Development of an Iridium-Based Catalyst for High-Pressure Evolution of Hydrogen from Formic Acid

Masayuki Iguchi,[a, d] Yuichiro Himeda,[b, d] Yuichi Manaka,[c, d] and Hajime Kawanami[a, d]

A highly efficient and recyclable Ir catalyst bearing a 4,7-dihydroxy-1,10-phenanthroline ligand was developed for the evolution of high-pressure H₂ gas (> 100 MPa), and a large amount of atmospheric pressure H₂ gas (> 120 L), over a long term (3.5 months). The reaction proceeds through the dehydrogenation of highly concentrated aqueous formic acid (FA, 40 vol%, 10 mol L⁻¹) at 80 °C using 1 µmol of catalyst, and a turnover number (TON) of 5 000 000 was calculated. The Ir catalyst precipitated after the reaction owing to its pH-dependent solubility in water, and 94 mol % was recovered by filtration. Thus, it can be treated and recycled like a heterogeneous catalyst. The catalyst was successfully recycled over 10 times for high-pressure FA dehydrogenation at 22 MPa without any treatment or purification.

Growing concerns over the depletion of fossil fuels and anthropogenic global warming have led to the search for alternative renewable energy resources. Molecular H₂ is considered as one of the perfect choices to act as a future energy source because of its high energy density and environmentally benign properties.[1] Although H₂ is a promising energy source, the gaseous nature of H₂ makes it difficult to store, transport, and use in mobile applications.[2] H₂ can be stored by physical adsorption on some specific materials, by chemical bonding, or in a complexed form that is incorporated into small molecules.[1a, c, 2] Chemical storage of H₂ in liquid materials gives several advantages over other hydrogen storage materials, such as a high H₂ storage capacity and easy handling and transportation with the existing infrastructures used for gasoline and diesel.[2a, 3] It is necessary that both the process of releasing storage of H₂ should occur at mild temperature for the reduction of material losses and energy consumption during the reactions.[2c, 3] Releasing compressed H₂ from a storage material for mobile applications, such as transportation, is a challenging issue because of space limitations, as typically a large volume system is required. H₂-fueled vehicles currently use H₂ in the gaseous form from high-pressure H₂ gas tanks that they carry.[1, c, 2b] The generation of high-pressure H₂ consumes a large amount of energy during compression, which corresponds to approximately 10–15% of the H₂ energy content.[1a, b, 2b] The energy consumed during the compression of H₂ could be reduced by generating high-pressure H₂ through a chemical reaction.

Recently, formic acid (FA) has attracted considerable attention as a liquid hydrogen storage material because it is stable, moderately flammable, and readily biodegradable under ambient conditions.[4] FA contains a relatively high content of H₂, and the low reaction enthalpy permits the release of H₂ at mild temperature[2c, 4e] through dehydrogenation, which is a thermodynamically favorable process.[4e] CO₂, a co-product of FA dehydrogenation, can also be converted to FA by photo- or electro-chemical reduction in the presence of catalysts.[4e–d] FA has been recognized as a H₂ storage material since 1978.[5] However, the development of a suitable process for the generation of H₂ gas from FA has progressed slowly because of the requirement of severe reaction conditions, low product selectivity, and regeneration of the catalyst.[2c] In addition, the occurrence of CO as a by-product deactivates the catalyst and hampers the application of the generated H₂ in fuel cells.[6]

In the presence of homogeneous catalysts, FA can be decomposed selectively at mild temperature. Various catalysts have been developed for the selective decomposition of FA to produce H₂ with a high rate at temperatures of less than 100 °C.[7] Many researchers investigated the catalytic dehydrogenation of FA under atmospheric pressure conditions, which releases high-pressure H₂ gas, and although the process is energy-efficient, it faces the problem of H₂ separation. To date, there have been very few reports of the dehydrogenation of FA under high-pressure conditions, above 10 MPa,[8] because the catalyst must be capable of withstandingsevere reaction conditions, especially high pressures and high concentrations of FA over long time periods. In practical applications of FA as a H₂ carrier, a high concentration of FA is generally used for

