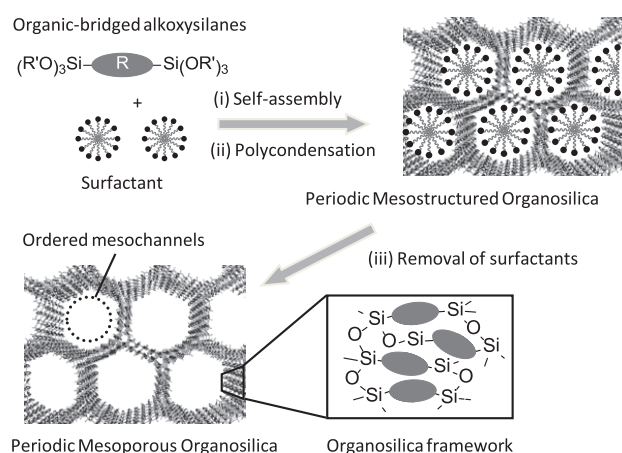

Fig. 5   A schematic showing preparation of periodic mesostructured or mesoporous organosilica.
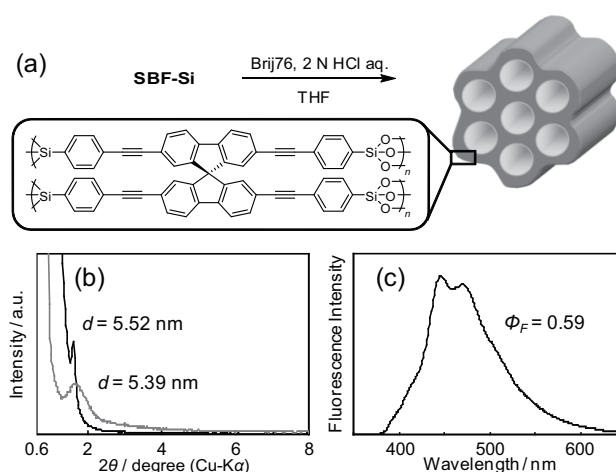

Fig. 6   (a)   Preparation of spirobifluorene-bridged mesostructured organosilica film **SBF-Si-F**, and its (b) XRD patterns before (black) and after (grey) extraction of the template surfactant, and (c) fluorescence spectrum upon excitation at 360 nm.

3. 2 Functionalization of PMO by Immobilization Protocol

Organoallylsilanes are also powerful reagents for further functionalization of organosilica hybrids such as PMOs. Our group reported on functionalization of the inner pore surface of biphenyl (Bp)-PMO with **Bpy-Si** as a fluorescent receptor, aiming for construction of a novel metal-ion detection system based on a light-harvesting PMO.[7] Briefly, the Bpy receptor was covalently anchored onto the inner pore surface of Bp-PMO by coupling of the allylsilyl groups of **Bpy-Si** with the silanol groups of Bp-PMO in the presence of trifluoroacetic acid as a catalyst in toluene under reflux (**Fig. 7**(a)). The obtained Bpy-functionalized Bp-PMO (Bpy/Bp-PMO) exhibited strong fluorescence emission from the Bpy receptor upon excitation of the Bp group in the framework via a light harvesting antenna mechanism; the excitation energy funneling into the Bpy receptor originated from a large number of Bp groups in the PMO framework (Fig. 7(b)). This system could successfully detect metal ions (e.g. ~ 0.15×10^{-6} M for Cu^{2+}) based on changes in the enhanced fluorescence (Fig. 7(c)).

