Hydrogen generation via dehydrogenation of formic acid using an immobilized Ir-complex catalyst, which combines the catalytic ability of the homogeneous catalyst and ease in handling of the heterogeneous catalyst, was investigated. The immobilization process was analyzed by scanning electron microscopy, Fourier transform infrared spectroscopy, and nitrogen adsorption-desorption measurement. Analytical methods for the heterogeneous catalyst remained appropriate for immobilized catalyst analysis. Hydrogen generation using the immobilized catalyst showed the same activation energy ($E_a = 72.5$ kJ mol$^{-1}$) as the analogous homogeneous catalyst ($E_a = 72.1$ kJ mol$^{-1}$). However, the reaction rate for the immobilized catalyst was 70% of that achieved for the homogeneous catalyst because of the reduced collision frequency. The $\zeta$ potential measurement implied that immobilized catalyst did not form a stable dispersion during the catalytic reaction. Effective agitation control is needed for efficient dehydrogenation reaction using immobilized catalyst. Immobilization of the homogeneous catalyst represents a new technology for practical hydrogen generation.

**Keywords**
Immobilized catalyst, Hydrogen generation, Formic acid, Iridium catalyst, Microparticle

1. Introduction
Renewable energy sources such as wind and solar irradiation have the potential to provide large but unpredictable quantities of electrical energy, so storage of the energy until use requires new energy storage technologies. Conversion into hydrogen ($H_2$) via electrolysis is a very attractive energy storage technology with low environmental burdens, as only water is needed as the reagent, and the reverse reaction for energy discharge produces only water. Such technology has been widely developed as the hydrogen fuel cell. However, $H_2$ gas is difficult to handle and store because of the high risk of explosion. Consequently, $H_2$ conversion into some other chemical substance has been proposed in recent years$^{[1,2]}$. Chemical $H_2$ storage materials, called hydrogen carriers, have high density and volume storage capacities, together with safe and easy handling characteristics.

Formic acid (FA) has been investigated as a hydrogen carrier in recent years. FA is a stable liquid at room temperature, contains 53 g of $H_2$ per liter (4.4 wt% hydrogen), and the endothermic reaction energy required for conversion into $H_2$ and $CO_2$ in aqueous media is only +4 kJ/mol$^{[3]}$. FA is widely available as a byproduct of industrial acetic acid synthesis from carbon monoxide ($CO$) and water, and FA can also be obtained by conversion of biomass or carbon dioxide ($CO_2$). In particular, FA synthesis via $CO_2$ reduction in conjunction with FA dehydrogenation can be regarded as a $CO_2$ neutral energy storage cycle (Fig. 1)$^{[5]}$. FA has many advantages as a hydrogen carrier, but selective $H_2$ production from FA requires a well-designed catalyst because FA has two decomposition

![Fig. 1 CO2 Neutral Energy Storage Cycle](image-url)
paths: dehydrogenation as above, and dehydration dependent on the thermal conditions, reaction pH, etc. (Scheme 1).  
FA dehydrogenation can be catalyzed by industrial catalysts such as heterogeneous metal catalysts, but this process is often accompanied by undesirable dehydration side reaction. The dehydrogenation pathway generates CO, which acts as a catalytic poison in fuel cells. H₂ generated by nonspecific heterogeneous catalysts is unsuitable for practical applications, and slower dehydrogenation rates are common compared to homogeneous catalysts. In contrast, FA dehydrogenation using well-designed homogeneous catalysts can achieve good reaction selectivity and reaction rate. Reports of efficient reaction in 2008,7, were followed by development of various homogeneous catalysts for FA dehydrogenation. In particular, highly selective FA dehydrogenation for H₂ supply using homogeneous iridium complex catalysts was described in 2009. We have improved on such reported catalysts and developed new catalysts with high reaction selectivity, very high reaction rates, and excellent robustness according to reported procedures. Mixing of FA and our developed catalyst in a closed pressure-tight vessel resulted in evolution of highly compressed H₂ without need for a compressor. The combination of FA and the iridium complex catalyst can provide high purity and highly compressed H₂ gas with low energy consumption. The advantages of homogeneous catalyst over heterogeneous catalyst are mentioned above. However, treatment of homogeneous catalyst in operation is not convenient.  
We report the immobilization of homogeneous iridium complex catalyst onto microparticles for efficient and highly selective FA dehydrogenation with easy handling. Specifically, our homogeneous catalyst ([Cp*Ir(pyridylimidazoline)(H₂O)][SO₄]), Cp* = η⁵-C₅Me₅) was immobilized, and the dehydrogenation of FA in the presence of water was carried out. FA dehydrogenation using immobilized catalyst has been reported, but previous studies focused on the chemical characteristics such as reaction rate and reaction mechanism. Practical application needs a chemical engineering perspective, so the present study investigated the engineering aspects by evaluation of the physical properties of immobilized catalyst and established analytical methods. The immobilization process was characterized by several methods, e.g. scanning electron microscopy (SEM), energy dispersion X-ray spectroscopy (EDS) mapping, Fourier-transform infrared (FT-IR) spectroscopy, and nitrogen (N₂) adsorption-desorption measurement. Catalytic performance was compared with a homogeneous catalyst using quantitative catalytic reaction parameters such as reaction rate and activation energy, and ζ potential measurement for understanding the particle conditions.