[a] Dr. M. Iguchi, Prof. Dr. H. Kawanami Research Institute for Chemical Process Technology Department of Material and Chemistry National Institute of Advanced Industrial Science and Technology Sendai, Miyagi 983-8551 (Japan) E-mail: m-iguchi@aist.go.jp

[b] Dr. Y. Himeda Research Institute of Energy Frontier Department of Energy and Environment National Institute of Advanced Industrial Science and Technology Tsukuba, Ibaraki 305-8565 (Japan)

[c] Dr. Y. Manaka Renewable Energy Research Center Department of Energy and Environment National Institute of Advanced Industrial Science and Technology Koriyama, Fukushima 963-0298 (Japan)

[d] Dr. M. Iguchi, Dr. Y. Himeda, Dr. Y. Manaka, Prof. Dr. H. Kawanami Core Research for Evolutional Science and Technology Japan Science and Technology Agency Tokyo, 102-0076 (Japan)

© 2016 The Authors. Published by Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

DOI: 10.1002/cssc.201600697
the fast and efficient production of large amounts of high-pressure H₂.

Recently, we developed water-soluble Ir catalysts for fast and selective FA decomposition under mild temperatures. The introduction of hydroxyl groups into a bipyridine ligand activated pentamethylcyclopentadienyl Ir (Cp*Ir) complexes toward FA dehydrogenation. We also reported that the Cp*Ir complex containing 4,4'-dihydroxy-2,2'-bipyridine (4DHBP, catalyst 1 in Figure 1) catalyzed selective FA decompo-

![Figure 1. Cp*Ir complexes for the development of a FA recycling system.](image)

sition at the high pressure of 123 MPa. However, the main drawback is the separation and consequent recycling of the catalyst. Even though catalyst 1 has a long lifetime of over 33 h with turnover number (TON) of 100 000 and turnover frequency (TOF) of 3100 h⁻¹ at 60 °C under atmospheric pressure, both the TON and TOF decreased to 38 100 and 2510 h⁻¹, respectively, under the high-pressure conditions of 30 MPa and 80 °C owing to the deactivation of the catalyst (Figure S1 in the Supporting Information). As the gas pressure increases owing to the decomposition of FA, the catalyst undergoes partial hydrogenolysis as a result of the presence of high-pressure H₂ in the system, resulting in a change to an insoluble compound, which then precipitates after the reaction (Scheme S1). We predicted that the bipyridine ligand might be changing from its chelating conformation in 1 to another conformation under the high-pressure H₂ conditions (Figure S2 in supporting information). Thus, after precipitation, the catalyst loses its activity towards decomposition of FA.

In this work, we have developed an effective catalyst for the dehydrogenation of FA under high-pressure conditions, which has a long lifetime and that can be recycled several times. Here, we introduce an Ir catalyst containing 1,10-phenanthroline-4,7-diol (catalyst 2) as a chelating ligand, which prevents cis/trans isomerization of the pyridine skeleton by bridging, and investigate its potential in terms of catalytic activity, durability, and reusability.