4. Improvement of Hydrolytic Reactivity of Organoallylsilanes by Solvent Effect

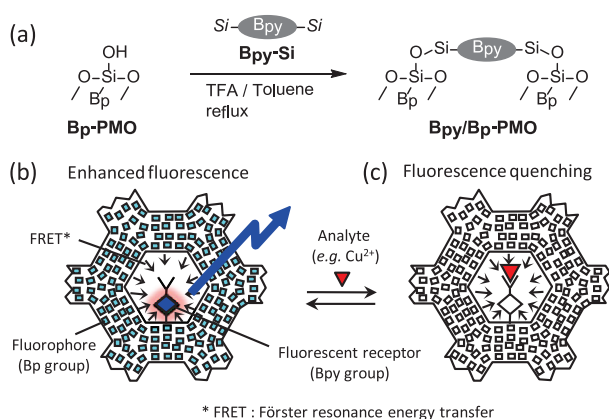Organoallylsilanes are useful precursors for preparing functional organosilica hybrids as shown in the previous section. However, they undergo hydrolysis and polycondensation with difficulty due to their low hydrolytic reactivity. For example, acid-catalyzed hydrolysis and polycondensation of organoallylsilanes usually require harsh conditions (e.g. > 0.2 M hydrochloric acid (HCl) at 60°C) as compared with those used for organoalkoxysilanes (e.g. < 0.01 M HCl at rt),[15] which can cause decomposition of the bridging organic groups and/or undesired Si-C bond cleavage between silyl groups and the bridges.[16] Thus, it is of great importance to identify mild hydrolytic conditions for organoallylsilanes.

Recently, we identified a significant solvent effect acting on the acid-catalyzed sol-gel polymerization (deallylation) of organoallylsilanes. The deallylation rates were strongly influenced by the reaction solvents [17] as shown in **Table 1**, which summarizes the initial deallylation rate v_0 at 0.5 h. **Figures 8**(a)-(c) show changes in the ^{1}H NMR spectra (signals from the β-hydrogens of the allylsilyl groups) of sol solutions of **3a** in (a) acetonitrile-d_3 (MeCN-d_3), (b) acetone-d_6 and (c) dimethyl sulfoxide-d_6 (DMSO-d_6) after the addition of HCl. MeCN was found to most effectively enhance the deallylation rates of **3a** and **3b** and gave complete deallylation within 4 h together with vigorous evolution of propene gas. The sol solutions formed solid organosilica films by solvent evaporation. Acetone also effectively provided deallylation of **3a**, but did not enhance deallylation of **3b** due to the lower

Fig. 7 (a) Covalent immobilization of the bipyridine receptor **Bpy-Si** onto the inner pore surface of Bp-PMO, schematic illustrations of (b) enhanced fluorescence of the receptor by a light-harvesting antenna mechanism and (c) its quenching by an analyte.

Table 1 Acid-catalyzed sol-gel polymerization of model organoallylsilane precursors **3a** and **3b** in various solvents.

Entry	Precursor	Solvent	$v_0{}^b$/M s^{-1}	Solid film formation
1	**3a**	MeOH	2.40×10^{-5}	No
2		THF	2.14×10^{-5}	No
3		DMSO	0.90×10^{-5}	No
4		Acetone	8.64×10^{-5}	Yes (24 h)^c
5		MeCN	4.53×10^{-4}	Yes (3 h)^c
6	**3b**	Acetone	1.23×10^{-5}	No
7		MeCN	3.88×10^{-5}	Yes (4 h)^c

^{a} Reactions of the allylsilane precursors **3a** and **3b** (0.10 mmol) were carried out at 60 ºC for 3–48 h in each solvent (0.25 mL) in the presence of HCl (0.2 M). ^{b} The deallylation rate after the initial 0.5 h. ^{c} The reaction time required for the formation of a solid organosilica film from the sol solution.

reactivity of the triallylsilyl group in **3b**. The use of other solvents such as methanol (MeOH), tetrahydrofuran (THF) and DMSO resulted in relatively slow deallylation. For example, in DMSO more than 90% of the allyl groups in **3a** remained after 4 h.