2. Experimental  
2.1. Materials  
Silica microparticles (G-10, average diameter = 3 mm) were purchased from Fuji Silysia Chemical Ltd. 3-Glycidyloxypropyltrimethoxysilane was purchased from Tokyo Chemical Industry Co., Ltd. 2-(4,5-Dihydro-1H-imidazol-2-yl)pyridine was purchased from Bepham. Dichloro(Cp*Ir(III)) dimer ([Cp*IrCl₂]) was purchased from Strem Chemicals. Silver sulfate was purchased from Junsei Chemical Co., Ltd. [Cp*Ir(H₂O)]₃[SO₄] was synthesized according to reported procedures.  
2.2. Characterizations  
2.2.1. SEM/EDS Mapping Analysis  
Sample morphologies were observed using a Quanta 250 FEG SEM (FEI Company) at 10,000- and 30,000-times magnifications. Ethanol dispersion SEM samples were dropped on a Cu transmission electron microscopy grid (Cu 300 mesh, JEOL Ltd.) and were well dried. Accelerating voltage was 3 kV, and working distance was 8 mm. EDS mapping analysis used an Octane PRO silicon drift detector (EDAX Inc.) at 30,000 × magnification for 60 min. Accelerating voltage was 15 kV, and working distance was 10 mm. Obtained analysis results were compensated (background X-ray cut-off) automatically by TEAM software (EDAX), and characteristic X-ray intensities of each element in the total X-ray spectrum (%) were obtained.  
2.2.2. FT-IR Analysis  
FT-IR spectra were recorded using a Nicolet iS50 FT-IR spectrometer (Thermo Fisher Scientific) with a diffuse reflection cell (Diffuse Reflectance 9067, SpectraTech). Background spectrum was obtained under air. The wavelengths were measured from 4000 to 6000 cm⁻¹ at intervals of 0.5 cm⁻¹.  
2.2.3. N₂ Adsorption-desorption Analysis  
Nitrogen adsorption-desorption isomers were obtained at −196 °C using a BELSORP-mini II
Prior to the measurement, the samples were degassed under a vacuum at 100 °C for 3 h. The pore size distributions were calculated by Barrett-Joyner-Halenda (BJH) analysis, and the specific surface area of the samples were estimated by the Brunauer-Emmett-Teller (BET) method.

2. 2. 4. Zeta Potential Measurement

Zeta potentials of the particles were measured using a Zetasizer Nano NS (Malvern Instruments Ltd). Water was used as the dispersant, and pH was adjusted using 0.1 M H₂SO₄ and 0.1 M NaOH solutions. The ζ potential measurement was repeated three times, and the averaged value was reported.

2. 3. Immobilization of Complex

The immobilization procedure is shown in Fig. 2.

Washing silica: Silica particles were treated prior to use with 1 : 1 methanol/HCl solution for 30 min. The cleaned silica particles were washed with water and were dried in an oven to obtain washed silica particles (1. Washed-Si).

