ギ酸からの水素生成に有効な水溶性触媒の開発

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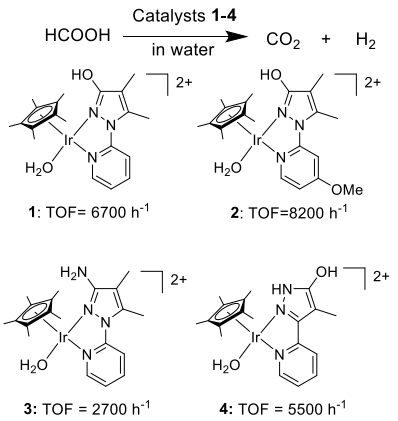
Development of water-soluble catalysts for hydrogen production from formic acid (*National Institute of Advanced Industrial Science and Technology*) ○Naoya Onishi, Yuichiro Himeda

Reducing our dependence on fossil fuels is of great importance, and in this connection, the use of hydrogen is attracting much attention. Formic acid (HCOOH), which contains 4.4% H_2, has been considered as one of the candidates for a convenient H_2 carrier because it is liquid at room temperature and pressure, soluble in water, and can be safely transported. In this study, we have developed a catalyst for dehydrogenation of formic acid to produce hydrogen (HCOOH → $H_2 + CO_2$).

We have already found that catalyst 1 was highly active in the dehydrogenation of formic acid. In this study, various derivatives were synthesized and their catalytic performances were evaluated. The introduction of an electron-donating group (OMe) on the pyridine, as in catalyst **2**, enhanced the catalytic activity. On the other hand, catalyst **3**, which has an amino group on pyrazole, showed no improvement in catalytic activity. The isomer of pyrazole with catalyst **1** showed good activity, but not as good as catalyst **1**.
Keywords : Hydrogen generation; Formic acid; Water-souble catalyst

化石燃料への依存度減らすことは重要視されており，それに関連して水素を利用する試みが注目されている．水素を安全な水素貯蔵体へと変換させることは高い重要性を持っている．4.4% の H_2 を含むギ酸（HCOOH）は，常温・常圧で液体であり，水に溶け，安全に輸送できることから，便利な H_2 キャリアの候補の 1 つとして考えられてきた [1]．本研究では，ギ酸を脱水素化して水素を発生させる（HCOOH→$H_2 + CO_2$）触媒の開発に取り組んだ(**Scheme 1**).



Scheme 1.Dehydrogenation of Formic Acid by Ir Catalysts. (Conditions: $[HCOOH]_{aq}$ = 1.0 M, [cat] = 1.0 mM, at 60 ºC).

これまでに触媒 **1** がギ酸の脱水素化に高活性を示すことを明らかにしていた [2]．本研究では，種々の誘導体を合成し，触媒性能について評価した．触媒 **2** のようにピリジン上に電子供与性基（OMe）を導入すると触媒活性が向上した．一方で，ピラゾール上にアミノ基を有する触媒 **3** は触媒活性の向上は見られなかった．また，触媒 **1** とはピラゾール上の N の位置が異なる異性体（触媒 **4**）は触媒 **1** ほどではないが良好な活性示した．

1) M. Beller et al., *Chem. Rev.* **2018**, *118*, 372–433.
2) N. Onishi, R. Kanega, E. Fujita, Y. Himeda, *Adv. Synth. Catal*. **2019**, *361*, 289-296.