The Ir catalysts 1 and 2 were synthesized as reported in the literature. First, we investigated the FA dehydrogenation using catalyst 2. When we tested the catalyst durability with 1 μmol of catalyst under atmospheric pressure using 10 mL of FA, catalyst 2 continued the dehydrogenation of FA for 2600 h (about 3.5 months), and almost 100% of FA was transformed to H₂ and CO₂ (Figure 2). The evolved gas volumes (H₂ and CO₂) increased linearly and the evolution rate was in the region of 0.11–0.12 mL h⁻¹ for the first 1000 h. The calculated TON value of catalyst 2 was 500000. Table 1 compares the results of the dehydrogenation of FA with catalysts 2 and 1. The obtained TOF value of catalyst 2 was 3010 h⁻¹ (Table 1, entry 2), which is superior to that of catalyst 1 (Table 1, entry 1), and CO was below the detection limit (< 5 ppm, Figure S3). With increasing concentration of FA, the TOF reaches its maximum between 3 and 6 M (Table 1, entries 2-6). Interestingly, the TOF decreased when 80% of highly concentrated FA was used, but the catalyst maintained its activity during the reaction. Moreover, the TON increased to 203 000 (Table 1, entry 6). With increasing reaction temperature, a high TOF of 62 900 h⁻¹ and high TON of 320 000 were obtained at 98.8 °C. Hence, catalyst 2 shows comparable activity with catalyst 1 for the dehydrogenation of FA under atmospheric pressure, as well as good durability, even from a highly-concentrated FA solution.

![Figure 2. The time courses of the volume of evolved gases/rate of evolution of gases from FA decomposition in 10 molL⁻¹ of FA aqueous solution (500 mL) at 60 °C, catalyzed by catalyst 2 (1 μmol) in a glass autoclave.](image)

![Figure 3. Reaction conditions and results of FA dehydrogenation.](image)

**Table 1. Dehydrogenation of FA under atmospheric pressure conditions.**

| Entry | Cat. | Catal. Conc. | FA Conc. | Bath temp. (°C) | React. time (h) | TOF (h⁻¹) | TON          |
|-------|------|--------------|----------|----------------|----------------|------------|--------------|
| 1     | 1    | 100          | 1        | 60             | 7              | 2020       | 10000       |
| 2     | 2    | 100          | 1        | 60             | 5              | 3010       | 10000       |
| 3     | 2    | 100          | 3        | 60             | 12             | 3640       | 30000       |
| 4     | 2    | 100          | 6        | 60             | 20             | 3220       | 60000       |
| 5     | 2    | 25 [f]       | 12.9 [g] | 60             | 45             | 2480       | 120000      |
| 6     | 2    | 100          | 20.3 [h] | 60             | 178            | 910        | 200000      |
| 7     | 2    | 25 [i]       | 4        | 79.8 [j]       | 12             | 17000      | 160000      |
| 8     | 2    | 25 [i]       | 4        | 89.8 [j]       | 7              | 33800      | 160000      |
| 9     | 2    | 12.5 [i]     | 4        | 98.8 [j]       | 6.5            | 62900      | 320000      |

[a] The reaction was carried out in degassed aqueous FA solution (20 mL) until gas evolution ceased; the volume of the evolved gas was temperature-corrected. [b] The TOF was determined 30 min after beginning the reaction. [c] The TOF was determined 30 min after beginning the reaction. [d] 50 wt % FA. [e] 80 wt % FA. [f] Temperature of the reaction solution was measured by a thermocouple. [g] Catalyst 1. [h] Catalyst 2. [i] Reaction temperature was 60 °C. [j] Reaction temperature was 98 °C.
We further evaluated the catalyst durability under high-pressure conditions. Previously, we reported that catalyst 1 could generate high-pressure gas over 100 MPa by FA dehydrogenation, but the catalytic activity gradually decreased as the reaction progressed. Catalyst 2 can also produce high-pressure gas at 110 MPa due to the dehydrogenation of FA from a 16 mM FA solution (Figure 3). It was observed that the rate of increase of pressure was comparatively faster than that of catalyst 1 (Figure S4).