**Linker immobilization via silane coupling:** 3-Glycidoxypropyltrimethoxysilane as the silane coupling regent (0.1 g, 4.2 × 10⁻⁴ mol) was dissolved in toluene and the solution was added dropwise to a Washed-Si (1 g)/toluene suspension and refluxed for 22 h. The suspension was filtered, and the residue was washed with toluene and n-hexane. The washed residue was dried under Ar to obtain 3-glycidoxypropyltrimethoxysilane-modified silica (2. Linker-Si, 1.09 g).

Immobilization of ligands: Linker-Si (0.52 g, theore-
ical epoxy group = $1.9 \times 10^{-4}$ mol)/dry DMF suspension was prepared and maintained at 50 °C. 2-(4,5-Dihydro-1H-imidazol-2-yl)pyridine as an N,N-bidentate ligand (150 mg, $5.1 \times 10^{-4}$ mol) was added to the suspension. Sodium carbonate (262.6 mg, $1.9 \times 10^{-3}$ mol) was added for immobilization of the ligand on the Linker-Si surface. After 39 h of stirring at 50 °C, the suspension was cooled to room temperature. Deionized water was added to the suspension, followed by filtration and washing the residue with deionized water. The residue was dried under Ar to obtain ligand-modified silica (3. Ligand-Si, 0.49 g).

Preparation of iridium complex catalyst: Aqueous suspension of the Ligand-Si (0.25 g) was prepared. A solution of $[\text{Cp}^\text{Ir}(\text{H}_2\text{O})_3][\text{SO}_4]$ (112.9 mg, $2.4 \times 10^{-4}$ mol) was added to the suspension, and the suspension was mixed at room temperature for 5 days and 16 h, after which the suspension was filtered and the residue was washed with deionized water. The residue was dried under Ar to obtain catalyst-immobilized silica (4. Catalyst-Si, 0.25 g).

2.4. Dehydrogenation of FA

The experimental setup for FA dehydrogenation is shown in Fig. 3. All manipulations were conducted under an Ar atmosphere. FA aqueous solutions were degassed via freeze-thaw cycling prior to use. In a typical reaction, 4 mg of Catalyst-Si was added to 10 mL of deaerated 1 M formic acid solution. The solution was stirred, and gas was evolved via dehydrogenation of formic acid. The evolved gas volume was monitored by a gas meter (W-NK-05, Shinagawa Corp.). After completion of the dehydrogenation reaction, the residual formate anion concentration in the reaction solution was determined by high-performance liquid chromatography (HPLC, ACQUITY UPLC, Waters) on an anion-exclusion column (TSK gel SCX(H+), Tosoh Corp.) with an aqueous phosphate solution (20 mM) as the eluent and a UV detector ($\lambda = 210$ nm). The conversion was calculated based on the amount of consumed formic acid.

3. Results and Discussions

3.1. Characterization of Silica Modification

3.1.1. SEM/EDS Mapping Analysis

The silica particles in each modification stage (Washed-Si, Linker-Si, Ligand-Si, and Catalyst-Si) were observed by SEM and EDS mapping. Figures 4a-4d show the surface morphologies of silica particle stage. The particle diameters (~3 mm) did not change after each modification. Moreover, the surface roughness also remained unchanged (Figs. 4e-4h). Therefore, the methods of silica particle modification employed in this study did not affect the particle form.

Figure 5 shows the results of EDS mapping measurement of each particle stage. Washed-Si particles showed the presence of carbon, nitrogen, and iridium atoms, despite the absence of surface modification. Presumably the energies of the characteristic X-rays emitted from nitrogen (Kα = 0.392 keV) and carbon (Kα = 0.277 keV) are close to that of the strong oxygen peak of the sample (Kα = 0.525 keV); so that the peaks of nitrogen and carbon detected near the oxygen peak are artifacts. The characteristic X-ray emitted by iridium (Mα = 1.977 keV) was also observed near the strong peak of silicon (Kα = 1.739 keV), and presumably was also an artifact. Therefore, the peaks of Washed-Si were treated as the base spectrum for qualitative identification of the peaks. Comparison of the EDS mapping of particles of Washed-Si, Linker-Si, Ligand-Si, and Catalyst-Si showed that the carbon percentage of the sample increased with modification. This result is expected because each modification step increases the percentage of carbon in the sample particle. Nitrogen percentage was also apparently increased by modification; however, the standard error obtained was very large. In contrast, the iridium percentage increased only during the complexation step because of iridium loading. We conclude that EDS mapping analysis can qualitatively detect the presence of a metal element in an immobilized catalyst.
Inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of Catalyst-Si was outsourced to Sumika Chemical Analysis Service, Ltd. (Niihama, Japan). The Ir content of Catalyst-Si was measured as 1.7 wt%. The value obtained by ICP-AES was close to the value by EDS mapping, suggesting that Ir is immobilized near the silica particle surface similar to the transmission depth of EDS X-rays.