From a mechanistic viewpoint, deallylation can be influenced by three factors: (i) proton activity, (ii) stability of the β-silyl cation intermediate and (iii) nucleophilicity of water (silanol species). These factors are closely related to the Catalán solvent basicity (SB), dielectric constant (D_C) and Gutmann's acceptor number (AN), respectively. **Figures 9**(a)-(c) show the relationship between the initial deallylation rate v_0 of
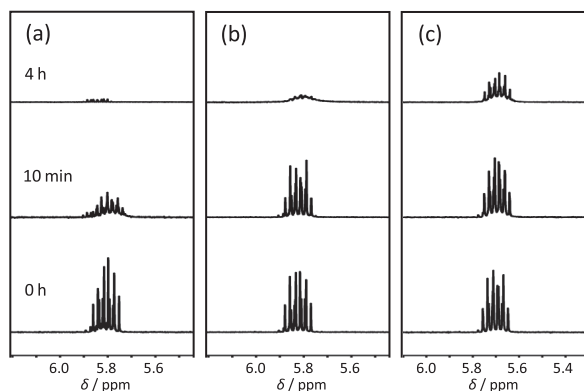
3a and the SB, D_C and AN parameters, respectively, for various solvents. A correlation was apparent for v_0 vs SB, but not for v_0 vs D_C or v_0 vs AN. The strong SB-dependence of v_0 suggests that the observed strong solvent effect results from differences in the proton activities in the solvents. We concluded that low-SB solvents such as MeCN lead to high proton activity, accelerating electrophilic addition of the proton to the allyl group in the deallylation step.

The solvent effect was also confirmed for highly functional organic-bridged allylsilanes such as **SBF-Si**. The use of a mixed solvent of THF/CH$_3$CN (2:1) clearly enhanced the acid-catalyzed hydrolysis and polycondensation of **SBF-Si** even at a low acid concentration (0.02 M HCl at 60°C) and the resulting sol solution gave a solid film after stirring for only 3 h. In contrast, when using pure THF as a solvent, the sol solution did not form a solid film even after stirring for 24 h. These results suggest that the solvent effect can be generally applied to the preparation of highly functional organosilica hybrid materials from a variety of functional and stable organoallylsilane precursors.

Fig. 8   Changes in the ^{1}H NMR spectra (signals from the β-hydrogens of the allylsilyl groups) of the sol solutions of **3a** in (a) MeCN-d_3, (b) acetone-d_6 and (c) DMSO-d_6 after the addition of HCl.

5. Conclusion

This review described advances in the development of organoallylsilanes as alternatives to conventional organoalkoxysilanes in preparation of organosilica hybrid materials. The use of allylsilanes that are chemically stable but hydrolyzable and the development of MBAS have opened up the potential for organoallylsilanes to be used as precursors for functional organosilica hybrids, as confirmed by the synthesis of novel spirobifluorene- and bipyridine-bridged allylsilane precursors and their utilization. A study of solvent effects showed that the low hydrolytic reactivity of organoallylsilanes can be improved by a proper selection of the reaction solvent. These findings should enable the synthesis of further functional organosilane precursors and their conversion to organosilica hybrids, and broaden their potential application.
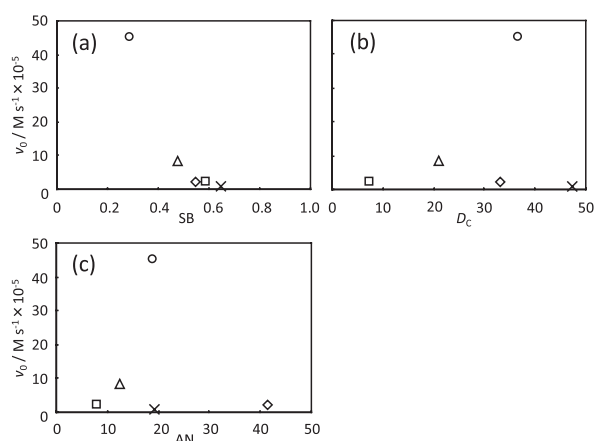

Fig. 9   Relationship between the initial deallylation rate (v_0) of **3a** and (a) solvent basicity (SB), (b) dielectric constant (D_C) and (c) acceptor number (AN) for various solvents. Solvents are labeled as follows: MeCN (○); acetone (△); MeOH (◊); THF (□); and DMSO (×).

References

(1) Loy, D. A. and Shea, K. J., *Chem. Rev.*, Vol.95, No.5 (1995), pp.1431-1442.