To compare the durability of catalysts 1 and 2, we recycled both of the catalysts under 22 MPa gas evolution conditions (Figure 4) by simply removing the aqueous FA under reduced pressure after the reaction. When catalyst 2 was used, the gas evolution rate remained practically unaltered in the 1st and 2nd runs. However, by the 4th run, it had decreased to 1/3 of that of the 1st run. The rate in the case of catalyst 2 was much faster (initial rate of 1.3 MPa h⁻¹) than that of catalyst 1 (<0.1 MPa h⁻¹). Interestingly, after the reaction, catalyst 1 was completely dissolved in aqueous solution, whereas catalyst 2 had precipitated (Figure 5c). The precipitate could be easily separated and recovered by filtration. The structural stability of the precipitated catalyst 2 was confirmed by NMR (Figure S5). After cooling down the system to 4°C, catalyst 2 was filtered and the Ir complex remaining in the filtrate was less than 6 mol% of the initial catalyst loading [31 ppm by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis]. Catalyst 2 in each of its conformations has a pH-dependent solubility in aqueous medium. [12a] We observed that before the reaction, the pH of the 6.5 mol L⁻¹ FA solution was 0.9, which changed to pH 1.9 after the decomposition of FA at 22 MPa (0.65 molL⁻¹). Thus, the catalyst precipitated as the reaction progresses owing to the change in pH of the system (Figure 4 and S6). As a result, catalyst 2 spontaneously precipitated and 94 mol% was recovered from the reactant without further pH adjustment.

Recycling of catalyst 2 was conducted for high-pressure dehydrogenation of FA at a pressure above 22 MPa (Figure 6). Catalyst 2 can be successfully recycled over 10 times while...
Figure 6. Recycling experiments of high-pressure gas evolution from FA in the presence of catalyst 2. The catalyst was recycled after the former reaction without any purification except filtration. Reaction conditions: 50 °C, 2 MPa He, FA aqueous solution (7 mol L\(^{-1}\), 4 mL), catalyst (2 mmol L\(^{-1}\), 8 μmol). FA was added after depressurization (1 mL). The upper horizontal axis represents times of high-pressure gas release.

maintaining its activity, and it has a durability of over 200 h of total reaction time under 22 MPa. In each experiment, all the evolved gases were confirmed as H\(_2\) and CO\(_2\) without any detectable amount of CO (< 0.6 ppm, Figure S7). Catalyst 2 is homogeneous but can be recycled like a heterogeneous catalyst many times under high-pressure conditions.

In conclusion, we have developed an Ir catalyst (catalyst 2) bearing the 1,10-phenanthroline-4,7-diol ligand, which can be used for the generation of high-pressure hydrogen from FA with an obtained highest TON value of 50 000.00. It can be successfully recycled over 10 times without losing any catalytic activity. Catalyst 1 with a 4,4'-dihydroxy bipyrindine ligand has the ability to generate high-pressure gas from FA aqueous solution effectively, but it is not suitable for the development of a high-pressure H\(_2\) evolution system for practical use. The developed catalyst 2 has comparable activity with the catalyst 1 with the advantage that after the reaction, it can be easily separated owing to its pH-dependent solubility properties. This work will be extended to develop a high-pressure H\(_2\) evolution system from highly-concentrated FA and to confirm the practical application of FA as a H\(_2\) storage material.

**Experimental Section**

FA (> 99.0%) was used as received from Wako Pure Chemical Industries, Ltd. Deionized water was prepared through a filtration system (EMD Millipore Corp., ZFSQ240P4) and distillation system (Toyo Roshi Kaisha, Ltd., GS-590). All liquid reagents were degassed with an obtained highest TON value of 50 000.00. It can be successfully recycled over 10 times without losing any catalytic activity. Catalyst 1 with a 4,4'-dihydroxy bipyrindine ligand has the ability to generate high-pressure gas from FA aqueous solution effectively, but it is not suitable for the development of a high-pressure H\(_2\) evolution system for practical use. The developed catalyst 2 has comparable activity with the catalyst 1 with the advantage that after the reaction, it can be easily separated owing to its pH-dependent solubility properties. This work will be extended to develop a high-pressure H\(_2\) evolution system from highly-concentrated FA and to confirm the practical application of FA as a H\(_2\) storage material.