3.1.2 FT-IR Analysis

Figure 6a) shows the results of diffuse reflection FT-IR measurement of the four particle stages. The silyl SiO-H stretch broad band (3000-3600 cm⁻¹) and Si-O-Si asymmetric stretch (1000-1250 cm⁻¹) were observed, attributable to the base silica support. The difference spectrum between Ligand-Si and Washed-Si...
The specific surface areas of the particles were calculated using the BET method. The specific surface area of Washed-Si was 316 m² g⁻¹. After linker modification, the surface area decreased to 270 m² g⁻¹, because the silane coupling reagent covering the particle surface reduced the surface roughness. Both the ligand molecule and the catalyst modification slightly increased the surface area (286 m² g⁻¹ and 302 m² g⁻¹, respectively). Presumably molecular-level surface modification increased the surface roughness. The specific surface area did not change significantly at any modification stage.

A quantity of 4.0 × 10⁻³ mol of the silane coupling reagent is required to completely cover the surface area of 1 g of Washed-Si (Washed-Si = 316 m² g⁻¹, cross-sectional area of the silane coupling reagent = 0.13 nm²). This study used only 4.2 × 10⁻⁴ mol reagent, so the theoretical coverage is only 10 %. The modification step involving a ligand molecule and a catalyst required excess molecules in each step, so the maximum theoretical coverage of the immobilized catalyst is 10 %. The SEM/EDS mapping results and pore size distribution results show that the immobilization process used in this study can be further improved.

### 3.2. Characterization of Catalyst-Si
#### 3.2.1. Dehydrogenation Activity
Investigation of FA dehydrogenation using Catalyst-Si in 1 M FA solution found that CO₂/H₂ gas was generated. After completion of the dehydrogenation reaction, the concentration of the residue formate anion was determined by HPLC. **Figure 8** shows the gas generation volume as a function of the reaction time using Catalyst-Si under several temperature conditions. Residual FA was detected in every case; e.g., 0.1 mM at 70 °C, 0.1 mM at 60 °C, 0.1 mM at 50 °C (after 20 h), and 0.1 mM at 40 °C (after 20 h). In contrast, the homogeneous catalyst analogue dehydrogenates FA completely, as we reported previously. These results imply that catalyst immobilization on microparticles reduces the contact of catalyst with FA in the solution.

The dehydrogenation velocity obtained using Catalyst-Si at 60 °C was 0.87 mL mg⁻¹ min⁻¹, as calculated from **Figure 8**. The Ir content of Catalyst-Si was 1.7 wt% from the ICP-AES analysis, so that the dehydrogenation velocity based on Ir amount is 51.2 mL mg⁻¹(Ir) min⁻¹. The turnover frequency of the homogeneous catalyst analogue was 16,900 h⁻¹, which converted gives 72.7 mL mg⁻¹ min⁻¹ (Mw of homogeneous catalyst = 588.70, Mw of Ir = 192.22, gas temp. = 25 °C). Therefore, the dehydrogenation velocity of Catalyst-Si is 70 % of that of its homogeneous analogue, presumably as a result of immobilization. Immobilization probably reduced the collision frequency between the catalyst and FA, which reduced the reaction velocity. Stirring of the solution may increase the catalytic activity, and this topic is under investigation.