(2) Shea, K. J., Loy, D. A. and Webster, O., *J. Am. Chem. Soc.*, Vol.114, No.17 (1992), pp.6700-6710.

(3) (a) Shimada, T., Aoki, K., Shinoda, Y., Nakamura, T., Tokunaga, N., Inagaki, S. and Hayashi, T., *J. Am. Chem. Soc.*, Vol.125, No.16 (2003), pp.4688-4689: (b) Aoki, K., Shimada, T. and Hayashi, T., *Tetrahedron: Asymmetry*, Vol.15, No.11 (2004), pp.1771-1777.

(4) Kapoor, M. P., Inagaki, S., Ikeda, S., Kakiuchi, K., Suda, M. and Shimada, T., *J. Am. Chem. Soc.*, Vol.127, No.22 (2005), pp.8174-8178.

(5) Maegawa, Y., Nagano, T., Yabuno, T., Nakagawa, H. and Shimada, T., *Tetrahedron*, Vol.64, No.46 (2007), pp.11467-11474.

(6) Tanaka, N., Mizoshita, N., Maegawa, Y., Tani, T., Inagaki, S., Jorapur, Y. R. and Shimada, T., *Chem. Commun.*, Vol.47, No.17 (2011), pp.5025-5027.

(7) Waki, M., Mizoshita, N., Maegawa, Y., Hasegawa, T., Tani, T., Shimada, T. and Inagaki, S., *Chem.-Eur. J.*, Vol.18, No.7 (2012), pp.1992-1998.

(8) (a) Inagaki, S., Guan, S., Ohsuna, T. and Terasaki, O., *Nature*, Vol.416, No.6878 (2002), pp.304-307: (b) Hoffmann, F., Cornelius, M., Morell, J. and Fröba, M., *Angew. Chem. Int. Ed.*, Vol.45, No.20 (2006), pp.3216-3251: (c) Wang, W. D., Lofgreen, J. E. and Ozin, G. A., *Small*, Vol.6, No.23 (2010), pp.2634-2642: (d) Mizoshita, N., Tani, T. and Inagaki, S., *Chem. Soc. Rev.*, Vol.40, No.2 (2011), pp.789-800.

(9) (a) Ohashi, M., Aoki, M., Yamanaka, K., Nakajima, K., Ohsuna, T., Tani, T. and Inagaki. S., *Chem.-Eur. J.*, Vol.15, No.47 (2009), pp.13041-13046: (b) Takeda, H., Ohashi, M., Tani, T., Ishitani, O. and Inagaki, S., *Inorg. Chem.*, Vol.49, No.10 (2010), pp.4554-4559.

(10) Stein, A., Melde, B. J. and Schroden, R. C., *Adv. Mater.*, Vol.12, No.19 (2000), pp.1403-1419.

(11) Melde, B. J., Johnson, B. J. and Charles, P. T., *Sensor*, Vol.8, No.8 (2008), pp.5202-5228.

(12) (a) Mizoshita, N., Goto, Y., Tani, T. and Inagaki, S., *Adv. Funct. Mater.*, Vol.18, No.22 (2008), pp.3699-3705: (b) Mizoshita, N., Goto, Y., Tani, T. and Inagaki, S., *Adv. Mater.*, Vol.21, No.47 (2009), pp.4798-4801: (c) Mizoshita, N., Goto,Y., Maegawa, Y., Tani, T. and Inagaki, S., *Chem. Mater.*, Vol.22, No.8 (2010), pp.2548-2554.

(13) Mizoshita, N., Ikai, M., Tani, T. and Inagaki, S., *J. Am. Chem. Soc.*, Vol.131, No.40 (2009), pp.14225-14227.

(14) (a) Inagaki, S., Ohtani, O., Goto, Y., Okamoto, K., Ikai, M., Yamanaka, K., Tani, T. and Okada, T., *Angew. Chem. Int. Ed.*, Vol.48, No.22 (2009), pp.4042-4046: (b) Takeda, H., Goto, Y., Maegawa, Y., Ohsuna, T., Tani, T., Matsumoto, K., Shimada, T. and Inagaki, S., *Chem.Commun.*, No.40 (2009), pp.6032-6034: (c) Maegawa, Y., Mizoshita, N., Tani, T. and Inagaki, S., *J. Mater. Chem.*, Vol.20, No.20 (2010), pp.4399-4403.