Acknowledgements

The authors thank Dr. David C. Grills of Brookhaven National Laboratory, and Dr. Maya Chatterjee of AIST for their help with manuscript preparation. The authors would like to acknowledge the financial support of Japan Science and Technology Agency (JST), CREST, and the International Joint Research Program for Innovative Energy Technology of the Ministry of Economy, Trade, and Industry (METI) of Japan.

**Keywords:** catalysis · formic acid · high pressure · hydrogen · indium

---

[1] a) N. Armaroli, V. Balzani, ChemSusChem 2011, 4, 21–36; b) P. Jena, J. Phys. Chem. Lett. 2011, 2, 206–211; c) S. Niazi, T. Manzoor, A. H. Pandith, Renewable Sustainable Energy Rev. 2015, 50, 457–469; d) L. Schlapbach, Nature 2009, 460, 809–811.

[2] a) A. F. Dalebrook, W. Gan, M. Grasemann, G. Laurenczy, Chem. Commun. 2013, 49, 8735–8735; b) U. Eberle, M. Felderhoff, F. Schütz, Angew. Chem. Int. Ed. 2009, 48, 6608–6630; Angew. Chem. 2009, 121, 6732–6757; c) P. Makowski, A. Thomas, P. Kuhn, F. Goettmann, Energy Environ. Sci. 2009, 2, 480–490.

[3] a) F. Alhumaidan, D. Cresswell, A. Garforth, Energy Fuel 2011, 25, 4217–4234; b) D. Teichmann, W. Ait, P. Wasserscheid, R. Freymann, Energy Environ. Sci. 2011, 4, 2767–2773; c) Q.-L. Zhu, Q. Xu, Energy Environ. Sci. 2011, 4, 478–512.

[4] a) W.-H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck, E. Fujita, Chem. Rev. 2015, 115, 12936–12937; b) J. L. White, M. F. Baruch, J. E. Pander, I., Y. Hu, I. C. Fortmeyer, J. E. Park, T. Zhang, K. Liao, J. Gu, Y. Yan, T. W. Shaw, E. Abele, A. B. Bocarsly, Chem. Rev. 2015, 115, 12888–12935; c) C. Costentin, M. Robert, J.-M. Saveant, Chem. Soc. Rev. 2013, 42, 2423–2436; d) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbeck, D. L. Dubois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, Chem. Rev. 2013, 113, 6611–6658; e) E. Enthaler, J. von Langermann, T. Schmidt, Energy Environ. Sci. 2010, 3, 1207–1217.

[5] R. Williams, R. S. Crandall, A. Bloom, Appl. Phys. Lett. 1978, 33, 381–383.

[6] a) X. Cheng, Z. Shi, N. Glass, L. Zhang, J. Zhang, D. Song, Z.-S. Liu, H. Wang, J. Shen, J. Power Sources 2007, 165, 739–756; b) R. Borup, J. Meyers, B. Pivovar, Y. S. Kim, R. Mukundan, N. Garland, D. Myers, M. Wilson, F. Garzon, D. Wood, P. Zelenay, M. More, K. Stroh, T. Zawodzinski, J. Boncella, J. E. McGrath, M. Inaba, K. Miatake, M. Hori, K. Ota, Z. Ogumi, S. Miataya, A. Nishikata, Z. Siroma, Y. Uchimoto, K. Yasuda, K.-I. Kiijima, N. Ishikawa, Chem. Rev. 2007, 107, 3904–3951.