**Figure 7** BJH Plot of Each of the Four Particle Stages Calculated from the Adsorption-desorption Method
Dehydrogenation of FA using Washed-Si, Linker-Si, and Ligand-Si as negative controls was also investigated as shown in Fig. 8. FA without iridium beads did not show any dehydrogenation activity, confirming that iridium catalyzed the dehydrogenation. The Arrhenius plot obtained using Catalyst-Si is shown in Fig. 9. The $E_a$ of Catalyst-Si was 72.5 kJ mol$^{-1}$ calculated from Fig. 9. The $E_a$ of the homogeneous analogue was 72.1 kJ mol$^{-1}$, so both catalysts had the same activation energy. This result implies that the immobilized catalyst has the same reaction mechanism as the homogeneous catalyst. Therefore, the immobilization technique employed in this study preserves the catalytic reaction mechanism of the iridium complex during immobilization. The frequency factor of Catalyst-Si is $5.1 \times 10^{12}$ mL mg$^{-1}$ (Ir) min$^{-1}$, whereas that of its homogeneous analogue is $1.5 \times 10^{13}$ mL mg$^{-1}$ (Ir) min$^{-1}$. This difference also reflects the effect of immobilization on the catalyst.

### 3.2.2. Dispersion Activity of Catalyst-Si

The decrease of collision frequency between Catalyst-Si and FA might be the main reason for the reduced dehydrogenation velocity. To evaluate the dispersion stability of Catalyst-Si, the $\zeta$ potential was investigated (Fig. 10). The $\zeta$ potential of Catalyst-Si was $+11.6$ to $+7.3$ mV at room temperature as the pH was changed from 1.8 to 6.8. The absolute value of the $\zeta$ potential of Catalyst-Si remained below that of stable dispersion (approximately 20 mV in absolute value) in this pH range. The pH value of aqueous 1 M FA solution at room temperature is 1.8; therefore, stirring the catalytic solution is essential to increase the collision frequency during the reaction because Catalyst-Si might not form a stable dispersion in the solution (pH value of reaction solution is not stable at 1.8 accurately because the pH value decreases with lower temperature). The isoelectric point of the Catalyst-Si dispersion was about pH 7, as presumed from Fig. 10. At the isoelectric point, fine particles lose charge and precipitate in general. If the catalytic FA dehydrogenation is increased, more FA is consumed, and the pH of the reaction solution approaches the neutral value. Complete FA consumption may be achieved by efficiently stirring the solution.
4. Conclusions

Immobilization of Ir-complex catalyst on Si-support and characterization of the immobilized silica particles showed no change in particle form during the modification, as confirmed by SEM and N₂ adsorption-desorption measurement. Surface analysis by EDS mapping and FT-IR confirmed immobilization of the Ir-complex. The immobilized catalyst had the same activation energy as its homogeneous analogue for FA dehydrogenation. However, the reaction velocity was reduced because of the decrease in collision frequency. Effective agitation control and verification of the immobilization effect are necessary to ensure future practical hydrogen technology via dehydrogenation of FA.

Acknowledgment

We acknowledge Mr. Kumakawa (Renewable Energy Research Center, AIST) for SEM/EDS-mapping measurements.

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要 旨

ギ酸からの実用的な水素製造を目指したシリカ担体上へのイリジウム錯体触媒の固定化と特性評価

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均一系触媒の触媒能と固体触媒の段いやすさを併せ持つ固定化イリジウム錯体触媒によるギ酸の脱水素反応による水素製造の研究を行った。触媒固定化の過程は走査電子顕微鏡、赤外分光光度計、原子吸光等を用いて検討した。これらの固体触媒の活性エネルギー（Eₐ=72.5 kJ mol⁻¹）は均一系触媒と同じ値（Eₐ=72.1 kJ mol⁻¹）と同様であった。しかし、固定化触媒の触媒反応速度は、均一系触媒の50%であった。これには触媒の衝突エネルギーが減少したことが原因と考えられる。ゼータ電位測定の結果から、固定化触媒は反応溶液中で安定分散できないことが示された。効率的な触媒反応のためには、触媒技術の検討を行う必要があると考えられる。固定化触媒は実用的な水素製造への有望な技術であるが、より多くの研究が求められる。

J. Jpn. Petrol. Inst., Vol. 60, No. 4, 2017