(15) (a) Kapoor, M. P., Yanagi, M., Kasama, Y., Yokoyama, T., Inagaki, S., Shimada, T., Nanbu, H. and Juneja, L. R., *J. Mater. Chem.*, Vol.16, No.32 (2006), pp.3305-3311: (b) Kapoor, M. P., Kasama, Y., Yanagi, M., Yokoyama, T., Inagaki, S., Shimada, T., Nanbu, H. and Juneja, L. R., *Microporous Mesoporous Mater.*, Vol.101, No.1-2 (2007), pp.231-239.

(16) Shirai, S., Goto, Y., Mizoshita, N., Ohashi, M., Tani, T., Shimada, T., Hyodo, S. and Inagaki, S., *J. Phys. Chem. A*, Vol.114, No.19 (2010), pp.6047-6054.

(17) Maegawa, Y., Mizoshita, N., Tani, T., Shimada, T. and Inagaki, S., *J. Mater. Chem.*, Vol.21, No.36 (2011), pp.14020-14024.

Yoshifumi Maegawa
Research Field:
- Organic Synthesis for Functional Organosilica Hybrids
Academic Societies:
- The Chemical Society of Japan
- The Society of Synthetic Organic Chemistry, Japan

Norihiro Mizoshita
Research Field:
- Synthesis and Functionalization of Organosilica Hybrid Materials
Academic Degree: Ph.D.
Academic Societies:
- The Chemical Society of Japan
- The Society of Polymer Science, Japan
- Japanese Liquid Crystal Society
Awards:
- Japanese Liquid Crystal Society Paper Award (A), 2000
- Young Scientist Award of Japanese Liquid Crystal Society, 2006

Minoru Waki
Research Field:
- Synthesis and Functionalization of Periodic Mesoporous Organosilicas
Academic Degree: Ph.D.
Academic Society:
- The Chemical Society of Japan

Takao Tani
   Research Fields:
      - Functionalization of Periodic
        Mesoporous Organosilicas
      - Flame Synthesis of Metal Oxide
        Nanoparticles and Their Applications
   Academic Degree: Dr. sc. techn. ETH
   Academic Societies:
      - The Ceramic Society of Japan
      - The Japanese Sol-Gel Society
   Award:
      - 40th Tokai Chemical Industry Association Award,
        2005

Toyoshi Shimada*
   Research Fields:
      - Synthetic Organic Chemistry
      - Silicon Chemistry
      - Organometallic Chemistry
   Academic Degree: Dr. Eng.
   Academic Societies:
      - The Chemical Society of Japan
      - American Chemical Society
      - The Society of Synthetic Organic Chemistry, Japan
      - The Kinki Chemical Society, Japan
      - The Society of Silicon Chemistry, Japan
      - The Japanese Sol-Gel Society
      - The Society of Iodine Science
   Award:
      - The Society of Synthetic Organic Chemistry Kansai
        Award, 2006

* Nara National College of Technology

Shinji Inagaki
   Research Field:
      - Synthesis and Applications of
        Mesoporous Materials
   Academic Degree: Dr. Eng.
   Academic Societies:
      - The Chemical Society of Japan
      - Catalysis Society of Japan
      - Japan Association of Zeolite
      - The Japan Society on Adsorption
      - The Society of Polymer Science, Japan
      - International Mesostructured Materials Association
      - International Zeolite Association
   Awards:
      - The Award of Chemistry on Catalyst Preparation, 1994
      - The Promotion Award of the Japan Society on
        Adsorption, 2001
      - The Chemical Society of Japan Award for Creative
        Work for 2004
      - The Minister Award of Education, Culture, Sport,
        Science and Technology, 2005
      - The Japan Society on Adsorption Award, 2008