[7] a) A. Boddien, B. Loges, H. Junge, M. Beller, ChemSusChem 2008, 1, 751–758; b) A. Boddien, D. Mellmann, F. Gärnter, R. Jesschell, H. Junge, P. J. Dyson, G. Laurenczy, R. Ludwig, M. Beller, Science 2011, 333, 1733–1736; c) Y. Maenaka, T. Suenobu, S. Fukuzumi, Energy Environ. Sci. 2012, 5, 7360–7367; d) J. H. Barnard, C. Wang, N. G. Berry, J. Xiao, Chem. Sci. 2013, 4, 1234–1244; e) S. Oldenhorst, B. de Bruin, M. Lutz, M. A. Siegler,
F. W. Patureau, J. I. van der Vlugt, J. N. H. Reek, Chem. Eur. J. 2013, 19, 11507−11511; f) T. Zell, B. Butschke, Y. Ben-David, D. Milstein, Chem. Eur. J. 2013, 19, 8068−8072; g) E. A. Bielinski, P. O. Lagaditis, Y. Zhang, B. Q. Mercado, C. Würtele, W. H. Bernskoetter, N. Hazari, S. Schneider, J. Am. Chem. Soc. 2014, 136, 10234−10237; h) G. A. Filonenko, R. van Putten, E. N. Schulpen, E. J. M. Hensen, E. A. Pidko, ChemCatChem 2014, 6, 1526−1530; i) T. W. Myers, L. A. Berben, Chem. Sci. 2014, 5, 2771−2777; j) J. J. A. Celaje, Z. Lu, E. A. Kedzie, N. J. Lo, T. J. Williams, Nat. Commun. 2016, 7, 11308.

[8] a) C. Fellay, P. J. Dyson, G. Laurenczy, Angew. Chem. Int. Ed. 2008, 47, 3966−3968; Angew. Chem. 2008, 120, 4030−4032; b) C. Fellay, N. Yan, P. J. Dyson, G. Laurenczy, Chem. Eur. J. 2009, 15, 3752−3760.

[9] a) Y. Himeda, Green Chem. 2009, 11, 2018−2022; b) Y. Himeda, S. Miyazawa, T. Hirose, ChemSusChem 2011, 4, 487−493; c) J. F. Hull, Y. Himeda, W.-H. Wang, B. Hashiguchi, R. Periana, D. J. Szalda, J. T. Muckerman, E. Fujita, Nat. Chem. 2012, 4, 383−388; d) Y. Manaka, W.-H. Wang, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, Catal. Sci. Technol. 2014, 4, 34−37; e) W.-H. Wang, S. Xu, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, ChemSusChem 2014, 7, 1976−1983; f) Y. Suna, M. Z. Ertem, W.-H. Wang, H. Kambayashi, Y. Manaka, J. T. Muckerman, E. Fujita, Y. Himeda, Organometallics 2014, 33, 6519−6530; g) W.-H. Wang, M. Z. Ertem, S. Xu, N. Onishi, Y. Manaka, Y. Suna, H. Kambayashi, J. T. Muckerman, E. Fujita, Y. Himeda, ACS Catal. 2015, 5, 5496−5504; h) N. Onishi, M. Z. Ertem, S. Xu, A. Tsurusaki, Y. Manaka, J. T. Muckerman, E. Fujita, Y. Himeda, Catal. Sci. Technol. 2016, 6, 988−992.

[10] M. Iguchi, Y. Himeda, Y. Manaka, K. Matsuoka, H. Kawanami, ChemCatChem 2016, 8, 886−890.

[11] a) K. Fujita, Y. Tanaka, M. Kobayashi, R. Ymaguchi, J. Am. Chem. Soc. 2014, 136, 4829−4832; b) J.-P. Zhang, Y.-Y. Lin, Y.-Q. Weng, X.-M. Chen, Inorg. Chem. Acta 2006, 359, 3666−3670; c) A. Zucca, G. L. Pettetto, S. Stoccoro, M. A. Cinellu, M. Manassero, C. Manassero, G. Minghetti, Organometallics 2009, 28, 2150−2159.

[12] a) Y. Himeda, N. Onozawa-Komatsuzaki, H. Sugihara, K. Kasuga, Organometallics 2007, 26, 702−712; b) Y. Himeda, N. Onozawa-Komatsuzaki, S. Miyazawa, H. Sugihara, T. Hirose, K. Kasuga, Chem. Eur. J. 2008, 14, 11076−11081.

Received: May 25, 2016
Revised: July 9, 2016
Published online on August 17, 2016